PREPARATION AND PROPERTIES OF METHYLGERMYLSILANES

Dutton

PREPARATION AND PROPERTIES OF METHYLGERMYLSILANES AND SOME RELATED COMPOUNDS

by

Walter Arthur Dutton, B.Sc.

A thesis submitted to the Faculty
of Graduate Studies and Research
of McGill University in partial
fulfilment of the requirements for
the degree of Doctor of Philosophy

From the Inorganic Chemistry Laboratory
under the supervision of Dr. M. Onyszchuk

McGill University
Montreal, Canada.

July, 1965

To My Parents
whose quiet encouragement helped
to make this work possible.

ACKNOWLEDGEMENTS

The author wishes to express his thanks and gratitude to Dr. M. Onyszchuk whose interest and support helped make this investigation possible.

The author is indebted to Dr. A. Taurins and Dr. C. Stammer for instruction in the use of the infrared and n.m.r. spectrometers, to Dr. J.E. Griffiths of the Bell Telephone Laboratories for checking the infrared assignments made in this work, and to Dr. M.A. Whitehead and his research group for helpful discussions concerning the n.m.r. data.

The freely given advice and encouragement of colleagues in the laboratory, especially that of Dr. T.N. Srivastava and Dr. J.M. Miller is acknowledged.

Thanks are also due to the Province of Quebec for a Scholarship and to the National Research Council of Canada for three Studentships during the course of this investigation.

TABLE OF CONTENTS

Page

INTRODUCTION

EXPERIMENTAL

RESULTS

DISCUSSION

INDEX OF TABLES

INDEX OF FIGURES

INTRODUCTION

Germane (GeH_4), the germanium analog of methane, was first prepared by Voegelen (1) in 1902 by the action of zinc and sulphuric acid on germanium tetrachloride. No further work on the hydrides of germanium was done until 1922 when Müller and Smith (2) studied the preparation of germane with a view to using the hydride in a reaction, similar to the Marsh test, for the detection of minute quantities of germanium. That same year, Paneth and Schmidt-Hebbel (3) produced germane by the reaction of sulphuric acid with a mixture of zinc, magnesium and germanium, and Schenck (4) obtained germane from the action of acid on magnesium germanide.

Since that time much work has been done on the preparation and characterization of germane, substituted germanes and germanium hydrides up to Ge_9H_{20} (5). In recent years, this field has been reviewed in detail by Johnson (6) up to 1950, by Rijkens (7) up to 1960, and by Quane and Bottei (8), whose review is intended as a supplement to Johnson's, up to 1962. Since it is not the purpose of this introduction to rewrite these reviews, only a brief summary of those topics which are relevant to this work will be given. These topics include the classification of compounds containing the germyl group, methods of preparation of these compounds and a summary of their physical properties (Appendix I).

CLASSIFICATION OF GERMYL COMPOUNDS

There are about seventy compounds containing the germyl (GeH_3) group reported in the literature to the end of 1964. They are conveniently divided into the following six groups.

1) Germanium hydrides, from GeH_4 to Ge_9H_{20} (9,5).

2) Alkylgermanes, from methylgermane (CH_3GeH_3) (10) to n-octylgermane ($n\text{-}C_8H_{17}GeH_3$) (11), including 1,1,1-trifluoro-3-germyl propane (12), vinylgermane (13) and 3-germyl-2-propylene (12).

3) Germyl halides, including digermanyliodide (14) and pseudo halides such as germylcyanide, -isocyanate and -isothiocyanate (15,16,17).

4) Germyl oxygen and sulphur compounds, including germyl acetate (16), methoxygermane (18,19), digermoxane (20), and digermthian (20).

5) Alkali metal salts (21,10) of the type GeH_3M, where M = Li, Na, K.

6) Mixed hydrides of germanium with silicon (22,23,24), arsenic, phosphorous, and nitrogen (25), including some fifteen germanium-silicon hydrides of the general type $Ge_xSi_yH_{2x+2y+2}$ where x=1 to 3 and y=1 to 5 (26).

PREPARATION OF GERMYL COMPOUNDS

1. Germanium Hydrides

Germane has been prepared by a variety of methods with yields ranging from 10 to 99 per cent. These methods include reduction of germanium tetrachloride with lithium aluminum hydride, lithium (t-butoxy) aluminum hydride (27) or sodium borohydride (28), acid hydrolysis of the metal (3) or alloy (4,29), acid or alkaline reduction of the oxide (2,30), reduction of the alloy with dichlorohydrazine in anhydrous hydrazine (31), electrolytic reduction of an acid solution of the oxide (32), and reduction of an acidic oxide solution with sodium borohydride (33). Of these methods, the best yield is obtained by the reduction of germanium dioxide in hydrobromic acid by sodium borohydride. In the original preparation, described by Piper and Wilson (33), germanium dioxide was dissolved in boiling hydrobromic acid and the solution was then cooled in an ice bath for the addition of aqueous sodium borohydride. Germane was obtained with a yield of 73 per cent. If the mixture of germanium dioxide in hydrobromic acid is refluxed for 6 hours and the solution of sodium borohydride is added to this solution without cooling, almost quantitative yields of germane are obtained.

The higher germanium hydrides occur as by-products in the preparation of germane by most of the methods mentioned previously. The yield of a germanium hydride decreases as the number of germanium atoms in the chain increases, and although the hydrides up to Ge_9H_{20} have been prepared and identified, those from Ge_6H_{14} to Ge_9H_{20} have been observed only as peaks on a gas chromatogram or mass spectrogram(5). Although the hydrides up to pentagermane (Ge_5H_{12}) have been prepared in low yields, sufficient quantities have been obtained to allow determination of their physical properties (5,62).

Digermane was first described by Dennis and his co-workers (29) in 1924. They obtained it by the action of hydrochloric acid on magnesium germanide but the yield was only 5 per cent of the germanium used. Digermane has also been prepared in low yield from germane in a gas discharge (5), along with the higher hydrides in smaller amounts. No specific method has yet been described for the preparation of digermane in high yield.

2. Alkylgermanes

The alkylgermanes, which include all the normal aliphatic compounds from methyl- to n-octylgermane as well as vinylgermane, 1-germyl-2-propylene and 1,1,1-trifluoro-3-germyl propane, have been prepared by the reduction of the appropriate alkyl germanium trihalide with lithium aluminum hydride or lithium hydride. Some have also been prepared by the reaction of germyl sodium in liquid ammonia with alkyl halides.

Methylgermane was prepared by Teal and Kraus (10) by the action of a methyl halide (iodide or bromide) on germyl sodium in liquid ammonia.

$$GeH_3Na + CH_3X \longrightarrow NaX + CH_3GeH_3 \quad \ldots 1)$$

Ponomarenko et al (34) obtained methylgermane by reducing methyltrihalogermane with lithium hydride in dioxane. Amberger and Boeters (35) used lithium aluminum hydride as a reducing agent to prepare the same compound.

Lithium aluminum hydride was also used to reduce vinyltrichlorogermane to vinylgermane (13) and 1-trichlorogermyl-2-propylene to 1-germyl-2-propylene (12).

Ethylgermane was prepared (36,10) by bubbling ethyl bromide through a solution of germyl sodium in liquid ammonia, as was iso-amylgermane from iso-amylhalide. Ponomarenko et al (34) prepared ethylgermane by the lithium hydride reduction of an ethyl germanium halide (chloride or bromide).

Teal and Kraus (10) were the first to report the preparation of n-propylgermane from the reaction of n-propylbromide with germyl sodium in liquid ammonia. Johnson and Jones (37) prepared n-propyltrichlorogermane from germanium tetrachloride and n-propyl lithium in petroleum ether, and then reduced it with lithium aluminum hydride in iso-propyl ether to n-propylgermane in 85 per cent yield.

The series of compounds from n-butylgermane to n-octylgermane were prepared by Satgé (11) by reduction of the appropriate alkylgermylhalide in ether solution with lithium aluminum hydride. The yield of alkylgermane by this method usually approached 90 per cent.

Ponomarenko et al (12) prepared 1,1,1-trifluoro-3-germylpropane by lithium hydride reduction of the trihalogermane.

3. Halides and Pseudo Halides

The monohalogermanes and digermanyliodide constitute a series of compounds containing a halide and the GeH_3 group. For purposes of classification, this series is expanded to include the pseudo halides, germylcyanide, -isocyanate, and -isothiocyanate. Germylhalides are usually prepared by the action of the pure halogen or hydrogen halide on germane. The pseudo halides are prepared from halogermanes by reaction with the appropriate silver salts.

Chloro- and bromogermane were prepared by Dennis and Judy (15) by the reaction of germane with hydrogen chloride or bromide in the presence of the appropriate aluminum trihalide as catalyst.

$$GeH_4 + HX \xrightarrow{AlX_3} GeH_3X + H_2 \qquad \ldots 2)$$

They attempted to prepare iodogermane by this method, but could not isolate it. In 1959 Sujishi (38) prepared and isolated iodogermane and he has used it to prepare other germyl compounds (20). More recently Srivastava et al (16) prepared bromogermane by the direct interaction of bromine with germane, with yields in excess of 60 per cent.

$$GeH_4 + Br_2 \longrightarrow GeH_3Br + HBr \qquad \ldots 3)$$

Srivastava and Onyszchuk (39) also prepared fluorogermane by passing bromogermane over dry silver fluoride.

Mackay and Roebuck (14) used the direct interaction of digermane with iodine at -63° to prepare digermanyliodide. Digermanylchloride appeared to be formed in the reaction of digermanyliodide with silver chloride but it could not be isolated.

The pseudo halogermanes have been prepared by Srivastava et al (16) by passing a halogermane over the appropriate silver salts, following the silver salt conversion series for silyl compounds proposed by MacDiarmid (40). The interaction of silver cyanide with chlorogermane produced germylcyanide, but a pure sample could not be isolated because it decomposed during purification. The pure compound has been obtained by the reaction of bromogermane with silver cyanide (38). The reaction between silver cyanate and bromogermane gave germylisocyanate in 93 per cent yield. Bromogermane and silver thiocyanate also react quantitatively (97 per cent yield) to produce germylisothiocyanate, which decomposes at 55° (16).

4. Oxygen and Sulphur Compounds

Compounds in which a germyl group is bound to an oxygen or sulphur atom comprise a series which includes germyl acetate, methyoxygermane, digermoxane and digermthian. These compounds are generally prepared from a halogermane by the action of the appropriate dry salt containing oxygen or sulphur.

Germyl acetate was prepared in almost quantitative yield (96 per cent) by Srivastava et al (16) by passing bromogermane over dry silver acetate. The reaction of liquid chlorogermane with dry sodium metholate at -50^{o} yielded about 60 per cent methoxygermane, but Griffiths (18) was unable to separate the pure material. The pure compound has recently been prepared by the mercury photosensitized reaction of methanol with germane (19). Goldfarb and Sujishi (20) prepared digermthian by the reaction of germyliodide with mercuric sulphide. Digermoxane was obtained (20) in 35 per cent yield by shaking digermthian with a large excess of granular red mercuric oxide at -40^{o}.

5. Alkali Metal Salts

Germyl alkali metal salts form a distinctive series of solid GeH_3 compounds. They are formed by the reaction of germane with alkali metals dissolved in liquid ammonia, and are relatively unstable at room temperature. The salt used exclusively in this work, germyl sodium, was prepared in 1934 by

Kraus and Carney (41). They bubbled germane through a solution of sodium in anhydrous liquid ammonia and, on removal of the ammonia, obtained a white solid which decomposed rapidly at room temperature, and more slowly at -33°. The reaction scheme proposed for the formation of germyl sodium from germane and sodium in liquid ammonia is (42):

$$\begin{tikzcd} \mathrm{GeH_4} \arrow[r, "\mathrm{Na}\ \ -63^{\circ}"] \arrow[d, "2\mathrm{Na}"'] & \tfrac{1}{2}\mathrm{H_2} + \mathrm{GeH_3Na} \\ \mathrm{H_2} + \mathrm{GeH_2Na_2} \arrow[ur, "\mathrm{GeH_4}"] \arrow[r, "\mathrm{NH_3}\ \ -45^{\circ}"] & \mathrm{NH_2Na} + \mathrm{GeH_3Na} \arrow[u, "-45^{\circ}", "\mathrm{GeH_4}"'] \end{tikzcd} \qquad \ldots\ 4)$$

Germyl sodium crystallizes first with 6 molecules of ammonia of crystallization, which are lost forming four solid phases consecutively at -33° (41):

$$\mathrm{GeH_3Na\cdot 6NH_3} \xrightarrow[315\mathrm{mm}]{} \mathrm{GeH_3Na\cdot 4.5NH_3} \xrightarrow[23\mathrm{mm}]{} \mathrm{GeH_3Na\cdot 2NH_3} \xrightarrow[3\mathrm{mm}]{} \mathrm{GeH_3Na} \quad \ldots\ 5)$$

Kraus and Carney initially used germyl sodium to obtain pure germane from the mixture of germanium hydrides which they had obtained by the action of ammonium bromide on magnesium germanide in liquid ammonia. They bubbled the mixture of hydrides through a solution of sodium in liquid ammonia to form germyl sodium. Ammonium bromide was then added to produce pure monogermane. Other workers, e.g. Glarum and Kraus (36), have used germyl sodium as a reagent for the preparation of alkylgermanes. Another germyl salt, germyl potassium, has been prepared by Teal and Kraus (10), from germane and potassium in liquid ammonia. They found that one mole of germyl potassium was soluble in 4.6 moles of ammonia, and it appeared to be more stable toward thermal decomposition than germyl sodium, but much less is known about its formation and properties. More recently, Amberger and Boeters (21) prepared germyl lithium by the reaction of germane with lithium in liquid ammonia. On removal of the liquid ammonia, the white solid germyl lithium retains two molecules of ammonia of crystallization at -78°, which are lost at room temperature.

6. Mixed Hydrides

The two main methods of preparation of mixed hydrides of germanium with silicon, phosphorous, arsenic and nitrogen are gas discharge of a mixture of two hydrides and acid hydrolysis of a mixed calcium or magnesium alloy. These methods generally yield such small quantities of mixed hydrides that vapour phase chromatography or mass spectrometry are required to identify them.

The simplest silicon-germanium hydride, germylsilane (or silylgermane) has been prepared by three different methods.

It was originally prepared and separated by Spanier and MacDiarmid (22) from an equimolar mixture of silane and germane in an electric discharge. Subsequently, Varma and Cox (24) used the reaction of silyl potassium with chlorogermane at room temperature to obtain a 20 per cent yield of germylsilane. Using the method of acid hydrolysis of calcium germanide-silicide, Royen and Rocktäschel (23) prepared germylsilane, germyldisilane and digermylsilane as well as some higher hydrides of germanium and silicon.

Timms et al (26) used acid hydrolysis of a germanium-silicon-magnesium alloy to obtain mixed hydrides of the type $Si_xGe_yH_{2x+2y+2}$, which they separated by vapour phase chromatography. They observed fifteen peaks characteristic of germanium-silicon hydrides with different total number of atoms, different germanium-silicon ratios, or different degrees of branching. All of the compounds appeared to have a terminal germyl group.

Drake and Jolly (43) prepared GeH_3PH_2, Ge_2PH_7, GeP_2H_6 and GeH_3AsH_2 by passing a mixture of germane and phosphine or arsine through an ozonizer at -78^o. They could not separate germyl phosphine from digermane and the higher germanes produced.

Royen et al (25) used acid hydrolysis of a solid solution of calcium germanide with calcium phosphide, calcium nitride, or calcium arsenide to produce germylphosphine,germylamine and germylarsine respectively.

OUTLINE OF THE RESEARCH PROBLEM

Prior to 1960 when this work was started, our knowledge of the preparation and properties of compounds containing the GeH_3 group was meagre, and only 20 germyl compounds were described in the literature. Alkylgermanes had been prepared in high yield by the coupling reaction of germyl sodium with alkyl halides, and it was of interest to determine if germyl sodium would couple with other halides. Since there was no method reported for the specific preparation of digermane in high yield, the first attempt was to react germyl sodium with a halogermane, in the hope of obtaining digermane in high yield.

The yields obtained from these experiments led to a further investigation of the usefulness of germyl sodium as a reagent for the preparation of compounds containing the germyl group. Germyl sodium was allowed to react with the methylchlorosilanes, and silicon tetrachloride, and the series of methylgermylsilanes was prepared. The change in the physical properties (including melting point, boiling point, infrared and n.m.r. spectra) of these compounds as methyl groups were successively replaced by germyl groups was determined.

During the course of this work, the preparation of germylsilane by an electric discharge method was reported in the literature (22) and it was of interest to see if this compound could also be prepared from germyl sodium and a halosilane.

The successful preparation of the methylgermylsilanes prompted preparation of an analogous series with germanium replacing silicon. The first member of this series, 1,1,1-trimethyldigermane was prepared.

EXPERIMENTAL

INTRODUCTION

Since most of the compounds used and prepared in this investigation were volatile and in some cases reacted with air or moisture, it was necessary to use high vacuum techniques for their manipulation. For this purpose, a standard high vacuum apparatus, similar to that described by Jolly (44), was constructed. A detailed description of vacuum techniques is not necessary here, since comprehensive reviews are available (44,45,46,47,48). However, the more important techniques that were used will be described briefly.

The use of high vacuum techniques has some advantages and disadvantages which were of special significance in this investigation. Some of the advantages are; a) materials of sufficient volatility may be transferred quantitatively by distillation, b) reactions may be done with small amounts of gas, c) small quantities of products may be isolated and identified, d) compounds can be confined in glass containers in the absence of air or moisture, and e) highly toxic or spontaneously inflammable compounds can be handled with comparative safety. Disadvantages are; a) materials with normal boiling points above about 200° cannot be conveniently transferred by distillation at room temperature, b) the complete separation of compounds with boiling points differing by less than about 30° is difficult by fractional distillation, and c) large scale preparations are usually impractical.

APPARATUS

The vacuum apparatus, shown schematically in Figure 1, was constructed of Pyrex glass and consisted of four main sections;

1. a pumping section.
2. storage vessels.
3. distillation line for the separation and purification of volatile compounds.
4. a central section for the measurement of pressure, molecular weight and other physical properties.

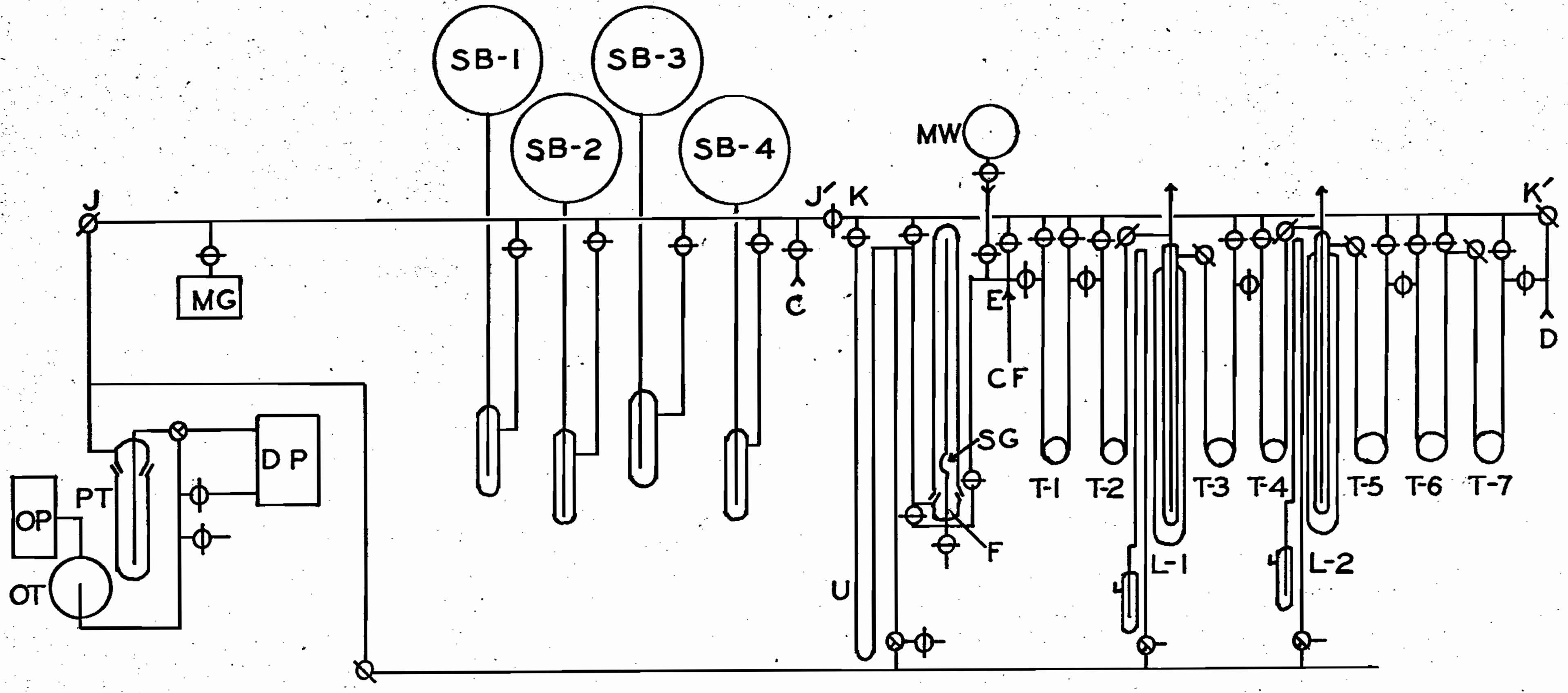
All stopcocks and ground glass joints were lubricated with Kel-F 90 fluorocarbon grease (Minnesota Mining and Manufacturing Co.), and regreased as needed. The apparatus was cleaned periodically using a concentrated solution of alkali permanganate followed by rinsing with concentrated HCl and distilled water.

Pumping System

The apparatus was evacuated using a single stage mercury diffusion pump, DP, backed by a rotary oil pump, OP.

<u>Figure 1</u>

Vacuum Apparatus


SB-1
SB-3
SB-2
SB-4
MW
J
J′
K
K′
MG
C
E
CF
SG
F
D
DP
PT
OP
OT
U
T-1
T-2
L-1
T-3
T-4
L-2
T-5
T-6
T-7

A ballast bulb, BB, reduced the back pressure, and a vacuum of 10^{-4} mm of mercury was obtained as measured with a tilting McLeod gauge, MG. A removable pump trap, PT, which was cooled in liquid air, protected the pumps from contamination by condensable vapours. A three-way stopcock allowed air to be pumped from the apparatus without passing through the mercury pump. This prevented contamination of the latter by mercuric oxide. The oil trap, OT, prevented oil being drawn back into the apparatus in the event of a power failure.

Storage System

Volatile materials were stored in 5-litre bulbs, SB 1, 2, 3, 4, connected to the manifold, JJ'KK', through condensation traps and stopcocks. Germane and hydrogen chloride were stored in these bulbs for long periods without decomposition. Less volatile materials were sealed in glass "break-seal" vials and stored at room temperature if stable, or at -78° or -194° (liquid air temperature) if unstable.

Distillation Line

Volatile materials were introduced into or removed from the system by means of stopcocks and ground glass joints C, D, and E, which also served as points of attachment for auxiliary apparatus. Seven distillation traps, T-1 to T-7, of about 70 ml capacity and two "LeRoy" low temperature fractionation columns (49), L1 and L2, were interconnected as shown in Figure 1. Purifications were done by distillation through traps immersed in "slush baths" or through "LeRoy stills" immersed in liquid air. The "LeRoy stills" were more useful because the temperature could be continuously varied by suitable adjustment of the pressure in the jacket and the current through the heating coil.

Measurement Section

This section consisted of a removable condensation tube, CF, a thin walled molecular weight bulb, MW, of accurately known volume (263.9 ml), a sensitive, soft glass spoon gauge (46), SG, used as a null point indicator, and a mirror backed mercury manometer, U. There were two advantages in using a spoon gauge for pressure measurements;

1) measurements could be made in the absence of mercury vapour, and

2) measurements at all pressures were done in a constant known volume.

TECHNIQUES

Temperature Measurement

Temperatures below 0° were measured to ±0.1° with copper constantan thermocouples in conjunction with a sensitive potentiometer (Rubicon Instruments, Model 2733). Approximate temperatures in the range 0° to -43° were measured with an alcohol in glass thermometer, and temperatures above 0° were measured with accurate mercury in glass thermometers.

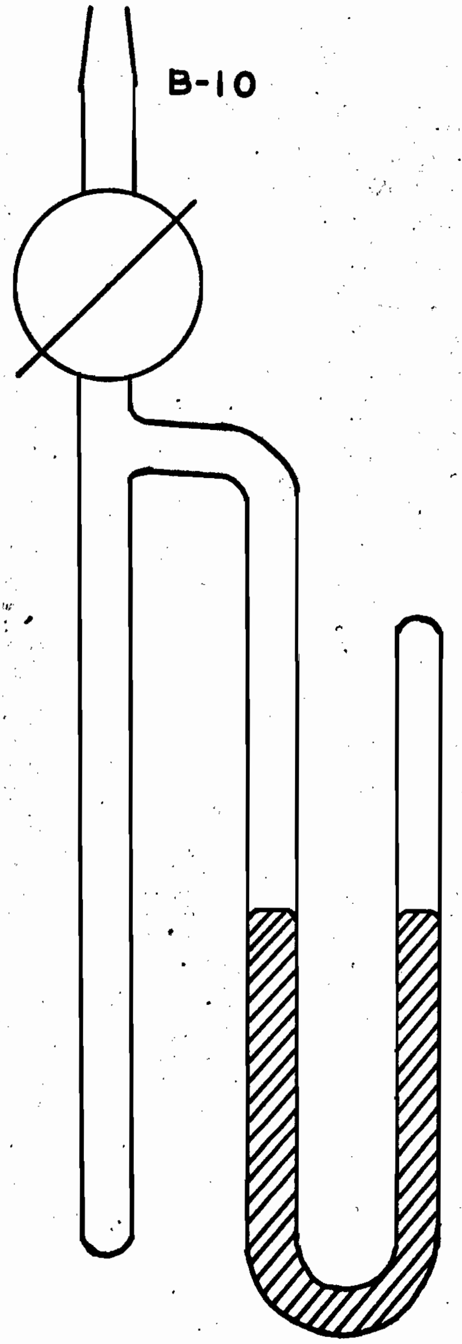
Pressure Measurements

Pressures were measured in most cases using the soft glass spoon gauge attached to the apparatus by means of the graded seal, F. The null point was indicated when the fine pointer surmounting the spoon was colinear with two fine diametrically opposite lines on the outer jacket. The air pressure required to equalize the spoon was then read directly from the manometer, to ±0.4 mm. If there was no danger of gas-mercury vapour interaction, pressures in the range 1 to 20 mm were measured with a cathetometer to ±0.02 mm, using a demountable mercury manometer, Figure 2, which was attached at ground joint E.

Vapour pressures below room temperature were measured

Figure 2

Demountable Manometer



DEMOUNTABLE MANOMETER

FIGURE 2

by condensing the sample in the cold finger, CF, surrounding it with the appropriate slush bath, and measuring the pressure with the spoon gauge. Measurements of vapour pressure in the range 1 to 20 mm, when there was no danger of gas-mercury vapour interaction, were done using the cold-finger of the demountable manometer instead of the cold-finger, CF. In this case the cathetometer was used to read the pressure.

Vapour pressures above room temperature were measured in a sealed all-glass vessel, to which a direct reading mercury manometer was attached. This assembly was immersed in an oil bath and pressures were measured using a cathetometer.

Determination of Molecular Weight and Purity

The molecular weight of a volatile compound was determined by direct weighing of the vapour in a bulb, MW, of known volume, at a measured pressure and temperature. Application of the Ideal Gas Equation gave the molecular weight with an accuracy of one per cent.

The purity of a new volatile compound was tested by measuring the vapour pressure at a fixed temperature of successive small samples of the compound. When the measurements were constant to within ±0.05 mm, the sample was considered tensiometrically pure. The purities of known volatile compounds were checked by measuring their vapour pressures at known temperatures and comparing these with the values reported in the literature.

Determination of Melting Point

Melting points below room temperature were determined by the dropping plunger technique described by Stock (47). The plunger consisted of a soft iron rod encased in glass, attached to a thin glass rod with a glass cross on the end. It was placed in the cold finger, CF, of the vacuum apparatus, Figure 1, and was raised magnetically about two inches and then allowed to rest on a ring of material which was condensed below it. The temperature of the cold finger, immersed in a slush bath, was raised slowly (0.5°/minute) and the temperature at which the plunger fell was taken as the melting point. Melting was confirmed by visual observation of the liquid phase.

Purification of Volatile Materials

Volatile compounds were purified by low temperature fractional distillation through the "LeRoy stills" or through the traps retained at the required temperature by slush baths. Liquid air was used to condense and transfer volatile compounds from trap to trap.

Infrared Spectra

Infrared spectra of gaseous compounds were recorded on one or more of the following Perkin-Elmer instruments:

1) Infracord Model 137 double beam spectrophotometer with sodium chloride optics for the range 4000-670 cm^{-1}.

2) Model 21 double beam spectrophotometer with sodium chloride optics for the range 4000-650 cm^{-1}.

3) Model 421 double beam grating spectrophotometer which recorded spectra in the range 4000-550 cm^{-1}.

The 10 cm gas cell used (Research and Industrial Instruments Co., England) had 5 mm thick NaCl or KBr windows, held in place by screw caps, using Viton "O" rings for sealing. The windows were repolished when necessary using an alcoholic suspension of alumina on a rotating wheel.

Spectra were recorded at various pressures in order to detect as many weak bands as possible and to resolve the strongest bands. Care was taken, in the case of materials having low vapour pressure, to avoid condensation of liquid on the cell windows. The spectra were recorded only in the gas phase because it was necessary to recover the small amount of sample available.

Proton Nuclear Magnetic Resonance Spectra

Proton nuclear magnetic resonance (n.m.r.) spectra were taken on a Varian Associates HR-60 high resolution spectrometer, operated at 60 Mc./second and room temperature. Samples of the neat liquid were sealed in capillary tubes which were then placed in a standard thin walled n.m.r. tube containing carbon tetrachloride. Small amounts of tetramethylsilane (TMS, τ= 10.0 ppm, Anderson Chemical Co.) were added to the carbon tetrachloride as an external standard and chemical shifts were reported in τ units. Calibration was by means of 60 cps sidebands on the TMS peak. Spectra were scanned several times in each direction and the average peak positions were reported.

Measurements were repeated on a Varian Associates A-60 spectrometer and the integrated areas of the peaks were also recorded. The n.m.r. spectra were recorded using samples in the pure liquid form rather than in dilute solution because it was necessary to recover the small amounts of sample available.

Inert Atmosphere

An evacuable, inert atmosphere "dry" box was used for manipulation of air or moisture sensitive materials such as the alkali metals or amalgams.

Gas Chromatography Using Infrared Detection

Since some of the compounds prepared are unstable in the presence of the thermal or ionization detectors usually used in vapour phase chromatography (VPC), the strong absorption band at 2050 cm^{-1} due to the GeH_3 stretching vibrations was used as the means of detecting the emergence of the sample from the column. A 10 cm gas cell with NaCl windows was fitted with an entrance and exit tube, and connected with Tygon tubing to the exit of the VPC column. The column, 17 mm internal diameter and 8 feet long, was packed with 20 per cent by weight silicone grease on acid washed firebrick (40-60 mesh; Matheson, Coleman and Bell). This column was used at room temperature, 22°, with nitrogen as a carrier gas at a flow rate of about 700 ml/minute. The infrared cell was placed in the sample beam of the Perkin-Elmer Model 421 spectrophotometer, the monochrometer was set at 2050 cm^{-1} and the scan clutch disengaged to allow use of the drum drive as a time scale. The exit tube of the gas cell was connected by means of Tygon tubing and stopcocks to one of three collection traps cooled in liquid air.

In order to avoid decomposition in the presence of air, it was necessary to use the following method to transfer the sample to the VPC column. The volatile liquid sample was sealed under vacuum in a small tube fitted with a serum cap. To facilitate removal of the sample with a syringe, about 10 cc (S.T.P.) of dry nitrogen was injected into the tube with a gas syringe. The sample was removed from the small tube using another syringe and then introduced into the inlet of the column by injection through a serum cap. The inlet system was maintained at 40^{o} to hasten volatilization of the sample.

If a VPC detector is capable of detecting only one component of a mixture, it cannot, obviously, give any information on the emergence of other components of the mixture from the column. Thus, it cannot indicate the extent of separation obtained on the column, or the purity of the detected component. In spite of these limitations, the absorption band due to the GeH_3 stretching vibrations was used as a means of detecting the emergence of compounds containing the GeH_3 group from the column. A very strong absorption band was necessary so that it could be detected when the compound was diluted with nitrogen. The elution curve was sharp and tailed out only slightly. Any material eluted before the GeH_3 containing sample was collected in one trap, the sample was collected in a second trap, and the tail of the sample peak, along with any material eluted after the required sample, was collected in a third trap.

Fractional Codistillation on a "Cady Column"

In addition to VPC, some materials were purified by fractional codistillation on a column described by Cady and Siegwarth (50). The column was a ¼ inch diameter copper U-tube with 40 cm arms, packed with 55 mesh silicon, and dry nitrogen was used as the carrier gas. The effluent gas from the "Cady column" was passed through an infrared gas cell attached to the Perkin-Elmer Model 421, as was done for the VPC separations.

Characterization of Compounds

New compounds were characterized by measuring as many of the following physical properties as possible with the amount of sample available.

1) Elemental analysis*
2) Molecular weight in the vapour phase.
3) Vapour pressure-temperature relationship.

---

[*] Elemental analyses were done by Scwarzkoff Microanalytical Laboratory, New York.

4) Boiling point at 760 mm (extrapolated or interpolated).
5) Latent heat of vaporization.
6) Trouton's Constant.
7) Melting Point.
8) Infrared spectrum.
9) Proton n.m.r. spectrum.

PREPARATION OF MATERIALS

Germane GeH_4

The reduction of germanium dioxide in aqueous hydrogen bromide by an aqueous solution of sodium borohydride proceeds smoothly at room temperature to give germane in almost quantitative yield. This preparation was originally done (33) by simply dissolving the germanium dioxide in boiling 1 M hydrobromic acid and cooling the solution in an ice bath before adding the sodium borohydride solution, and yields of germane of 60-75 per cent were reported. However, when the germanium dioxide is refluxed in 1 M hydrobromic acid for about 6 hours and the solution is not cooled during the addition of sodium borohydride, the yield is almost quantitative (18). This method of preparation of germane was chosen over the others available (27,28,29,30,31,32,41,51) because of its simplicity and high yield.

Germane was prepared in the apparatus shown in Figure 3. A one litre, 3-necked flask A, was equipped with a dropping funnel B, a magnetic stirring bar, a reflux condenser C, and a nitrogen inlet which extended below the level of the liquid in the flask. The condenser was maintained at -78° in order to retain the bulk of the solvent, and it was attached to a trap D, which in turn led to three traps E, F, G and a "LeRoy still" L, on the vacuum apparatus. A mercury "blow off" H, on the "LeRoy still" served to allow hydrogen produced in the reaction, and nitrogen to escape without the admission of air or moisture.

Germane was collected in the traps, and then purified by vacuum distillation through the "LeRoy still", maintained at -150°.

In a typical preparation, three grams (28.9 mmoles) of germanium dioxide was refluxed for 6 hours with 375 ml of 1 M hydrobromic acid solution (48 ml of 48% HBr with 327 ml of H_2O). Twenty-five grams of sodium borohydride was dissolved in 225 ml of water and added over a period of 1.5 hours to the GeO_2-HBr solution in a nitrogen atmosphere. The condensable gases were trapped in liquid air. The crude

Figure 3

Apparatus Used for the Preparation of Germane

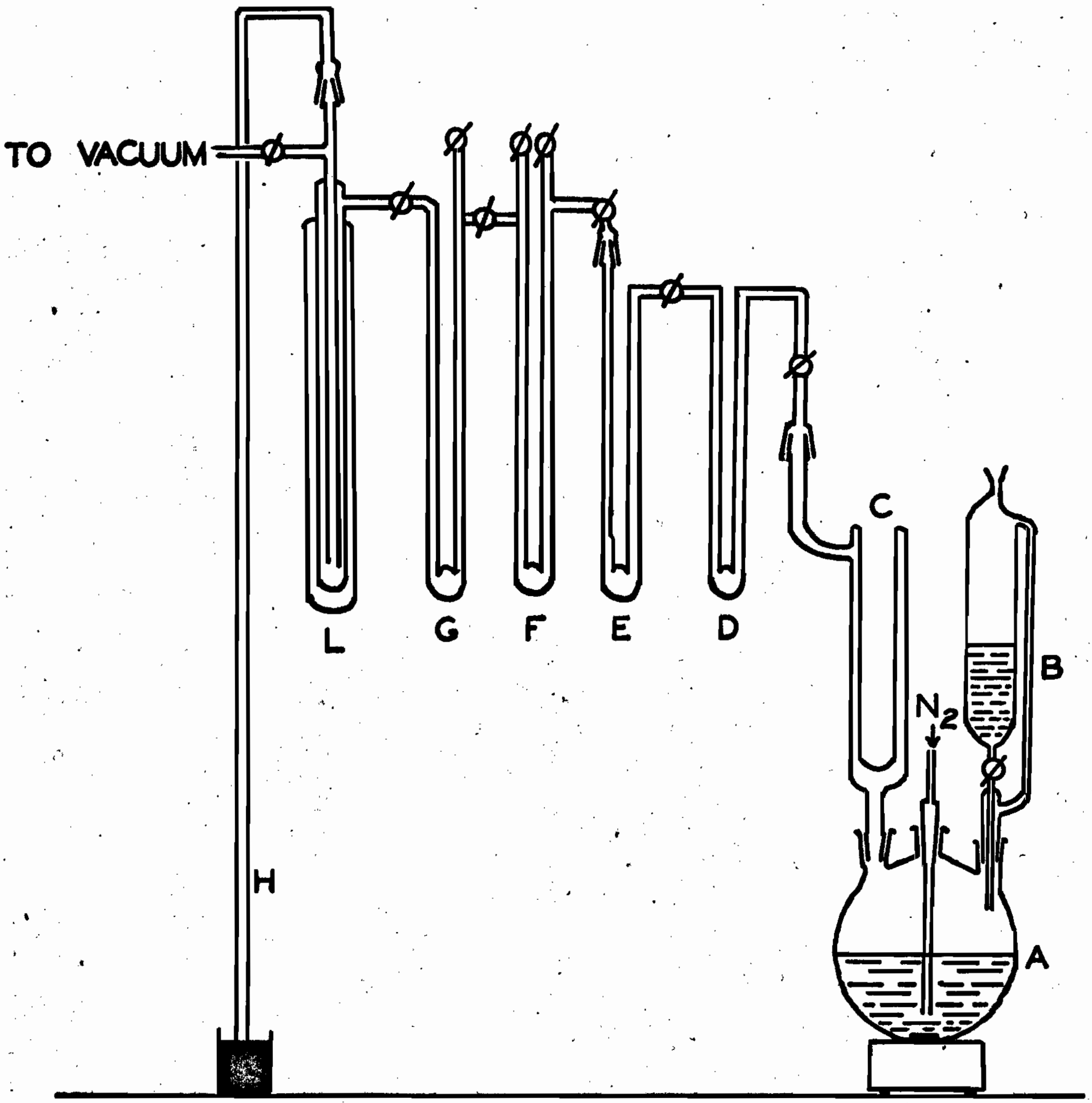


FIGURE 3

germane was purified by distillation at -150°. The yield of germane, volatile at -150°, was 27.8 mmoles (96% of GeO_2; Found: M, 76.6. Calcd. for GeH_4: M, 76.6). Germane was stored as a gas at room temperature for future use.

Bromogermane GeH_3Br

Monobromogermane was prepared by the direct action of bromine on germane:

$$GeH_4 + Br_2 \longrightarrow GeH_3Br + HBr \qquad \ldots 6)$$

This reaction also produces a mixture of di-, tri- and tetrabromogermanes, which are less volatile than monobromogermane, and are easily separated from it by low temperature fractionation. In a typical reaction, bromine (15.0 mmoles) was condensed in successive small portions on germane (15.0 mmoles) in a 500 ml flask cooled in liquid air, and the mixture was warmed slowly until the colour of bromine just disappeared. Monobromogermane was then separated from the mixture of products by several distillations at -64°. (Found: M, 158.0; v.p. 27.5 mm at -23°. Calcd. for GeH_3Br: M, 155.5; Lit. (15) v.p. 28.0 mm at -23°. Yield, 55%).

Germyl Sodium GeH_3Na

Germyl sodium was prepared according to the method of Kraus and Carney (41) by bubbling germane through a solution of sodium in liquid ammonia. A weighed amount of freshly cut metallic sodium was placed in the reaction vessel (Figure 4), and degassed at room temperature for several hours. About 10 ml of anhydrous ammonia was condensed in the bulb of the reaction vessel R, which was then kept at -45° while the sodium dissolved, giving a deep blue solution. A measured excess of germane from the 50 ml bulb B, was bubbled slowly through the liquid ammonia solution at -45° until well after the blue colour of sodium in liquid ammonia had disappeared. The excess germane and some ammonia were trapped in liquid air. In order to insure that all of the sodium had reacted to produce germyl sodium it was necessary to add germane even after the deep blue colour had disappeared. The liquid ammonia was pumped off at -45° and then the ammonia of crystallization was removed from the remaining white solid by continuous pumping for 4 to 8 hours at -23°. Ammonia is lost in the following four stages at -33° (41):

$$GeH_3Na\cdot 6NH_3 \xrightarrow{315\text{ mm}} GeH_3Na\cdot 4.5NH_3 \xrightarrow{23\text{ mm}} GeH_3Na\cdot 2NH_3 \xrightarrow{3\text{ mm}} GeH_3Na \quad \ldots 7)$$

The resulting pure, ammonia-free germyl sodium was stored in the reaction vessel at -78° under vacuum until it was used in

Figure 4

Reaction Vessel used for Germyl Sodium

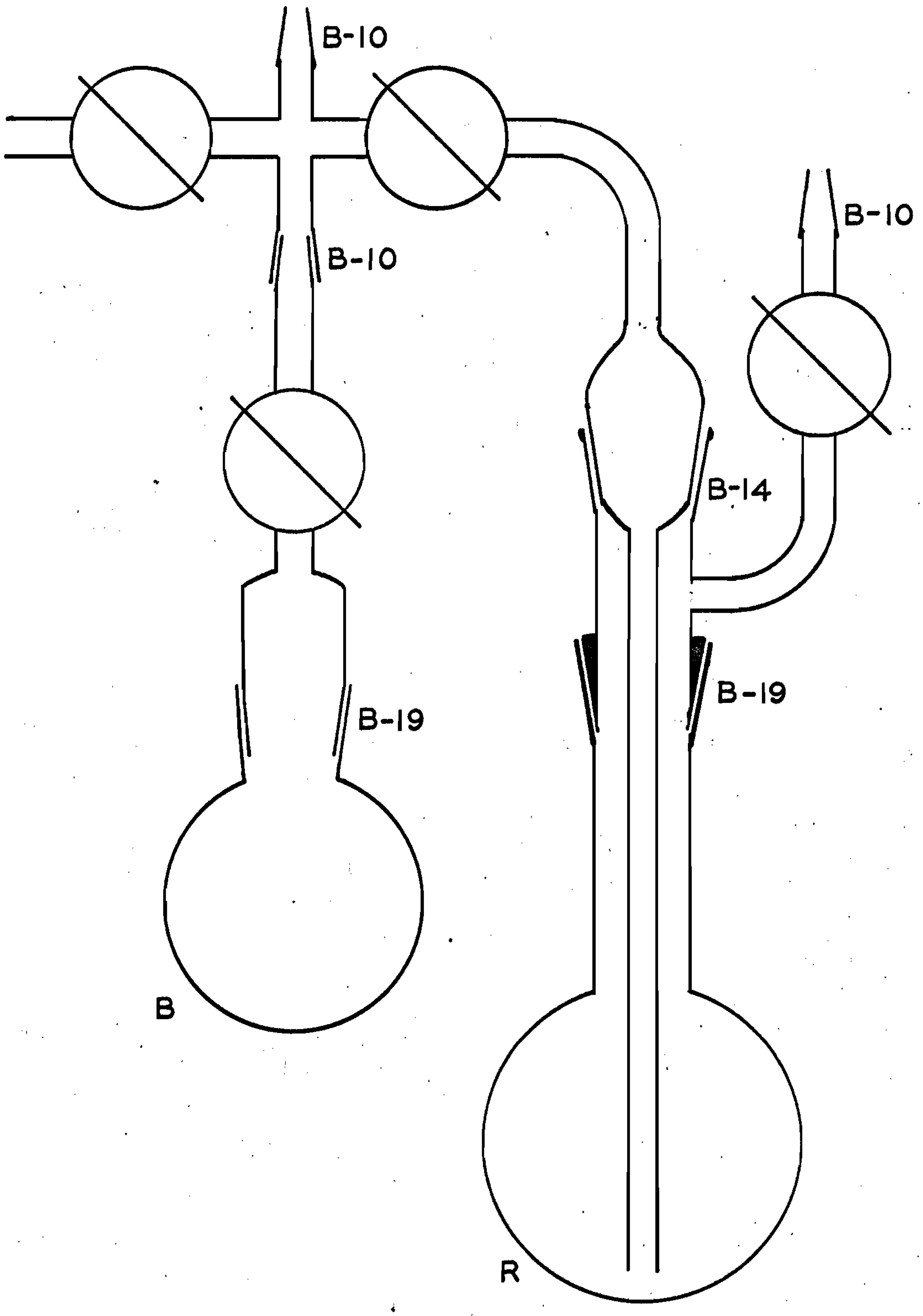


FIGURE 4

a reaction. Because of its instability, it was necessary to prepare germyl sodium for each reaction immediately before it was required.

Purification of Sodium

Sodium metal used in the reaction with bromogermane was purified by three trap-to-trap vacuum sublimations using a hand torch to heat the sodium. The purified sodium was then sublimed into the reaction vessel in the form of a mirror on the walls. Freshly cut pieces of sodium, prepared and transferred in the dry box were used in the preparation of germyl sodium.

Sodium Amalgam

Sodium amalgam was prepared in a nitrogen atmosphere by adding sodium metal to mercury and grinding them together. Sodium was added until the amalgam was just fluid. The resulting amalgam was filtered through paper to remove any oxide or undissolved sodium. The filtered amalgam was placed in a 100 ml round bottomed flask with a magnetic stirring bar, and was degassed with stirring for one hour before it was used.

Other Materials

Table I summarizes the methods of purification and purity of other reagents used.

TABLE I

Compound	Method of Preparation or Supplier	Method of Purification	Molecular Weight	
			Calcd.	Found
Trimethylchlorosilane $(CH_3)_3SiCl$	Dow Corning Corp. (Purified Grade)	Vacuum Distillation	108.6	110.0
Dimethyldichlorosilane $(CH_3)_2SiCl_2$	Dow Corning Corp. (Purified Grade)	Vacuum Distillation	126.0	128.8
Methyltrichlorosilane CH_3SiCl_3	Dow Corning Corp. (Purified Grade)	Vacuum Distillation	149.5	150.8
Trimethylfluorosilane $(CH_3)_3SiF$	$[(CH_3)_3Si]_2O + BF_3$	Vacuum Distillation	92.1	93.7
Silicon Tetrachloride $SiCl_4$	Fisher Scientific Co.	Refluxing over Cu and Distillation	169.9	169.2
Silicon Tetrafluoride SiF_4	Matheson Co.	Vacuum Distillation	104.1	104.2
Bromosilane SiH_3Br	$C_6H_5SiH_3$ + HBr	Vacuum Distillation	111.0	110.8
Chlorine Cl_2	Matheson Co.	Vacuum Distillation	70.9	70.4
Trimethylbromogermane $(CH_3)_3GeBr$	$(CH_3)_4Ge$ + HBr	Vacuum Distillation	197.6	199.8
Trimethylfluorogermane $(CH_3)_3GeF$	$[(CH_3)_3Ge]_2O + GeF_4$	Vacuum Distillation	136.7	136.6

Comparison was also made of the infrared spectra with those in the literature.

RESULTS

DIGERMANE Ge_2H_6

There are no methods available for the preparation of digermane in high yield. Digermane usually occurs as a by-product in yields of about 5 per cent in the preparation of germane (29,30,31,52,53). It has also been prepared in low yield by subjecting germane to an electric discharge (5). Several methods have been reported for the preparation of fully substituted digermanes, Ge_2R_6, where R = CH_3, C_2H_5, C_6H_5, C_6H_{11} or p-$CH_3C_6H_4$ (54,55,56,57,58). Some of these methods, with suitable modifications, have been used in an attempt to prepare digermane in high yield.

Germyl Sodium and Bromogermane

The reaction between germyl sodium and bromogermane was carried out a total of nine times under varying reaction conditions. Measurable amounts of digermane were produced in only three of these experiments, and the best yield of crude digermane was only 6.8 per cent. The other attempts did not yield sufficient digermane for it to be identified by infrared measurements. The best results were obtained when bromogermane (5.68 mmole) was condensed on a slight deficiency of freshly prepared ammonia-free germyl sodium (4.1 mmoles) and the mixture was allowed to react first at -45° and then at -23° for a total of two hours. The volatile products were separated by low temperature fractional distillation. The fraction volatile at -130° was germane (0.38 mmoles) and accounted for 9.4 per cent of the germyl sodium available. The fraction (0.28 mmoles, 6.8%) volatile between -120° and -100°, which was thought to contain digermane, had the vapour pressure of digermane (Found: v.p. 25.4 mm at -46°. Lit. (52) for Ge_2H_6: v.p. 24.0 mm at -46°) but its molecular weight was low (Found: M, 137. Calcd. for Ge_2H_6: M, 151.2) indicating the presence of a low molecular weight impurity which, however, could not be identified. An infrared spectrum of this fraction contained two peaks at 1141 cm^{-1} and 828 cm^{-1} which have not been observed in the spectrum of pure digermane (59) and hence must be due to the unidentified impurity. This fraction accounted for 6.8 percent of the germyl sodium available. Attempts to remove the unidentified impurity by fractional distillation were unsuccessful.

In an attempt to increase the yield of digermane, a five-fold excess of bromogermane (23.3 mmoles) over germyl sodium (4.2 mmoles) was used, so that a solid-liquid interaction might occur. The materials were allowed to react for two hours at -30°, after which time the volatile products were separated. Germane (1.42 mmoles) was produced to the extent of 33 per cent of the germyl sodium available but only a trace of digermane was present, as indicated by infrared measurements. Bromogermane (19.75 mmoles) was recovered, indicating that 3.5 mmoles were consumed in the reaction.

Three different solvents were also tried in a further attempt to increase the yield of digermane in the reaction of germyl sodium with bromogermane. In one experiment, about 2 ml of tetrahydrofuran (THF) which had been dried over and distilled from sodium was condensed on to the germyl sodium. The reaction vessel was held at -78° overnight, during which time the liquid THF changed from deep blue to light brown. The reaction products were distilled out of the reaction vessel and separated. Germane (2.49 mmoles) was present to the extent of 25 per cent of the germyl sodium available, and there was no evidence of any digermane.

The reaction was repeated using 2-3 ml of dried, redistilled benzene as a liquid medium and the mixture (5.6 mmoles of GeH_3Na, 9.2 mmoles of GeH_3Br) was allowed to react at 0° for two hours. The reaction products were separated by low temperature fractionation, and germane (2.8 mmoles) accounting for 50 per cent of the germyl sodium available, was recovered. The fraction volatile at -78° and trapped at -150° had a molecular weight of 137 (Calcd. for Ge_2H_6: M, 151.2. Calcd. for GeH_3Br: M, 155.5) and a vapour pressure of 13.8 mm at -51° (Calcd. for Ge_2H_6: v.p. 17.5 mm. Calcd. for GeH_3Br: v.p. 4.7 mm). Repeated slow distillations of this mixture through a trap at -78° resulted in fractions which increased in molecular weight to 143.2, but the vapour pressure of the final fraction was still lower than that of digermane. This material decomposed after about 3 weeks at room temperature, and since digermane is stable, the mixture must have contained a considerable amount of an unstable component, probably bromogermane. The measured infrared spectrum did not rule out the presence of bromogermane.

In another experiment, diethylene glycol dimethyl ether (diglyme) was used as a liquid medium. A deficiency of bromogermane (2.9 mmoles) was bubbled through the chocolate brown mixture of diglyme and germyl sodium (3.4 mmoles) at -23°, and then the reaction mixture was warmed slowly to room temperature. Vigorous bubbling occurred, probably due to hydrogen evolved in the decomposition of germyl sodium. After about one hour, the reaction products were removed but only germane (0.64 mmoles) could be separated from the large excess of diglyme.

Bromogermane and Sodium

Bromogermane (1.57 mmoles) was condensed in a reaction vessel the walls of which were coated with a freshly prepared sodium mirror. The reaction vessel was allowed to remain at room temperature overnight. Only 0.60 mmoles of volatile material, identified as bromogermane was recovered and no digermane was detected by infrared measurements.

Bromogermane and Sodium Amalgam

Bromogermane (3.0 mmoles) was condensed on a large excess of sodium amalgam previously prepared in a 50 ml. flask, and the flask was warmed to room temperature. Magnetic stirring was started as soon as the amalgam became liquid. After about 10 minutes, a large amount of fine black powder appeared on the walls of the vessel and on the surface of the amalgam. The mixture was stirred continuously overnight. When the reaction vessel was opened, only a small amount of volatile material was recovered at room temperature and more was recovered on heating the reaction vessel to about 60° with continuous pumping for several hours. Germane (1.58 mmoles, Found: M, 76,6. Calcd. for GeH_4: M, 76.6) was the only volatile product.

Germyl Sodium and Chlorine

A large excess of chlorine (34 mmoles) was condensed on the ammonia-free germyl sodium (7.3 mmoles) and as the liquid air bath was removed and replaced by a -78° bath, there was a bright yellow flash, followed immediately by a loud report. At the same time, the white germyl sodium turned black.

The reaction vessel was kept at -78° for an additional 10 minutes, and then cooled in liquid air to check for non-condensable gas. About 0.5 mmoles of non-condensable material, probably hydrogen, was found. The condensable materials were removed, and separated by low temperature fractionation. The results showed that 11.9 mmoles of chlorine were consumed, and 15.1 mmoles of hydrogen chloride (Found: M, 36.7. Calcd. for HCl: M, 36.46) and 0.63 mmoles of germanium tetrachloride (Found: M, 209. Calcd. for $GeCl_4$: M, 214.4) were recovered. In addition, the solid material remaining in the reaction vessel contained 4.5 mmoles of chloride ion. There was no evidence of digermane.

TRIMETHYLGERMYLSILANE $(CH_3)_3SiGeH_3$

Germyl Sodium and Trimethylchlorosilane

Five attempts were made to prepare trimethylgermylsilane by the reaction of ammonia-free germyl sodium with trimethylchlorosilane using essentially the same reaction conditions. In one of these attempts, no detectable amount of trimethylgermylsilane was produced, while only traces of the desired product were produced in two other experiments. In one of the experiments which produced an appreciable amount of trimethylgermylsilane, trimethylchlorosilane (9.1 mmoles) was condensed on ammonia-free germyl sodium (10.4 mmoles) in an evacuated reaction vessel, which was placed in a -23° bath and warmed over a period of 4 hours to 0°. The volatile reaction products were distilled through traps at -45° and -140°, and the small amounts of materials trapped at -45° or volatile at -140° were discarded. The material trapped at -140° was then distilled slowly at -78° until a fraction containing almost pure trimethylgermylsilane remained (Found: M, 148.0. Calcd. for $(CH_3)_3SiGeH_3$: M, 148.8). Since an infrared spectrum of this material showed an Si-O-Si absorption band at 1080 cm^{-1} the material was purified further by passing it through a VPC column using an infrared detector. In this way, 1.1 mmoles of pure material (Found: M, 148.4. Yield: 12.1% of $(CH_3)_3SiCl$ used) were recovered. The total yield of product was estimated to be 42 per cent by molecular weight determination of the fraction collected at -140°, based on the reaction:

$$(CH_3)_3SiCl + GeH_3Na \longrightarrow (CH_3)_3SiGeH_3 + NaCl \qquad \text{... 8)}$$

The following results were obtained by elemental analysis of the pure compound:

Found: C, 24.49%; H, 8.08%; Si, 18.76%; Ge, 48.67% (by difference)

Calculated: C, 24.21%; H, 8.12%; Si, 18.87%; Ge, 48.77%

Trimethylgermylsilane is a clear colourless liquid which melts at -77.4±0.2°, the average of four determinations. The vapour pressure (Table II and Figure 5) data show that the extrapolated boiling point is 73.6°, the heat of vaporization, ΔH_v, is -7.24 kcal./mole, and Trouton's Constant is 20.88 calories $degree^{-1}$ $mole^{-1}$. The following vapour pressure equation, valid in the range 15.0 to 41.4°, which best fits the measured values, was calculated using the method of least squares, as described in Appendix II.

TABLE II

VAPOUR PRESSURE OF TRIMETHYLGERMYLSILANE

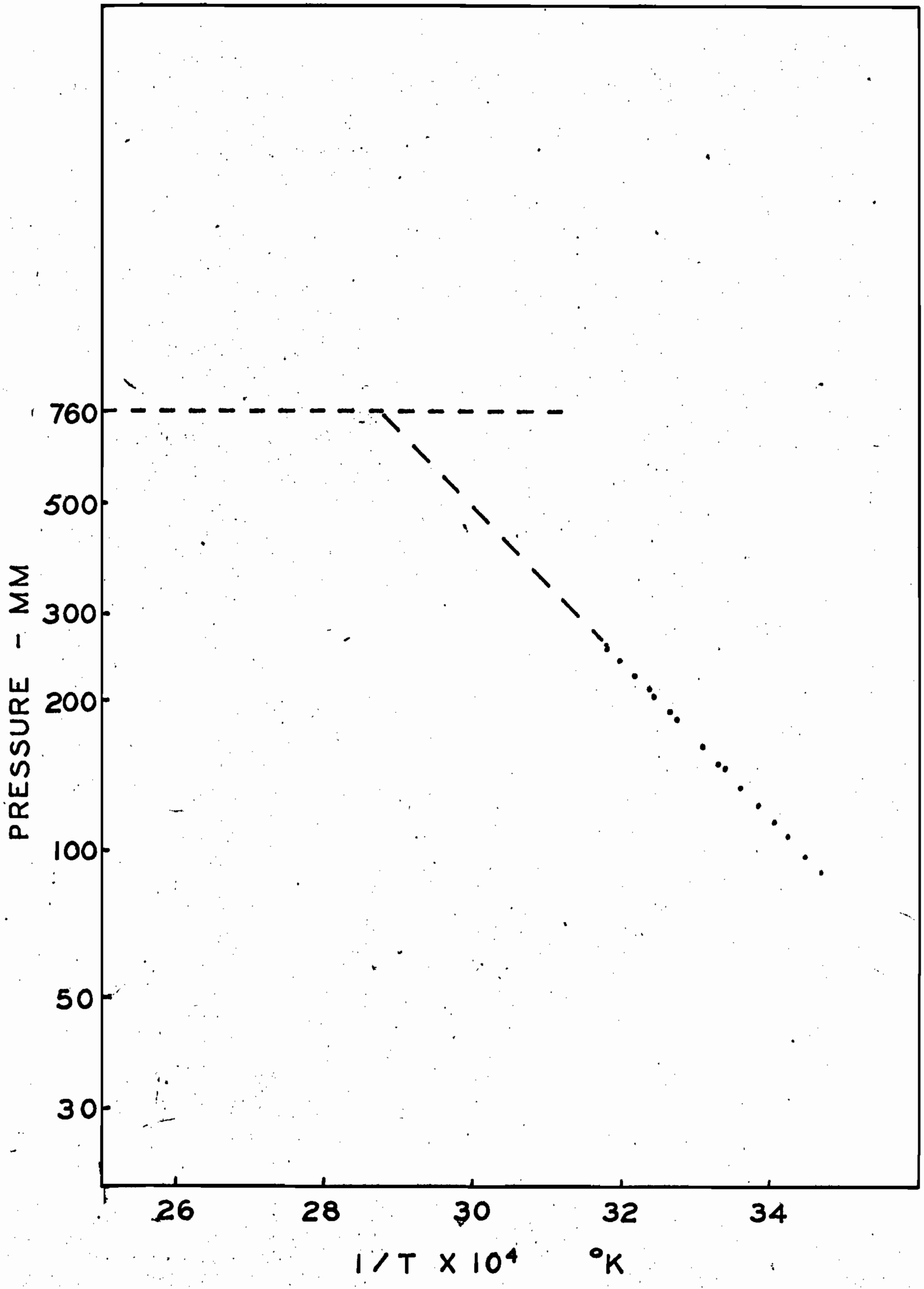
Temperature °C	Pressure mm Experimental	Pressure mm Calculated	Difference mm
15.00	90.00	89.90	0.10
16.90	97.81	97.65	0.16
19.00	106.70	106.87	-0.17
20.50	113.59	113.89	-0.30
22.50	123.34	123.85	-0.51
22.60	123.27	124.36	-1.09
24.50	134.75	134.53	0.22
26.30	146.06	144.79	1.27
27.20	149.57	150.17	-0.60
29.00	161.98	161.41	0.57
32.20	183.34	183.14	0.20
33.00	190.78	188.94	1.84
35.10	204.22	204.89	-0.67
35.70	211.52	209.65	1.87
37.50	224.02	224.47	-0.45
39.50	242.90	241.96	0.94
41.30	255.66	258.64	-2.98
41.40	259.00	259.60	-0.60

$$\log P_{mm} = 3.030182 - 0.001140\,T + 1.75 \log T - 1455.88/T$$

Figure 5

Vapour Pressure of Trimethylgermylsilane

Pressure vs 1/T


760
500
300
200
100
50
30
PRESSURE - MM
26
28
30
32
34
1/T X 10⁴ °K

$$\log P_{mm} = 3.03018 - 0.00114T + 1.75 \log T - 1455.88/T$$

The proton n.m.r. spectrum of the neat liquid consisted of two sharp peaks, having areas in the ratio of 3:1 and $\tau(CH) = 9.97$ ppm and $\tau(GeH) = 7.42$ ppm relative to dilute tetramethylsilane (TMS, $\tau = 10.0$ ppm) in carbon tetrachloride (Figure 6).

<u>Germyl Sodium and Trimethylfluorosilane</u>

Trimethylgermylsilane was also prepared by the reaction of trimethylfluorosilane with germyl sodium. A small excess of trimethylfluorosilane (6.37 mmoles) was condensed on ammonia-free germyl sodium (5.5 mmoles). The reaction mixture was warmed from -23° to -3° over a period of 5.5 hours. After removal of unreacted trimethylfluorosilane (1.6 mmoles) and most of the hexamethyldisiloxane impurity by distillation at -45°, trimethylgermylsilane (2.4 mmoles) (Found: M, 148.5. Calcd. for $(CH_3)_3SiGeH_3$: M, 148.8) was distilled at -78°. The latter fraction still contained hexamethyldisiloxane as an impurity as indicated by its Si-O-Si absorption band at 1080 cm^{-1}. Since this impurity could not be removed by distillation, the fraction was passed through the VPC column using the infrared detector. In this way pure trimethylgermylsilane (0.96 mmoles, Yield: 18%) was obtained. The infrared spectrum of this material is given in Figure 7 and Table III.

Figure 6

Proton n.m.r. Spectrum of Trimethylgermylsilane

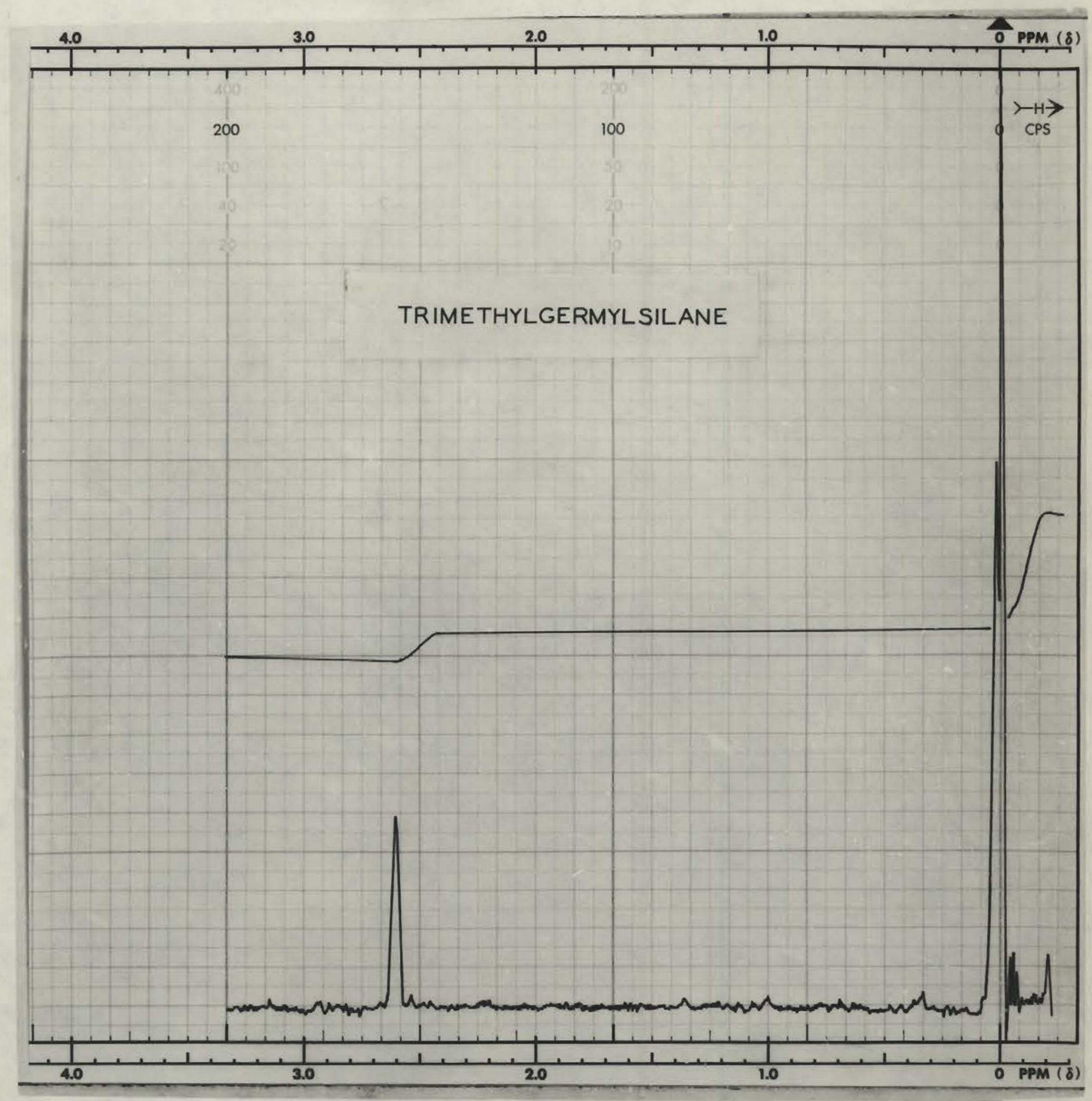

TRIMETHYLGERMYLSILANE

Figure 7

Infrared Spectrum of Trimethylgermylsilane

Pressure = 14 mm

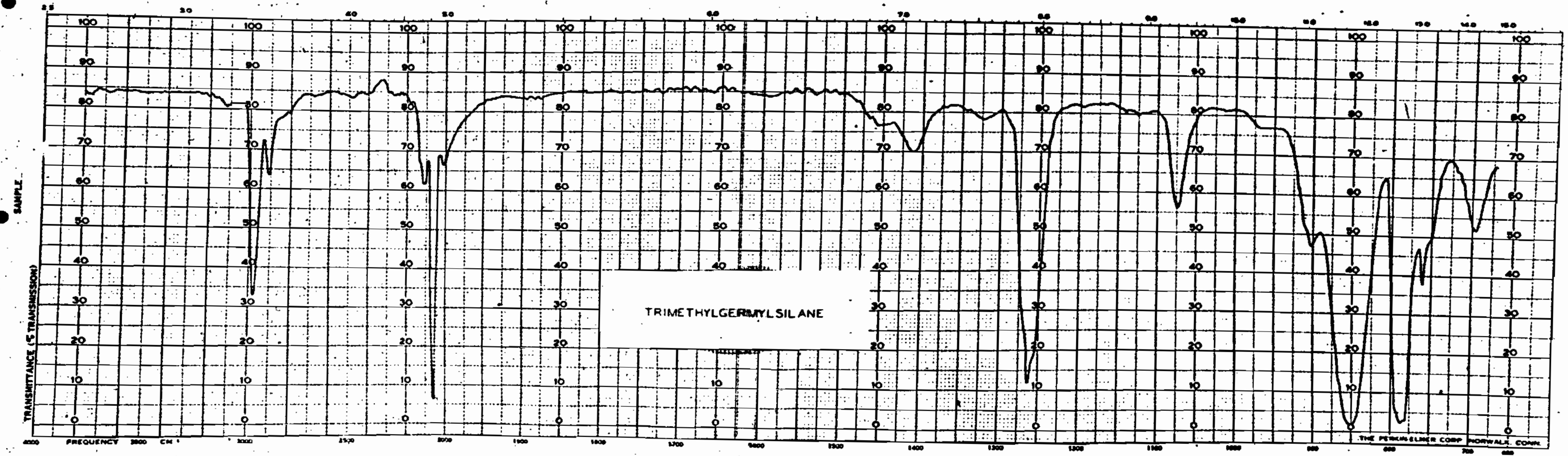

TRIMETHYLGERMYLSILANE
TRANSMITTANCE (% TRANSMISSION)
SAMPLE
FREQUENCY CM⁻¹
THE PERKIN-ELMER CORP. NORWALK, CONN.

TABLE III

INFRARED ASSIGNMENTS FOR TRIMETHYLGERMYLSILANE

Frequency cm^{-1}	Vibration
2978 s	CH_3 stretch (asym)
2910 m	CH_3 stretch (sym)
2805 vw	Combination of CH_3 deformation
2105 w-m 2060 s 2010 w-m	GeH_3 stretch
1412 w-br	CH_3 deformation (asym)
1262 s 1254 sh	CH_3 deformation (sym)
1074	SiO impurity
903 m	CH_3 rock
850 vs	GeH_3 deformation (asym) CH_3 rock
786 s	GeH_3 deformation (sym)
781 s	Si-C stretch (asym) + CH_3 rock
760 m	CH_3 rock
695 w-m	Si-C stretch (sym)

s = strong, m = medium, w = weak, br = broad, v = very, sh = shoulder
asym = asymmetric, sym = symmetric

DIMETHYLDIGERMYLSILANE $(CH_3)_2Si(GeH_3)_2$

Germyl Sodium and Dimethyldichlorosilane

Ten attempts were made to prepare dimethyldigermylsilane in good yield by the action of dimethyldichlorosilane on ammonia-free germyl sodium:

$$(CH_3)_2SiCl_2 + 2GeH_3Na \longrightarrow 2NaCl + (CH_3)_2Si(GeH_3)_2 \qquad \ldots\ 9)$$

In one of these attempts, the reaction mixture exploded. In four other experiments, only trace amounts of a compound containing the GeH_3 group, other than germane, were produced. This compound was probably the desired product, but could not be positively identified. The presence of the GeH_3 group was indicated by the occurrence of an infrared absorption band at about 2065 cm^{-1} due to the GeH_3 stretching vibrations. Dimethyldigermylsilane was produced in five other preparations in yields which varied from 18 to 28 per cent.

In a typical preparation, dimethyldichlorosilane (5.5 mmoles) was condensed on ammonia-free germyl sodium (7.1 mmoles). The reaction vessel was warmed over a period of 3 hours from -23° to $+2^\circ$. The products were separated by distilling them through traps at -23, -45 and -130°. Unreacted dimethyldichlorosilane (2.66 mmoles) was trapped at -130°, and dimethyldigermylsilane (1.0 mmole) was trapped mainly at -23°, although some was carried over to the -45° trap. The final purification was done by flashing off vapour at 0.7° until the vapour pressure became constant at 6.28 ± 0.05 mm. (Found: M, 208.8. Calcd. for $(CH_3)_2Si(GeH_3)_2$: M, 206.4).

The results of an elemental analysis were:

Found: C,11.45%; H,5.54%; Si,13.73%; Ge,69.28% (by difference)
Calculated: C,11.48%; H,5.78%; Si,13.42%; Ge,69.40%.

The melting point was $-93.1 \pm 0.1^\circ$, the average of three determinations. From the vapour pressure data, the interpolated boiling point is 117.4°, the heat of vaporization, ΔH_v, is -7.69 kcal/mole and Trouton's Constant is 19.7 calories degree^{-1} mole^{-1}. The vapour pressure equation which best fits the experimental data in the range 23.8 to 119.5° is:

$$\text{Log } P_{mm} = 5.27705 - 0.004334\ T + 1.75 \log T - 2046.05/T.$$

The proton n.m.r. spectrum of the neat liquid consisted of two sharp peaks of equal area, with $\tau(\text{CH}) = 9.67$ ppm and $\tau(\text{GeH}) = 7.00$ ppm relative to dilute TMS ($\tau = 10.0$ ppm) in carbon tetrachloride (Tables IV and V, Figures 8, 9 and 10).

Thermal Decomposition of Dimethyldigermylsilane

The products of the thermal decomposition of dimethyldigermylsilane were determined by sealing a sample (0.5 mmoles)

TABLE IV

VAPOUR PRESSURE OF DIMETHYLDIGERMYLSILANE

Temperature °C	Pressure mm Experimental	Pressure mm Calculated	Difference mm
23.80	26.91	26.75	0.16
28.40	33.72	33.43	0.29
31.00	37.82	37.79	0.03
35.20	45.82	45.84	-0.02
37.40	50.44	50.60	-0.16
39.30	54.60	55.03	-0.43
41.90	61.48	61.61	-0.13
44.40	68.12	68.54	-0.42
46.30	73.91	74.23	-0.32
48.30	80.60	80.63	-0.03
50.20	86.83	87.13	-0.30
52.30	94.64	94.80	-0.16
54.40	101.55	103.01	-1.46
56.40	110.70	111.36	-0.66
58.30	119.13	119.80	-0.67
60.30	128.87	129.24	-0.37
62.30	139.38	139.27	0.11
64.50	152.98	151.02	1.96

TABLE IV (cont.)

Temperature °C	Pressure mm Experimental	Pressure mm Calculated	Difference mm
66.10	160.99	160.05	0.94
68.20	172.99	172.57	0.42
70.30	186.70	185.85	0.85
72.30	200.00	199.25	0.75
74.20	214.16	212.68	1.48
76.20	227.55	227.58	-0.03
78.30	244.78	244.11	0.67
80.50	263.62	262.43	1.19
83.20	287.32	286.37	0.95
85.30	306.94	306.14	0.80
87.50	328.54	327.99	0.55
90.10	356.86	355.35	1.51
93.90	401.20	398.48	2.72
96.60	432.50	431.50	1.00
99.00	462.50	462.57	-0.07
101.70	499.50	499.54	-0.04
104.60	541.50	541.70	-0.20
107.80	590.00	591.29	-1.29
110.20	627.50	630.66	-3.16
113.70	688.95	691.54	-2.59
116.50	739.75	743.31	-3.56
119.50	797.08	801.89	-4.81

$$\log P_{mm} = 5.27705 - 0.004334T + 1.75 \log T - 2046.05/T$$

Figure 8

Vapour Pressure of Dimethyldigermylsilane

Pressure vs 1/T

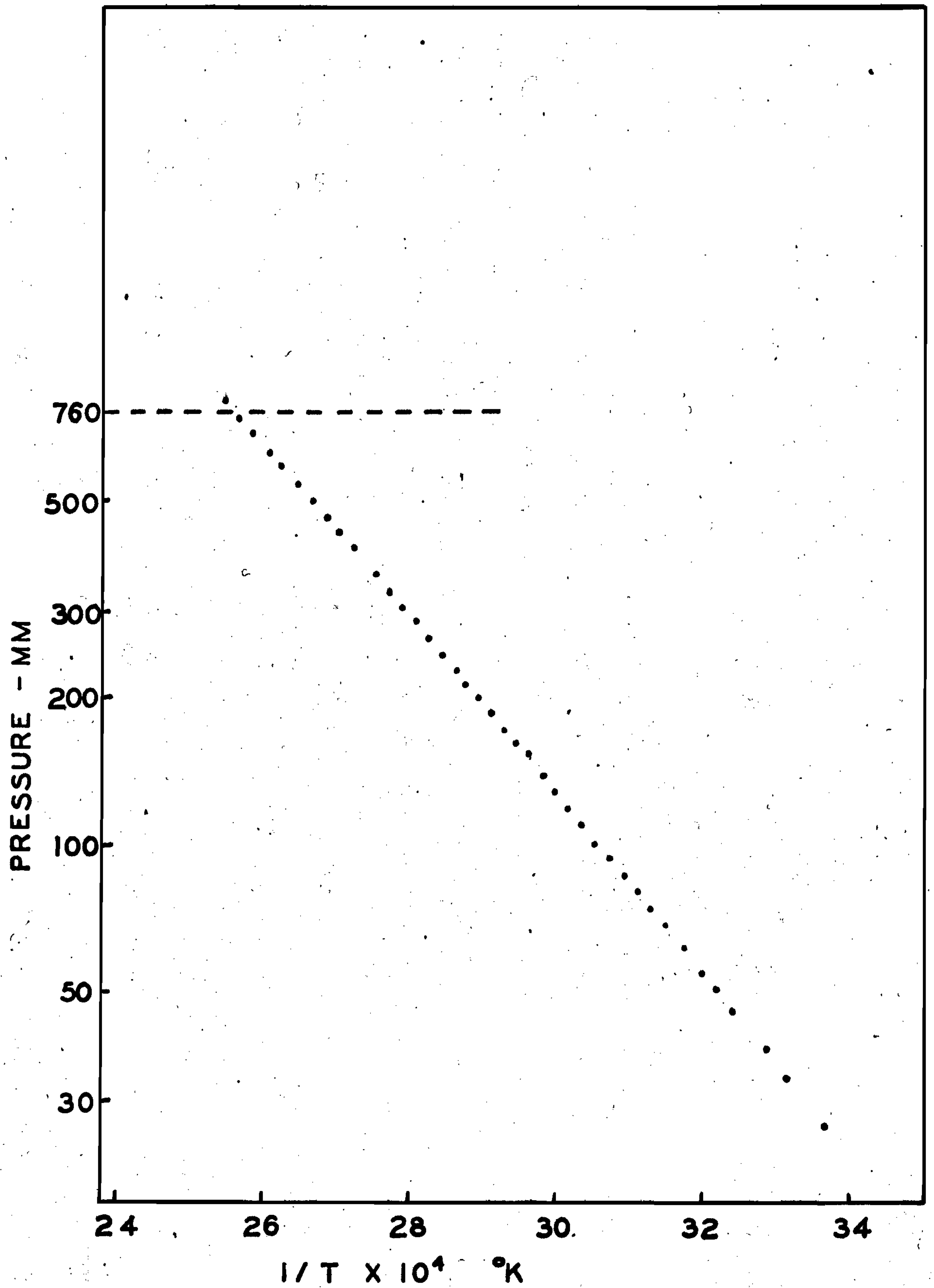

760
500
300
200
100
50
30
PRESSURE - MM
24
26
28
30
32
34
1/T X 10⁴ °K

Figure 9

Infrared Spectrum of Dimethyldigermylsilane

Pressure, A = 3.7 mm
B = 14.3 mm

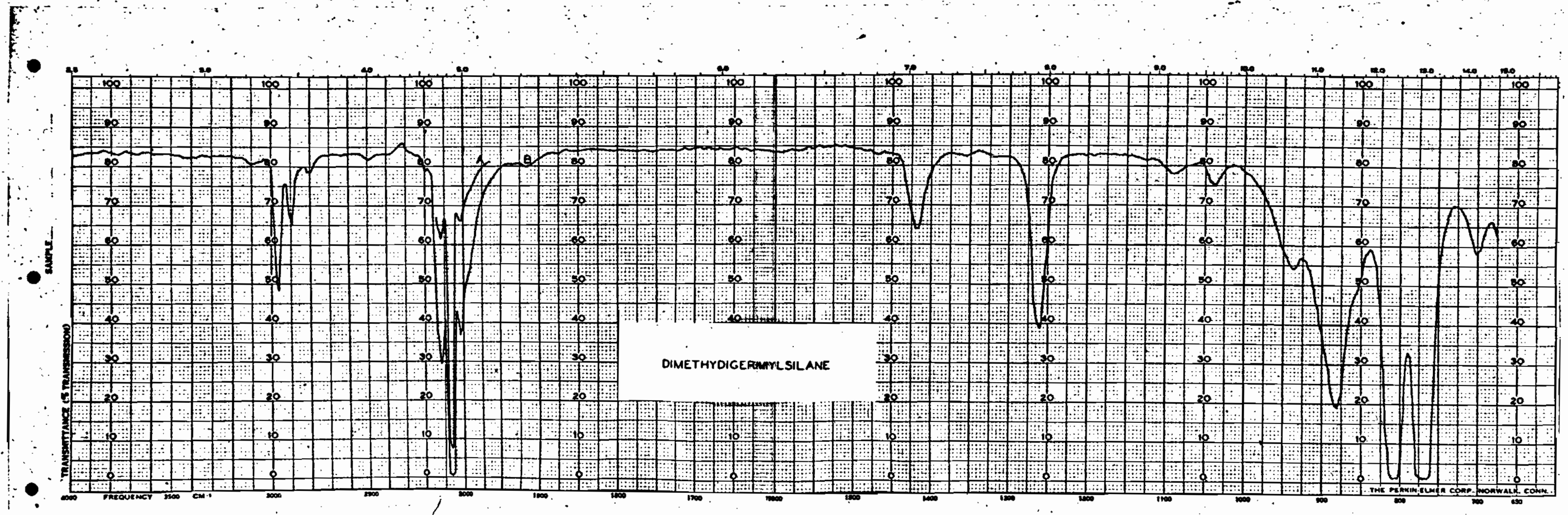
 DIMETHYDIGERMYLSILANE
A
B
TRANSMITTANCE (% TRANSMISSION)
SAMPLE
FREQUENCY CM⁻¹
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
900
800
700
650
100
90
80
70
60
50
40
30
20
10
0
THE PERKIN-ELMER CORP. NORWALK, CONN.

TABLE V

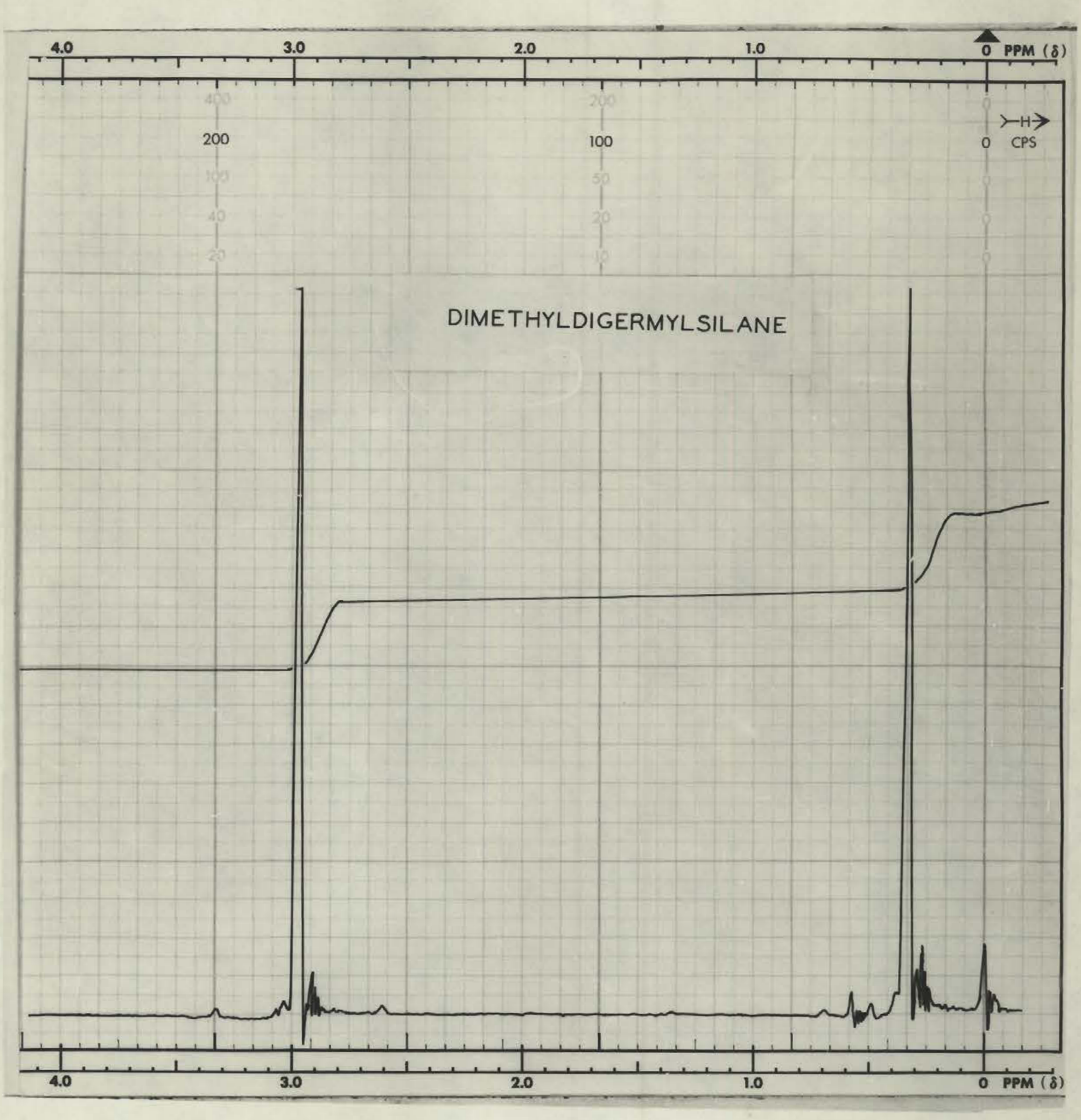
INFRARED ASSIGNMENTS FOR DIMETHYLDIGERMYLSILANE

Frequency cm^{-1}	Vibration
2970 m	CH_3 stretch (asym)
2900 w	CH_3 stretch (sym)
2800 vw	Combination of CH_3 deformation
2120 m 2065 s 2015 m	GeH_3 stretch
1418 w	CH_3 deformation (asym)
1258 m	CH_3 deformation (sym)
1037	Combination of ρ (GeH_3)($\sim$ 500 cm^{-1})
935 m-sh	CH_3 rock
883 s	CH_3 rock
840 sh	GeH_3 deformation (asym)
810 vs	SiC stretch (asym)
765 vs	GeH_3 deformation (sym)
702 w	Si-C stretch (sym)

s = strong, m = medium, w = weak, v = very, sh = shoulder
asym = asymmetric, sym = symmetric

Figure 10

Proton n.m.r. Spectrum of Dimethyldigermylsilane



4.0
3.0
2.0
1.0
0 PPM (δ)
400
200
100
40
20
200
100
50
20
10
0
H
0
CPS
DIMETHYLDIGERMYLSILANE
4.0
3.0
2.0
1.0
0 PPM (δ)

of the pure material in a 50 ml Pyrex tube, and placing it in an oven at the desired temperature. After 18.5 hours at 85°, dimethyldigermylsilane was recovered unchanged. However, after only 15 minutes at 200°, a mirror of metallic germanium covered the interior of the vessel. The tube was kept in the oven at 200° for 19.5 hours to assure complete decomposition. The volatile products were then passed through a series of traps at -78°, -150° and -194°. The non-condensable vapour (0.25 mmoles) was hydrogen (Found: M, 5.45. Calcd. for H_2: M, 2.01). The fraction (0.25 mmoles) trapped at -194° was germane (Found: M, 76.7. Calcd. for GeH_4: M, 76.6). The final fraction, (0.49 mmoles) trapped at -150°, was dimethylsilane (Found: M, 62.9; v.p. 26.4 mm at -86.3°. Calcd. for $(CH_3)_2SiH_2$: M, 60.2; Lit. v.p. 20 mm at -86.3°) and its infrared spectrum agreed exactly with that reported in the literature (60). The metallic mirror on the interior of the reaction vessel dissolved completely in 3 per cent hydrogen peroxide, indicating that it was mainly germanium.

METHYLTRIGERMYLSILANE $CH_3Si(GeH_3)_3$

Germyl Sodium and Methyltrichlorosilane

The preparation of methyltrigermylsilane was attempted seven times by reacting methyltrichlorosilane with freshly prepared, ammonia-free germyl sodium. Explosions occurred in three of these attempts, and no products were recovered. In another attempt, no trace of methyltrigermylsilane was found by infrared measurements. In three other preparations the yields of methyltrigermylsilane were 7.3, 9.0 and 34.4 per cent based on the reaction:

$$CH_3SiCl_3 + 3GeH_3Na \longrightarrow CH_3Si(GeH_3)_3 + 3NaCl . \qquad \ldots 10)$$

The highest yield was obtained when methyltrichlorosilane (9.1 mmoles) was condensed on ammonia-free germyl sodium (12.0 mmoles) and the reaction vessel was warmed slowly from -23° to $+9^{\circ}$ over 4.5 hours. The products were separated by distillation at -23°, at which temperature the methyltrigermylsilane (1.37 mmoles; Yield: 34.4%) was retained. The final purification was done by flashing off vapour at 0.6° to a constant vapour pressure of 1.60 ± 0.05 mm. Because of the very low vapour pressure of the compound, it was impossible to determine accurately the molecular weight of the vapour at room temperature.

The following results were obtained by elemental analysis of the pure material:

Found: C,4.38%; H,4.70%; Si,10.64%; Ge,80.51%

Calculated: C,4.45%; H,4.48%; Si,10.40%; Ge,80.66%.

The average of three melting point determinations on a sample of methyltrigermylsilane was $-101.0 \pm 0.1^{\circ}$. Vapour pressure data (Table VI and Figure 11) showed that the extrapolated boiling point of the compound is 153.5°, the latent heat of vaporization, ΔH_v, is -9.578 kcal./mole, and Trouton's Constant is 22.45 calories degree^{-1} mole^{-1}. The vapour pressure equation which best fits the experimental data in the range 27.9 to 105.1° is:

$$\log P_{mm} = 2.65334 - 0.000266\ T + 1.75 \log T - 1817.73/T.$$

The proton n.m.r. spectrum (Figure 12) of a sample of the neat liquid showed two sharp peaks having areas in the ratio of 1:3, with τ(CH) = 9.43 ppm and τ(GeH) = 6.69 ppm relative to dilute TMS (τ = 10.0 ppm) in carbon tetrachloride.

The infrared spectrum is shown in Figure 13 and Table VII.

TETRAGERMYLSILANE $(GeH_3)_4Si$

Germyl Sodium and Silicon Tetrafluoride

Silicon tetrafluoride was allowed to react with germyl sodium in two attempts to prepare tetragermylsilane. In the first attempt, germyl sodium (18.8 mmoles) was prepared in the usual way, but before the liquid ammonia was removed, an excess of silicon tetrafluoride (11.5 mmoles) was bubbled through the solution which then changed from white to black. This mixture was allowed to stand for 11 hours at -78° during

TABLE VI

VAPOUR PRESSURE OF METHYLTRIGERMYLSILANE

Temperature ^{o}C	Pressure mm Experimental	Pressure mm Calculated	Difference mm
27.90	7.54	7.46	0.08
32.30	9.41	9.33	0.08
36.90	11.68	11.70	-0.02
39.40	13.09	13.20	-0.11
42.00	14.96	14.93	0.03
44.40	16.70	16.71	-0.01
46.70	18.33	18.57	-0.24
51.70	23.47	23.27	0.20
54.20	25.64	25.98	-0.34
56.20	27.95	28.35	-0.40
58.30	30.78	31.03	-0.25
60.30	33.50	33.78	-0.28
62.30	36.40	36.74	-0.34
67.20	45.43	44.97	0.46
69.50	49.79	49.35	0.44
71.90	54.90	54.30	0.60
74.80	61.32	60.86	0.46
78.20	69.46	69.40	0.06
80.70	77.03	76.32	0.71
83.60	85.75	85.08	0.67
86.60	95.89	95.03	0.86
90.20	108.68	108.28	0.40
93.10	121.49	120.07	1.42
96.20	133.65	133.86	-0.21
99.10	147.40	147.97	-0.57
102.30	163.63	164.98	-1.35
105.10	177.86	181.20	-3.34

$$\log P_{mm} = 2.65334 - 0.000266T + 1.75 \log T - 1817.73/T$$

Figure 11

Vapour Pressure of Methyltrigermylsilane

Pressure vs 1/T

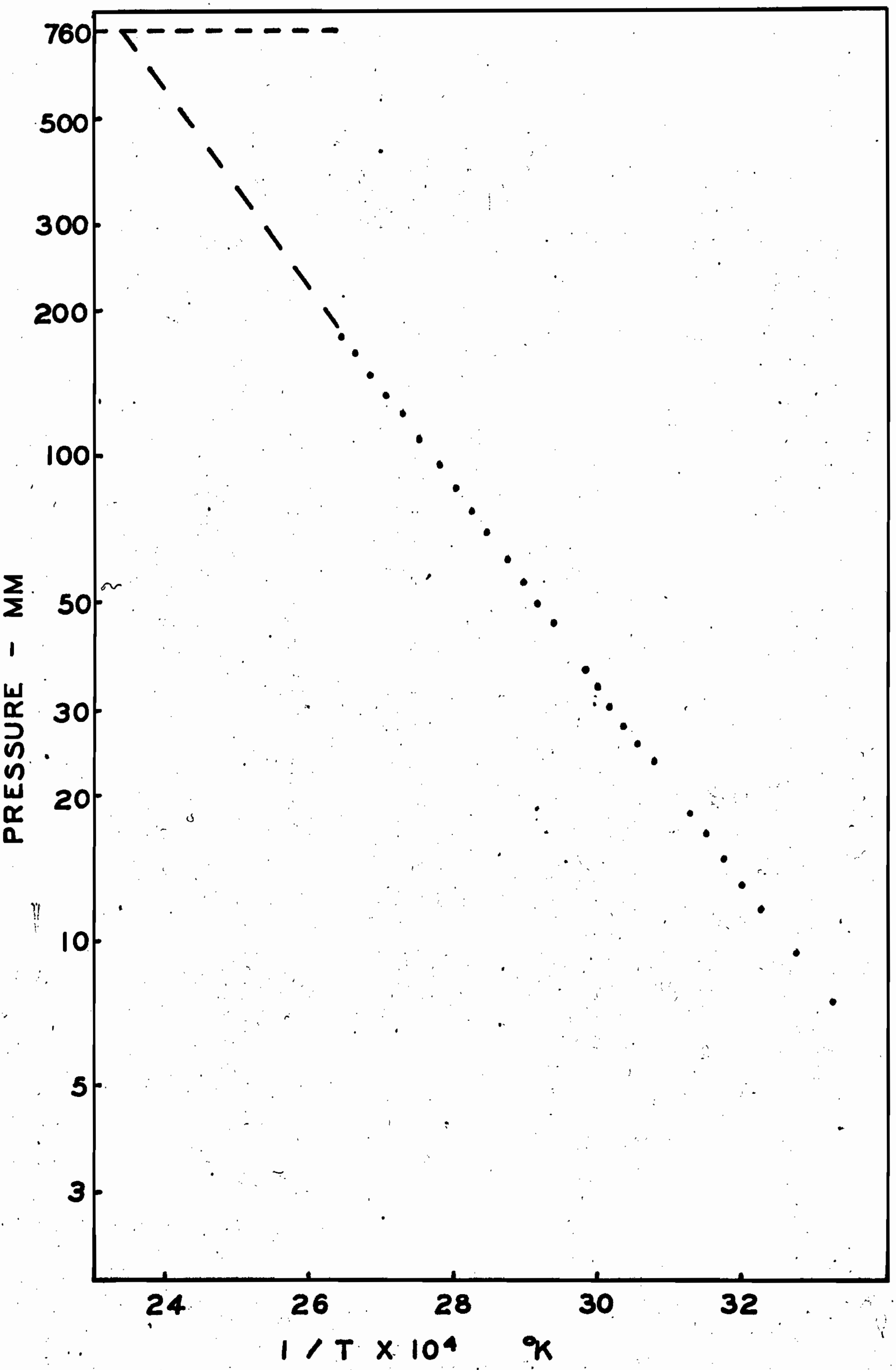
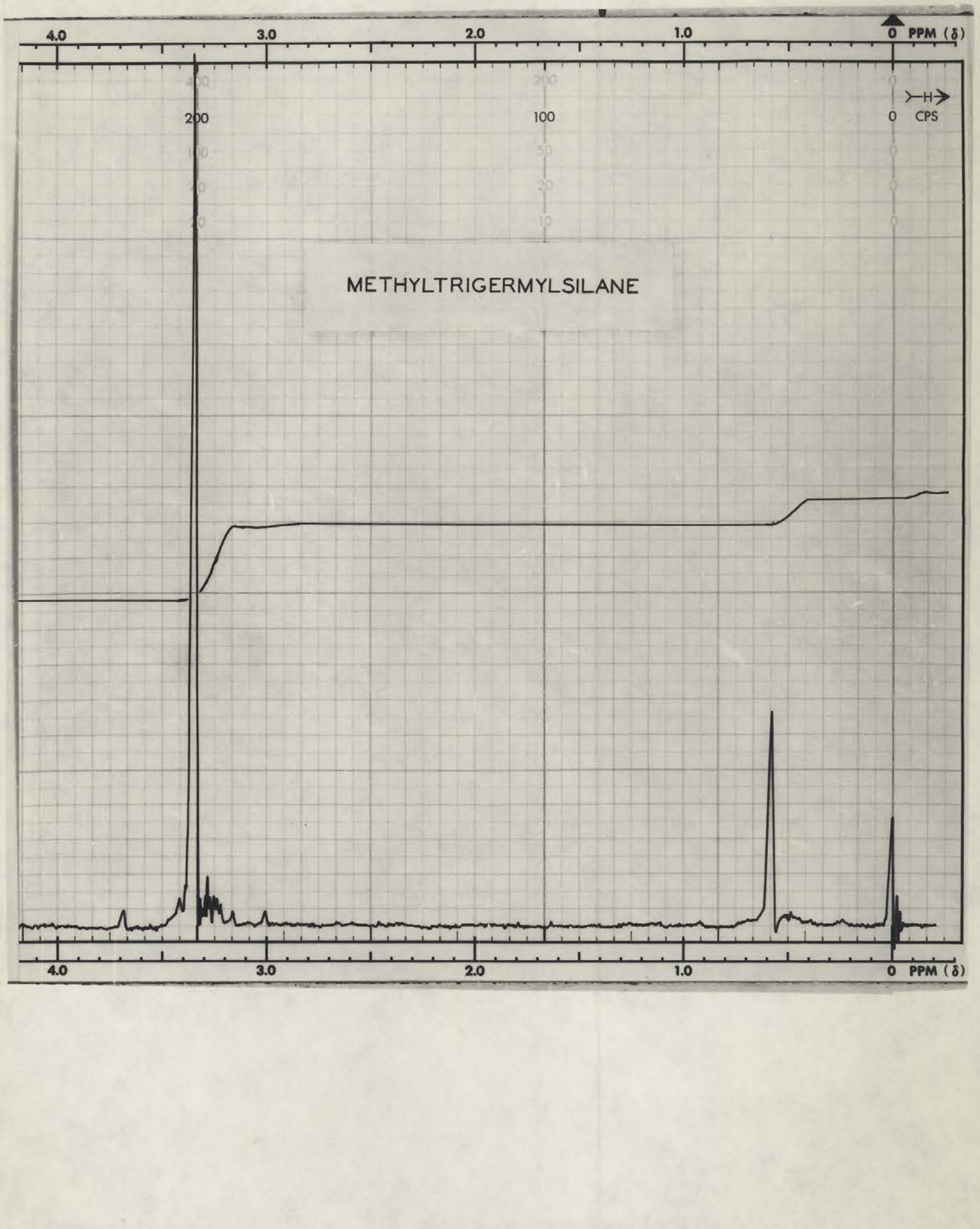

760
500
300
200
100
50
30
20
10
5
3
PRESSURE - MM
24
26
28
30
32
1 / T X 10⁴ °K

Figure 12

Proton n.m.r. Spectrum of Methyltrigermylsilane

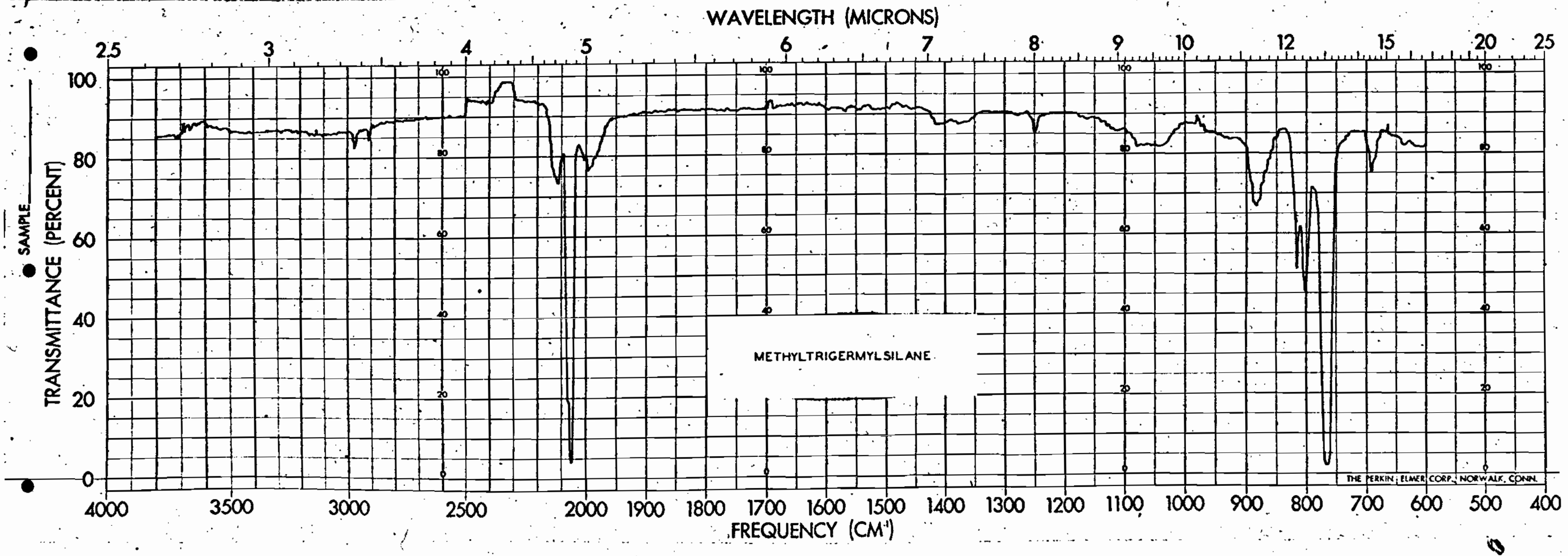


METHYLTRIGERMYLSILANE

Figure 13

Infrared Spectrum of Methyltrigermylsilane

Pressure = 6.3 mm



WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
25
TRANSMITTANCE (PERCENT)
SAMPLE
100
80
60
40
20
0
METHYLTRIGERMYLSILANE
THE PERKIN-ELMER CORP., NORWALK, CONN.
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

TABLE VII

INFRARED ASSIGNMENTS FOR METHYLTRIGERMYLSILANE

Frequency cm^{-1}	Vibration
2970 w	CH_3 stretch (asym)
2912 w	CH_3 stretch (sym)
2115 m 2080 sh 2065 vs 2010 m	GeH_3 stretch
1410 w-br	CH_3 deformation (asym)
1250 w	CH_3 deformation (sym)
885 m	GeH_3 deformation (asym)
818 m	GeH_3 out of phase deformation
802 m	CH_3 rock
768 vs	GeH_3 deformation (sym)
693 w	Si-C stretch (sym)

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder
asym = asymmetric, sym = symmetric

which time the pressure in the reaction vessel increased to about 620 mm of mercury. It was hoped that the resulting silicon tetrafluoride-ammonia adduct would react with germyl sodium in solution to give the desired tetragermylsilane. The volatile mixture was distilled through a trap at -78° to condense the tetragermylsilane, but none was recovered. Instead, germane (8.1 mmoles) was the only volatile product.

In a second experiment, a deficiency of silicon tetrafluoride (3.7 mmoles) was condensed onto ammonia-free germyl sodium (16.2 mmoles). The temperature of the reaction vessel was increased from -23° to +2° over a period of 4 hours, and then the temperature was held at 0° for 25 minutes. Silicon tetrafluoride was entirely in the gas phase under these conditions, and if any reaction had occurred, the pressure would have decreased due to its consumption. No decrease in the pressure was observed, and most of the silicon tetrafluoride (3.1 mmoles) was recovered, along with some germane (less than 0.1 mmoles).

Germyl Sodium and Silicon Tetrachloride

The reaction of silicon tetrachloride with ammonia-free germyl sodium was carried out twelve times. The reaction vessel exploded during the course of three of these experiments. Nine other preparations proceeded without exploding but only a minute drop of tetragermylsilane was produced each time, and the total amount of material prepared was only about 18 mg.

In a typical experiment, an excess of silicon tetrachloride (10.1 mmoles) was condensed onto ammonia-free germyl sodium (13.7 mmoles) and the mixture was allowed to react for 4 hours while it was warmed from -23° to -1°. The unreacted silicon tetrachloride (9.4 mmoles) was distilled at -23° and only a minute drop of liquid remained. This liquid had a vapour pressure of less than 2 mm at room temperature. The infrared spectrum of its gaseous phase showed only two main peaks; a strong band at 2072 cm^{-1} due to GeH_3 stretching vibrations and a very strong band at 772 cm^{-1} due to the symmetric GeH_3 deformation vibration (Figure 14 and Table VIII).

The proton n.m.r. spectrum of the neat liquid contained a single sharp peak at $\tau = 6.36$ ppm and two very small peaks at $\tau = 6.48$ ppm and $\tau = 6.61$ ppm which were due to an unidentified impurity (Figure 15).

The melting point of this compound was $-53.3 \pm 0.4^\circ$,

Figure 14

Infrared Spectrum of Tetragermylsilane

Pressure = about 3 mm

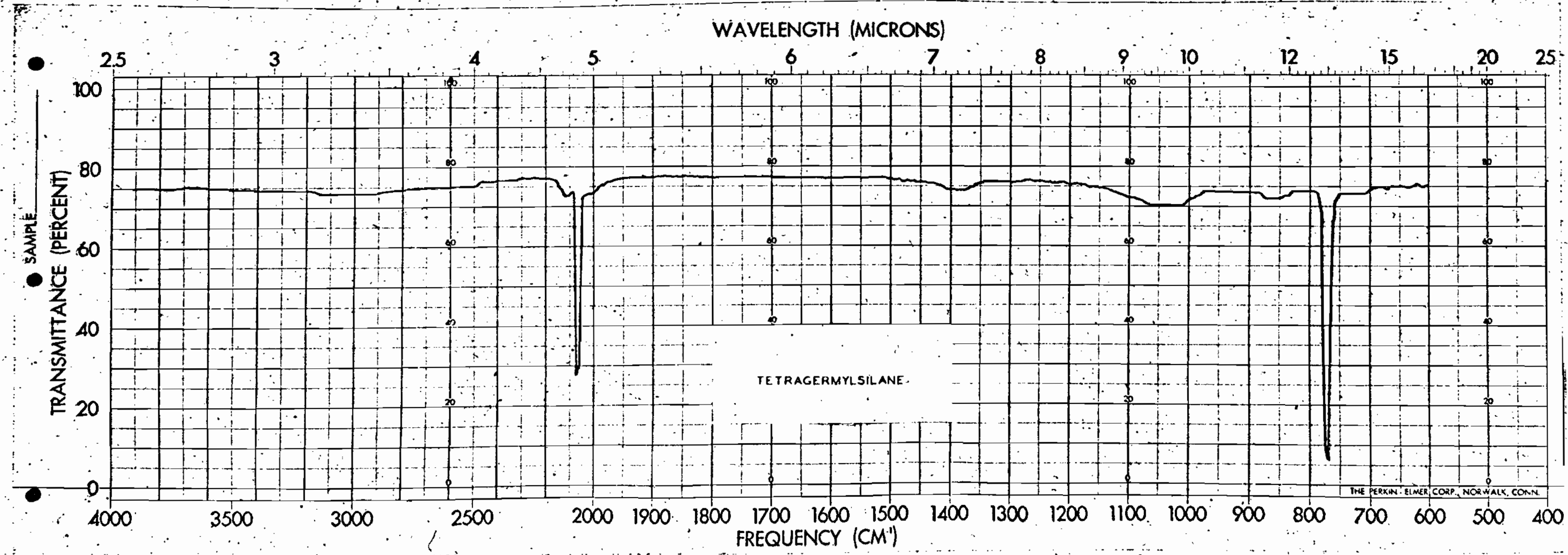

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
25
100
80
60
40
20
0
SAMPLE
TRANSMITTANCE (PERCENT)
TETRAGERMYLSILANE
THE PERKIN-ELMER CORP., NORWALK, CONN.
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)

TABLE VIII

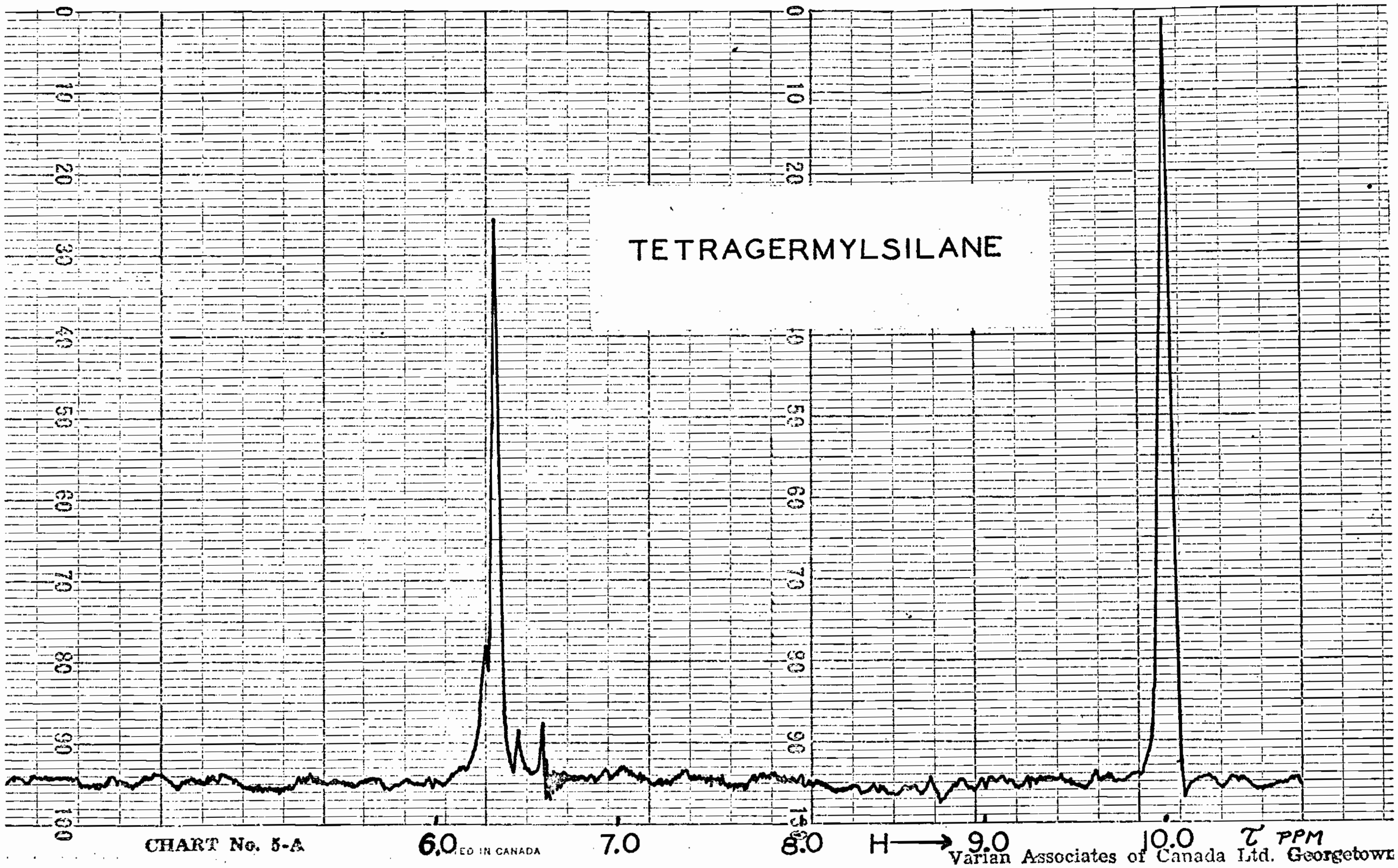
INFRARED ASSIGNMENTS FOR TETRAGERMYLSILANE

Frequency cm^{-1}		Vibration
2110 w	R	
2072 vs	Q	GeH_3 stretch
2000 w	P	
1390 vw		Combination band $\nu_{16} + \nu_3$
872 vw		GeH_3 deformation (asym)
772 vs		GeH_3 deformation (sym)

s = strong, w = weak, v = very, asym = asymmetric,
sym = symmetric

Figure 15

Proton n.m.r. Spectrum of Tetragermylsilane



TETRAGERMYLSILANE

from three determinations.

About 15 mg of tetragermylsilane was sent for analysis, but even this amount was not sufficient for a duplicate determination. The single determination done indicated no germanium and 10.94 per cent hydrogen (Calcd. for $(GeH_3)_4Si$: Ge, 87.8%; H, 3.66%). These results must be in error since infrared and proton n.m.r. results proved the presence of the germyl group in this compound.

GERMYLSILANE GeH_3SiH_3

Germyl Sodium and Bromosilane

Germylsilane was first prepared by Spanier and MacDiarmid (22) from germane and silane in an electric discharge, and more recently by Varma and Cox (24) from chlorogermane and silyl potassium in 20 per cent yield. It can also be prepared by the interaction of germyl sodium with bromosilane in 7.8 per cent yield. A deficiency of bromosilane (7.7 mmoles) was condensed onto ammonia-free germyl sodium (11.9 mmoles) and the reaction vessel was held at -78° overnight, then at -45° for one hour and subsequently warmed from -23° to $+1^{\circ}$ over a three hour period. After the removal of germane (0.6 mmoles) the volatile product mixture, containing bromosilane and germylsilane, was allowed to react with an excess of ammonia to consume the bromosilane. This reaction produced trisilylamine (0.62 mmoles) and a trace of silane, leaving germylsilane (0.6 mmoles; Yield: 7.8%). Germylsilane was identified by its infrared spectrum which agreed exactly with that reported in the literature (22). However the observed molecular weight of the vapour was lower than that calculated (Found: M, 99.0. Calcd. for GeH_3SiH_3: M, 106.72). No further attempts were made to purify and characterize this compound.

1,1,1-TRIMETHYLDIGERMANE $(CH_3)_3GeGeH_3$

Germyl Sodium and Trimethylbromogermane

Eight separate experiments were done to prepare 1,1,1-trimethyldigermane by the reaction of germyl sodium with trimethylbromogermane. One attempt was made using toluene as a liquid medium, but only a trace of material which might have been the desired product was found. In four other experiments using solid ammonia-free germyl sodium only a trace of material containing a GeH_3 group was identified by infrared measurements. Measurable amounts of a material which had the molecular weight of trimethyldigermane were obtained in three other experiments. In one preparation, trimethylbromogermane (6.29 mmoles) was condensed onto ammonia-free germyl sodium (5.71 mmoles) and allowed to react for one hour at -23° and then for one hour at 0°. Trimethyldigermane (0.48 mmoles) was recovered and purified by vacuum distillation at -78° and was identified by its molecular weight (Found: M, 191.7. Calcd. for $(CH_3)_3GeGeH_3$: M, 193.3). Its infrared spectrum confirmed the presence of GeH_3 and $(CH_3)_3Ge$ groups.

Germyl Sodium and Trimethylfluorogermane

In an attempt to increase the yield of 1,1,1-trimethyldigermane, and also to facilitate separation of product from starting materials, one experiment was done using trimethylfluorogermane (2.6 mmoles) with a large excess of ammonia-free germyl sodium (21.3 mmoles). The temperature of the reaction vessel was raised from -20° to -4° over a period of 2 hours, and then maintained at 0° for 4.5 hours and at +2° for an additional 1.5 hours. The volatile products were removed, and the trimethyldigermane was separated by condensation at -78° followed by fractional codistillation on a "Cady column" using the infrared detector. The final purification was done by flashing off vapour at 0° to a constant pressure of 24.6±0.04 mm. The yield of trimethyldigermane (0.96 mmoles) was 36.4 per cent of the trimethylfluorogermane used (Found: M, 192.3. Calcd. for $(CH_3)_3Ge_2H_3$: M, 193.3).

The results of an elemental analysis of the pure compound were:

Found: H, 6.50%; C, 18.85%; Ge, 75.07%

Calculated: H, 6.25%, C, 18.64%; Ge, 75.10%

The melting point was -89.6±0.2°, an average of two determinations. The vapour pressure equation which best fits the experimental data (Table IX and Figure 16) from 0° to 54° is:

$$\log P_{mm} = 8.1394 - 0.00824\ T + 1.75 \log T - 2393.09/T.$$

This equation indicates that the extrapolated boiling point is 77.6°. The heat of vaporization, ΔH_V, is -7.53 kcal./mole, and Trouton's Constant is 21.46 calories degree^{-1} mole^{-1}.

The proton n.m.r. spectrum of the neat liquid (Figure 17) consists of two sharp peaks having areas in the ratio of 3:1 and τ(GeH) = 7.07 ppm and τ(CH) = 9.75 ppm relative to dilute TMS (τ = 10.0 ppm) in carbon tetrachloride.

The infrared spectrum of the vapour is shown in Figure 18 and assignments given in Table X.

TABLE IX

VAPOUR PRESSURE OF 1,1,1-TRIMETHYLDIGERMANE

Temperature °C	Pressure mm Experimental	Pressure mm Calculated	Difference mm
0	24.63	24.66	-0.03
0	24.56	24.66	-0.10
0	24.60	24.66	-0.06
19.90	76.40	75.22	1.18
20.70	80.06	78.35	1.71
21.80	83.13	82.83	0.30
23.80	90.46	91.52	-1.06
25.80	99.33	100.93	-1.60
27.20	108.91	107.98	0.93
28.80	115.14	116.53	-1.39
31.40	129.05	131.58	-2.53
31.90	135.93	134.64	1.29
34.90	156.61	154.28	2.33
37.30	171.66	171.58	0.08
39.90	189.56	192.05	-2.49
43.20	220.53	220.76	-0.23
46.10	250.77	248.70	2.07
49.50	285.35	284.91	0.44
52.10	313.16	315.26	-2.10
54.00	340.11	338.97	1.14

$$\log P_{mm} = 8.1394 - 0.00824\ T + 1.75 \log T - 2393.04/T$$

Figure 16

Vapour Pressure of 1,1,1-Trimethyldigermane

Pressure vs 1/T

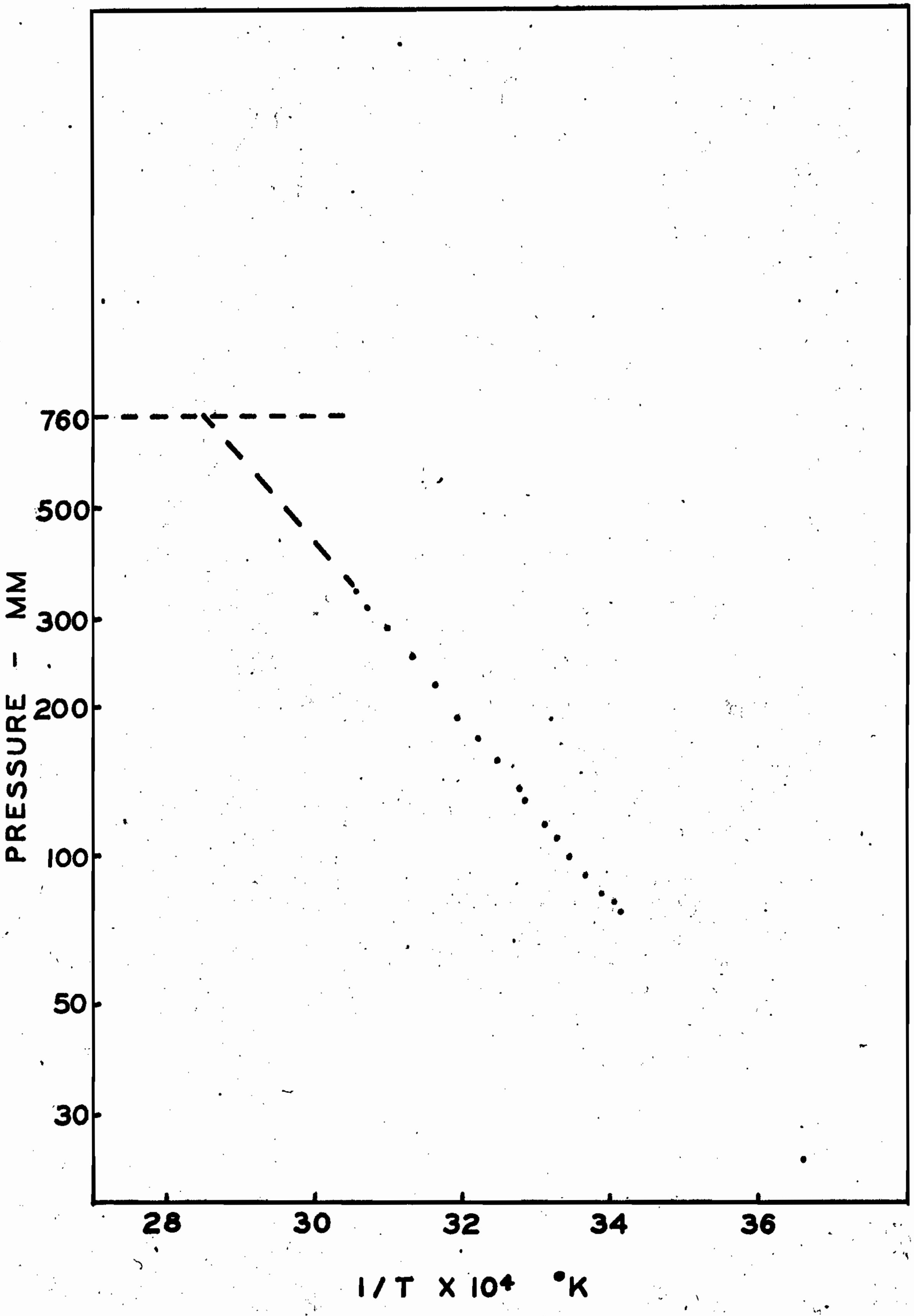
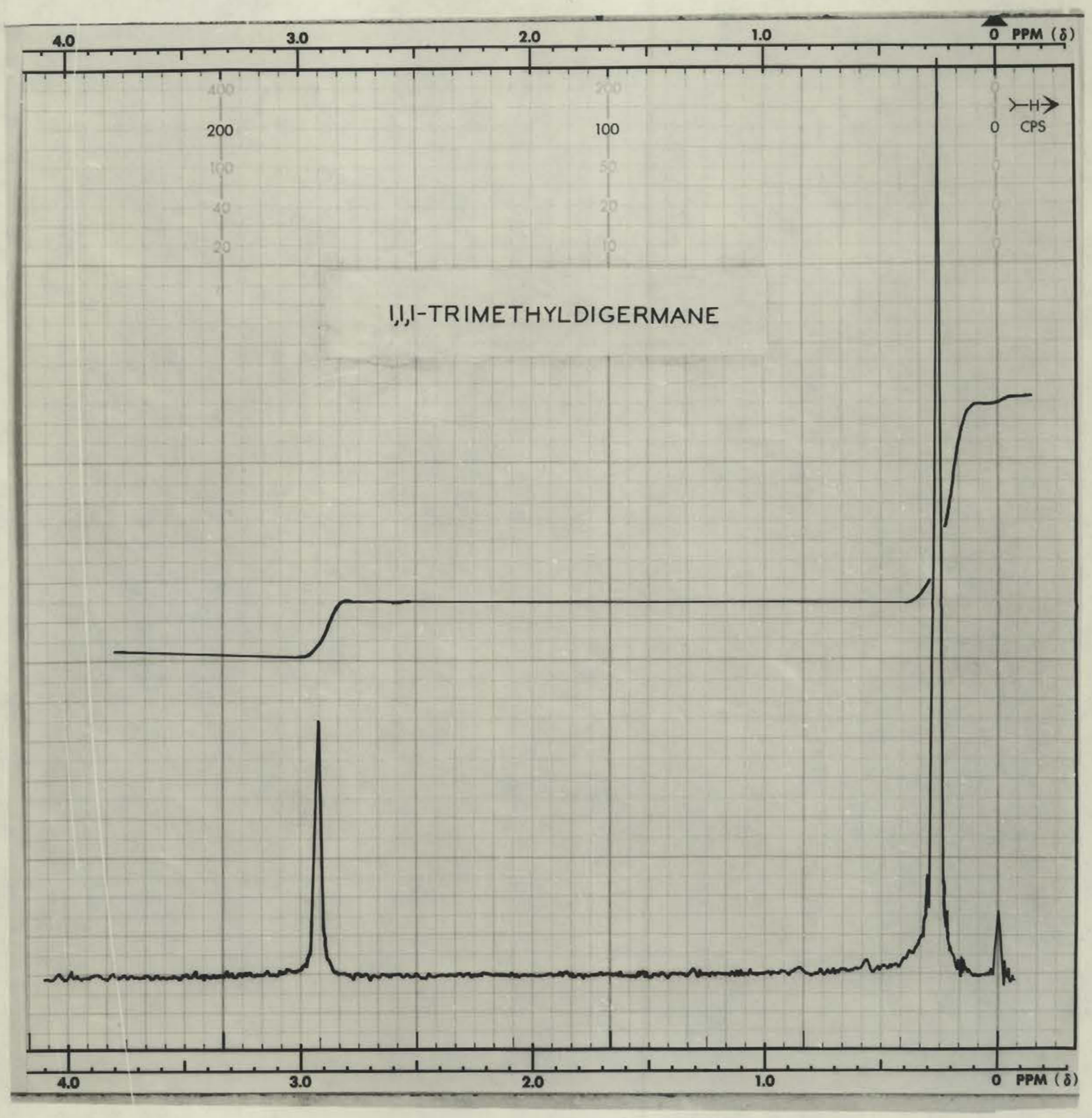

760
500
300
200
100
50
30
PRESSURE - MM
28
30
32
34
36
1/T X 10⁴ °K

Figure 17

Proton n.m.r. Spectrum of 1,1,1-Trimethyldigermane



1,1,1-TRIMETHYLDIGERMANE

Figure 18

Infrared Spectrum of 1,1,1-Trimethyldigermane

Pressure, A = 5.7 mm
B = 35.8 mm

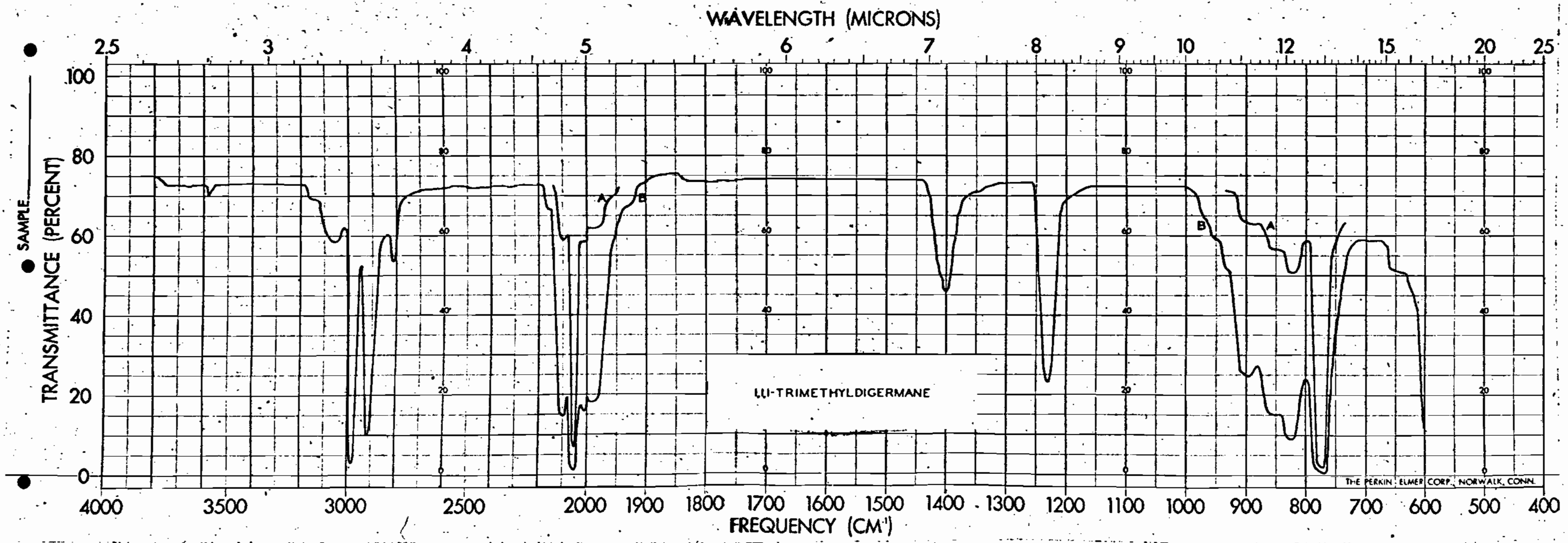

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
25
TRANSMITTANCE (PERCENT)
SAMPLE
100
80
60
40
20
0
A
B
B
A
1,1,1-TRIMETHYLDIGERMANE
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
FREQUENCY (CM⁻¹)
THE PERKIN - ELMER CORP., NORWALK, CONN.

TABLE X

INFRARED ASSIGNMENTS FOR 1,1,1-TRIMETHYLDIGERMANE

Frequency cm^{-1}		Vibration
3060 w-br		
2980 s		CH_3 stretch (asym)
2915 s		CH_3 stretch (sym)
2810 w		Combination of CH_3 deformation
2100 m	R	
2055 vs	Q	GeH_3 stretch
2010 m	P	
1400 m		CH_3 deformation (asym)
1232 s		CH_3 deformation (sym)
898 m-br		CH_3 rock
850 sh-m		GeH_3 deformation (asym)
824 s		CH_3 rock
772 vs		GeH_3 deformation (sym)
<600 s		Ge-C stretch

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder
asym = asymmetric, sym = symmetric

DISCUSSION

PREPARATION AND REACTIONS OF GERMYL SODIUM

The reaction of gaseous germane with a solution of sodium in liquid ammonia proceeds smoothly and quantitatively at -45° to yield germyl sodium and hydrogen. A conductimetric titration of sodium in liquid ammonia with germane coupled with measurements of the hydrogen evolved, showed (42) that the overall reaction was:

$$GeH_4 + Na \longrightarrow GeH_3Na + \tfrac{1}{2}H_2. \qquad \ldots\ 11)$$

At 63°, the amount of hydrogen evolved and the conductivity data indicated that both germyl sodium, GeH_3Na, and germylenedisodium, GeH_2Na_2, were formed. When more germane was added, all the disodium salt was converted to germyl sodium. At -45°, the same overall reaction (equation 11) occurred, but in two distinct steps. These were postulated to be the formation of sodamide by interaction of germylenedisodium with the solvent, and the subsequent reaction of germane with sodamide, as follows:

$$\begin{tikzcd}
GeH_4 \arrow[r, "Na\ -63^{\circ}"] \arrow[d, "2Na"'] & \tfrac{1}{2}H_2 + GeH_3Na \\
H_2 + GeH_2Na_2 \arrow[ur, "GeH_4"] \arrow[r, "NH_3\ -45^{\circ}"] & GeH_3Na + NH_2Na \arrow[u, "GeH_4", "-45^{\circ}"']
\end{tikzcd} \qquad \ldots\ 12)$$

The reaction of stannane with sodium in liquid ammonia proceeds in a similar fashion. The deep blue colour of sodium in liquid ammonia was discharged when the germane/sodium ratio was between 0.7 and 0.8, indicating that some of the sodium was consumed in the formation of germylenedisodium (42). In order to insure that the main product of these reactions is germyl sodium and does not include germylenedisodium, germane must be bubbled through the liquid ammonia solution after the blue colour has been discharged. In all of the preparations done in this work, an excess of germane was bubbled through the solution of sodium in liquid ammonia for just this reason. The unused germane was collected and separated and the amount of germyl sodium formed was calculated from the amount of germane consumed.

Since germyl sodium is extremely soluble in liquid ammonia, it begins to precipitate only after removal of some of the solvent. The temperature and rate of removal of liquid ammonia from the solution must affect the rate of precipitation of germyl sodium, and hence cause variations in the crystal size and surface area of the solid. The white crystaline solid which remains after removal of the liquid solvent still contains six molecules of ammonia of crystallization which it loses in four consecutive solid phases at -33° (41):

$$GeH_3Na\cdot 6NH_3 \xrightarrow{315mm} GeH_3Na\cdot 4.5NH_3 \xrightarrow{23mm} GeH_3Na\cdot 2NH_3 \xrightarrow{3mm} GeH_3Na \quad .. \; 13)$$

The rate of removal of ammonia of crystallization should also affect the crystal size and surface area of the resulting ammonia-free germyl sodium. These changes could in turn affect the rate or extent of reaction of the germyl sodium with the germyl or silylhalide used. Thus in these experiments, the surface area of the solid germyl sodium was not reproducible from one experiment to the next. Since these reactions were mostly solid-liquid interactions, the irreproducible surface area could at least in part explain the erratic results obtained.

Pure ammonia-free germyl sodium decomposes rapidly at room temperature, the white solid turning brown after several hours (41). At liquid ammonia temperatures (-33°) the decomposition is much slower, with only a slight yellowing of the product after 24 hours, and at -78°, no decomposition was detected after 24 hours. In the presence of ammonia, the rate of decomposition is greatly increased (41), but there was no evidence of decomposition during removal of ammonia at -45° since there was no colour change of the white product.

If there had been decomposition, the colour of the product would have changed from white to black, since it is known that with rising temperature, germyl sodium decomposes rapidly into sodium germanide and hydrogen, according to the equation

$$NaGeH_3 \longrightarrow NaGe \quad + \quad 1.5\ H_2 . \qquad \ldots\ 14)$$

Teal and Kraus (10) prepared germyl potassium, GeH_3K, by bubbling germane through a solution of potassium in liquid ammonia, and they found that it decomposed slowly at liquid ammonia temperatures and faster at room temperature or above. Although they stated that "it appears to be somewhat more stable than the corresponding sodium compound", they did not give any quantitative data.

In this work it was decided to use germyl sodium because more was known about the preparation and properties of germyl sodium than of germyl potassium. The potassium compound may have been better to use since Teal and Kraus (10) report that it crystallizes in the pure form from liquid ammonia solution and although they did not analyse their product, they inferred its composition from the weight of material formed. Since the ammonia of crystallization can be easily removed from germyl sodium, there was no real disadvantage in using it rather than germyl potassium. It was considered advantageous to use the less stable germyl sodium instead of germyl potassium, since there was the possibility that the less stable material would be the more reactive one. This order of stability is contrary to that found for the corresponding alkyl compounds, and the decomposition products also differ. Methyl sodium decomposes rapidly at 200° to give methane and Na_4C (63), whereas methyl potassium decomposes rapidly at only 100°, with the formation of potassium hydride.

The alkali metal alkyls undergo a coupling reaction with hydrocarbon halides of the general type

$$RM + R'X \longrightarrow RR' + MX \qquad \ldots 15)$$

with yields for amyl sodium ranging from 5 to 35 per cent. In general, the iodides and bromides react much more readily than the corresponding chlorides, and inert hydrocarbons are usually used as solvents (63) rather than the dry solid reagent.

Kraus (64) described the use of germyl sodium in liquid ammonia solution to prepare ethylgermane by reaction with ethylbromide, and others (10,36) have used germyl sodium in liquid ammonia to prepare methyl-, ethyl-, propyl- and isoamylgermane using the general reaction:

$$RX + GeH_3Na \xrightarrow[NH_3]{liquid} NaX + RGeH_3 \quad (X=Cl,Br). \quad \ldots 16)$$

Germyl sodium reacts with methylene bromide in a complex fashion to give mainly methylgermane (10), and the reaction of phenylbromide with germyl sodium proceeds according to the following equations (36)

$$GeH_3Na + C_6H_5Br \xrightarrow[NH_3]{liquid} NaBr + C_6H_6 + GeH_2 \quad \ldots 17)$$

$$3GeH_2 \longrightarrow GeH_4 + 2GeH \longrightarrow 2Ge + H_2 \quad \ldots 18)$$

to give benzene, germane, germanium and hydrogen. In this reaction, germyl sodium acts as a reducing agent rather than coupling to the benzene ring. No other coupling reactions of germyl sodium are reported, although reactions of some alkyl germyl sodium compounds (36) and the more stable triphenylgermyl lithium, sodium or potassium have been extensively studied (65,66,67,68,69,70,71). Reactions of trimethylstannyl sodium in liquid ammonia with alkyl halides have also been studied (72). All the reactions with germyl sodium were done in liquid ammonia solvent, while those with the triphenylgermyl metal salts were done in a variety of solvents, including ammonia, benzene, diethyl ether, tetrahydrofuran, and ethylene glycol diethyl ether. In some cases, when ammonia was used as a solvent, there was a secondary reaction with the solvent which reduced or prevented the formation of the required product (64) e.g.

$$3NaGe(C_6H_5)_3 + HCCl_3 + NH_3 \rightarrow 3NaCl + H_2C[Ge(C_6H_5)_3]_2 + (C_6H_5)_3GeNH_2 . \quad \ldots 19)$$

With some halides such as methylene bromide (10) or others containing an active halogen, ammonolysis occurs with the formation of ammonium halide which reacts rapidly and quantitatively with germyl sodium to produce monogermane. It is likely that the germane recovered in the reactions studied in this investigation was produced by the interaction of ammonium halide with germyl sodium. The ammonium halide was probably formed by ammonolysis of the methylsilylhalide by the small amounts of ammonia occluded in the solid germyl sodium, which may not have been removed by prolonged pumping. In order to minimize the formation of ammonium halide and the consequent loss of germyl sodium by formation of germane, most of the reactions using the silyl- and methylsilylhalides and germyl and methylgermylhalides were done using solid, ammonia-free germyl sodium. This, however, introduced the additional problem of physical mixing between the solid germyl sodium and the relatively small amounts of liquid halides. The lack of physical contact between the two reactants must have contributed to the very low yields obtained in most of the reactions.

In order to use germyl sodium as a reagent, it was necessary to employ reaction temperatures below about 0^{o} to decrease the rate of thermal decomposition. Even at these temperatures, reaction times of only a few hours could be used to keep the amount of decomposition comparatively small. Any thermal decomposition of the germyl sodium during the course of the reaction would decrease the amount of germyl sodium available for reaction and thus would decrease the yield of the desired product.

Preparation of Digermane

Various fully substituted digermanes have been prepared by the action of organogermylsodium on an appropriate organogermylhalide (67) in liquid ammonia.

$$R_3GeNa + R'_3GeX \xrightarrow[NH_3]{liquid} R'_3GeGeR_3 + NaX \qquad \ldots\ 20)$$

Several triphenylalkylgermanes have been prepared by the reaction of triphenylgermylsodium with alkylhalides in liquid ammonia as solvent (73,66), and germyl sodium dissolved in liquid ammonia will react with a variety of alkylhalides to form alkylgermanes (10). From the reactivity of germyl sodium, and by comparison with the coupling reactions of triphenylgermylsodium, it seemed reasonable to expect that germyl sodium would react with a halogermane to produce digermane in good yield. However, because of the interaction of the halogermanes with ammonia, the reaction with germyl sodium could not be done in liquid ammonia, and it was necessary to use solid, ammonia-free germyl sodium, or an inert solvent.

Solid, ammonia-free germyl sodium reacted to the extent of only 7 per cent with an equimolar amount of bromogermane, and the crude digermane thus formed could not be purified by low temperature fractionation. The low yield was not surprising considering the lack of adequate physical contact between the solid germyl sodium and the small amount of liquid bromogermane. "Poisoning" of the surface of germyl sodium with sodium bromide might also have occurred which would have decreased the amount of germyl sodium available for reaction. The extent of this "poisoning" probably depends on the surface area of the germyl sodium, the amount of liquid bromogermane present, and the amount of agitation of the reaction vessel. The agitation in these reactions was limited to occasional shaking of the reaction vessel, and the surface area of the germyl sodium, as mentioned previously, was not reproducible or controllable from one experiment to the next.

When a large excess of bromogermane was used to increase the relative amount of liquid present, only a trace of digermane was recovered. The use of various organic liquid media did not improve the yield of digermane. Although germyl sodium is very soluble in liquid ammonia, nothing is known of its solubility in other solvents except ethylamine, in which it is insoluble (41). Although several organic solvents have been used for reactions involving triphenylgermyl metal salts, the actual extent of solubility of the salts has only been mentioned in the case of diethyl ether, pure benzene and benzene saturated with ammonia (65). Moreover, the solubility of the triphenylgermyl metal salts in organic solvents would be due mainly to the phenyl groups and could not be expected to give any indication of the solubility of germyl sodium in the same solvents. In these experiments germyl sodium did not appear to dissolve in diglyme, benzene, or tetrahydrofuran.

Little is known about the stability of germyl sodium in the presence of solvents or other materials, but it is known that the rate of thermal decomposition is increased in the presence of ammonia. The amount of hydrogen produced in the reactions employing benzene and tetrahydrofuran indicate that the extent of thermal decomposition of germyl sodium during the reaction was less than 10 per cent of that initially present. With diglyme the amount of hydrogen given off seemed to be much larger, but it was not measured because of the necessity of pumping on the reaction vessel during the addition of bromogermane. Although the thermal decomposition of germyl sodium does not completely explain the extremely low yields of digermane, it may be at least partially responsible.

The same problems of solubility and thermal stability also apply to bromogermane, the other reactant used in the preparation of digermane. A liquid at room temperature, (m.p. -32^{o}) bromogermane is soluble in cyclohexane and diethyl ether, and it reacts instantly with ammonia (15). Bromogermane decomposes slowly at room temperature when pure and more rapidly in the presence of impurities. Nothing is known of its stability in the presence of solvents, and this could have a considerable effect on the yield of digermane.

The alkali metal alkyls are very reactive toward oxidizing agents such as chlorine, and the violent reaction which occurred on warming a mixture of chlorine and germyl sodium confirms the similarity between germyl sodium and the alkali metal alkyls.

Preparation of Trimethylgermylsilane

In a further attempt to evaluate the reactivity of germyl sodium in a coupling reaction, the preparation of trimethylgermylsilane from germyl sodium and trimethylchlorosilane was attempted:

$$GeH_3Na + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiGeH_3 + NaCl \quad \ldots \; 21)$$

A similar reaction using triphenylgermylpotassium and triethyl- or triphenylchlorosilane in ether solution (74) produced the expected substituted silylgermane. Also triphenylgermyllithium in tetrahydrofuran reacts quantitatively with triethylchlorosilane to give triphenylgermyltriethylsilane (70). Triphenylgermylpotassium and triphenylchlorostannane react to form the Ge-Sn analog of hexaphenylethane (69) while one of the most important reactions of the alkali metal alkyls is the coupling reaction with hydrocarbon halides (63) following the general reaction:

$$RM + R'X \longrightarrow RR' + MX \; . \qquad \ldots\ 22)$$

Because of the unsuitability of ammonia as a solvent and the lack of improvement found when organic solvents were used as a liquid phase in the preparation of digermane, the reaction of germyl sodium with trimethylchlorosilane was done in the absence of solvents. Three of the five reactions done with these reactants gave negative results, while the others produced yields of 20 and 42 per cent.

The use of trimethylfluorosilane did not result in an increase in the percentage yield over that obtained using trimethylchlorosilane, but there was an increase in the amount of pure material recovered because of the ease of separating the product from the starting materials.

Preparation of Dimethyldigermylsilane

Since the reaction of germyl sodium with trimethylchlorosilane produced the monosubstituted product, trimethylgermylsilane, it was logical to attempt the reaction of germyl sodium with dimethyldichlorosilane to see if the disubstituted product could also be formed. Similar reactions between methylene chloride and triphenylgermylsodium (66) or trimethylstannylsodium (72) in liquid ammonia have produced the expected disubstituted products in almost quantitative yields. Because of the reactivity of dimethyldichlorosilane toward ammonia, liquid ammonia could not be used as a solvent, and the reaction was done using solid ammonia-free germyl sodium. Five of the ten experiments done in this way did, in fact, produce the expected product, dimethyldigermylsilane, in yields of from 18 to 27 per cent. In four other experiments, only a trace of material containing a GeH_3 group was detected, and in one experiment, the reactants exploded.

The cause of the low yields obtained in these reactions is difficult to establish, but one possibility is the thermal decomposition of the germyl sodium which might have occurred during the reaction. In one experiment the amount of hydrogen formed accounted for decomposition of about 64 per cent of the germyl sodium available, and the yield of product was only 18 per cent. The decomposition of germyl sodium is not the only cause of low yields however, since in two of the experiments which yielded only traces of dimethyldigermylsilane, no hydrogen was detected in the reaction vessel, indicating that virtually no decomposition of germyl sodium had occurred. Other experiments gave erratic results with varying amounts of product and decomposition.

The most surprising fact about this reaction is that there was no evidence of the partially substituted product which must have been the intermediate of essentially a two step process. Similarly, the partially substituted product was not found in the reactions of trimethylstannylsodium, triphenylstannylsodium (66) and triphenylgermylsodium (72) in liquid ammonia with methylene chloride. In the case of the tin compounds, the reaction proceeded quantitatively, while for the germanium compound, there was some side reaction with the solvent. The first chlorine atom was quantitatively substituted by the germyl compound, while the second was only partially substituted. Owing to the affinity of carbon for hydrogen and of germanium for nitrogen, ammonia entered into the reaction forming the germylamine and the dechlorinated, monosubstituted methane (66).

$$CH_2Cl_2 + 2Ph_3GeNa + NH_3 \longrightarrow Ph_3GeNH_2 + CH_3GePh_3 + 2NaCl \quad \ldots \; 23)$$

In the reaction of dimethyldichlorosilane with germyl sodium, the latter did not act as a reducing agent since there was no evidence in any of the experiments for the formation of dimethylsilane.

Preparation of Methyltrigermylsilane

After the successful preparation of dimethyldigermylsilane using solid, ammonia-free germyl sodium as a reactant, it was of interest to determine if three chlorine atoms could be replaced by germyl groups. In a similar reaction, tris(triphenylgermyl)silane was prepared quantitatively by the reaction of triphenylgermylsodium with trichlorosilane in ether solution (75). However, the reaction of triphenylgermylsodium with chloroform in liquid ammonia produced only the disubstituted product, bis(triphenylgermyl)methane (66), while the similar reaction with trimethylstannylsodium produced the trisubstituted product only as an unstable intermediate which then decomposed according to the following equation:

$$2\left[(Me_3Sn)_3CH\right] \longrightarrow 2(Me_3Sn)_2 + Me_3SnCH{=}CHSnMe_3. \quad \ldots\ 24)$$

Three of the seven experiments performed to prepare methyltrigermylsilane from methyltrichlorosilane and solid germyl sodium exploded, and two others produced only a trace of material containing a GeH_3 group. In one experiment a 34 per cent yield of methyltrigermylsilane was obtained, and there was no trace of any partially substituted products, or any indication of the germyl sodium acting as a reducing agent.

There is no apparent reason for the wide variation of the yields. The explosions which occurred may have been due to the condensation of a large amount of methyltrichlorosilane in one spot on the solid germyl sodium. This may have started to react vigorously on melting, causing local heating and consequent rapid decomposition of germyl sodium. It is surprising that the yield of methyltrigermylsilane was greater than that of dimethyldigermylsilane, but it is dangerous to make any general assumptions on the basis of only one experiment which gave a better yield than four others.

Preparation of Tetragermylsilane

After preparing three members of the series of methylgermylsilanes, it was only natural to attempt the preparation of tetragermylsilane from solid germyl sodium and silicon tetrachloride. In a somewhat similar reaction, tetrakis(trimethylsilyl)-silane was obtained in a 70 per cent yield from trimethylchlorosilane, lithium and silicon tetrachloride in tetrahydrofuran (76). This reaction probably involved the initial formation of trimethylsilyllithium, and its subsequent reaction with silicon tetrachloride, the overall reaction being:

$$4Me_3SiCl + 8Li + SiCl_4 \xrightarrow{THF} (Me_3Si)_4Si + 8LiCl \quad \ldots\ 25)$$

The reaction of triphenylgermylsodium with carbon tetrachloride in liquid ammonia or benzene was reported (64) to be similar to the reaction of trimethylstannylsodium with carbon tetrachloride

(77):

$$4NaSnMe_3 + CCl_4 \xrightarrow{NH_3} 2(SnMe_3)_2 + 4NaCl + C \, . \qquad \ldots \; 26)$$

But in a later paper, Kraus (66) stated that there was no reaction between triphenylgermylsodium and carbon tetrachloride in liquid ammonia. The same reactants in diethyl ether also produce hexaphenyldigermane (73).

In seven out of twelve experiments, the reaction of solid, ammonia-free germyl sodium with silicon tetrachloride produced only minute drops of tetragermylsilane. The yields were consistently small and seemed to be independent of the amounts of starting materials or their ratios. The small yields were not unexpected, but the absence of any partially substituted products which must have been formed as intermediates in the overall reaction:

$$4GeH_3Na + SiCl_4 \longrightarrow 4NaCl + (GeH_3)_4Si \qquad \ldots \; 27)$$

was considered unusual. The presence of only tetragermylsilane was confirmed by the appearance of only a single large peak in the n.m.r. spectrum, and an infrared spectrum which was consistent with a molecule of tetrahedral symmetry. No other fractions containing the GeH_3 group, other than germane, were found. The very small peaks in the proton n.m.r. spectrum of tetragermylsilane at $\tau = 6.48$ and 6.61 ppm, upfield of the tetragermylsilane peak at $\tau = 6.36$ ppm might possibly be due to trace amounts of the partially substituted products. Their position at slightly higher field is consistent with the magnetic anisotropic effect causing a shift to higher field as germyl groups are replaced by much smaller chlorine atoms, modified by the opposing inductive effect as discussed in a later section.

An attempt was made to increase the yield of tetragermylsilane by bubbling silicon tetrafluoride through a solution of germyl sodium in liquid ammonia. Although silicon tetrafluoride forms an adduct with ammonia, it was hoped that some reaction would occur before or after adduct formation. The only product of this reaction was germane which undoubtedly resulted from the reaction of germyl sodium with ammonium fluoride which was produced by the ammonolysis of silicon tetrafluoride. This reaction was repeated in the absence of solvent but because of the volatility of silicon tetrafluoride at 0°, the result was an unsuccessful gas-solid interaction. The small amount of silicon tetrafluoride not recovered may have been adsorbed in the stopcock grease of the reaction vessel, or may have reacted to produce the trace of germane detected.

Preparation of Germylsilane

The preparation of germylsilane by a gas discharge method (22) prompted an attempt to prepare it using solid germyl sodium and bromosilane. A small yield was obtained, comparable with that produced in the preparation of digermane. The fact that there were no organic groups present as in the case of the methylchlorosilanes might explain the low yields of both digermane and germylsilane, since the organic groups might be expected to stabilize the intermediates formed. This is one explanation of the higher yields obtained with triphenyl- or trimethylgermylsodium compared with unsubstituted germyl sodium. As with the other reactions involving solid germyl sodium, the physical state of the germyl sodium and the extent of contact between the two reactants was probably an important factor affecting the yield. However, the presence of a solvent, 1,2-dimethoxyethane, did not appreciably increase the yield when silyl potassium was allowed to react with chlorogermane (24). After 15 minutes at room temperature, a 20 per cent yield of germylsilane was obtained.

Preparation of 1,1,1-Trimethyldigermane

The reaction of trimethylbromogermane with solid, ammonia-free germyl sodium is similar to that of bromogermane with germyl sodium, and equally small yields of 6.8 and 8.5 per cent respectively were obtained in both cases. However, when trimethylfluorogermane was used, a yield of over 35 per cent was obtained in the one experiment done. Although it may not be valid to base conclusions on only one experiment, it seems more than coincidental that yields were always less than 10 per cent when the bromides were used, but close to 40 per cent when the chlorides or fluorides were used. This can be explained in terms of the Si-X or Ge-X and the Na-X bond strengths. In the general equation

$$GeH_3Na + R_3MX \longrightarrow GeH_3MR_3 + NaX \qquad ...\ 28)$$

where M = Si or Ge and X = F, Cl, or Br, two bonds are broken, Ge-Na and M-X, while two are formed, Na-X and Ge-M. In any given series of reactions in which only the halogen X changes, the difference in the heats of reaction will depend on the difference in the bond strengths Na-X and M-X, since the values of Ge-Na and Ge-M are fixed for a given M. From the known bond strengths, given in Table XI, the relative heats of reaction are estimated to be 0.85, 0.96 and 0.80 eV. where M = Si and X = F, Cl, and Br respectively. When M = Ge and X = F, Cl, and Br, the relative heats of reaction are 0.65, 0.74 and 0.40 eV. respectively. This indicates that the reaction of germyl sodium with the bromide is much less favourable than with the fluoride or chloride, particularly in the formation of digermane or 1,1,1-trimethyldigermane (i.e. M = Ge).

TABLE XI

BOND STRENGTHS (FROM COTTREL (78))

	eV.		eV.		eV.
Ge-F	4.0±1.0	Si-F	3.8±0.4	Na-F	4.65±0.25
Ge-Cl	3.5-4.0?	Si-Cl	3.3±0.5	Na-Cl	4.24±0.05
Ge-Br	2.6-3.0?	Si-Br	3.0±0.5	Na-Br	3.8 ±0.1

? = doubtful values

OTHER REACTIONS

Attempts were made to prepare digermane by the use of reactants other than germyl sodium. These unsuccessful experiments involved the interaction of bromogermane with sodium and sodium amalgam.

Bromogermane with Sodium

Although most Wurtz reactions of the type

$$2RX + 2Na \longrightarrow 2NaX + RR \qquad \ldots 29)$$

are done in a boiling inert solvent, an attempt was made to prepare digermane using a freshly prepared sodium mirror at room temperature and pure bromogermane, in the absence of solvent.

This was done because the thermal instability of bromogermane would not permit the use of normal boiling solvents, and the use of pure materials would simplify the separation of products. The yield was expected to be low because of the relatively small surface area of the sodium available for reaction, and the poisoning by involatile products which would further decrease the amount of sodium available. There were no volatile products and most of the bromogermane was recovered.

Bromogermane with Sodium Amalgam

The use of a liquid sodium amalgam increased the surface of sodium available for reaction with the bromogermane. The only volatile product formed was germane, which accounted for one half of the germanium present and could only have been formed by reaction of bromogermane with the sodium amalgam. The decomposition of bromogermane according to equations 30 and 31 would produce the required germane, but hydrogen bromide would also be a product.

$$GeH_3Br \longrightarrow GeH_2 + HBr \qquad \ldots\ 30)$$

$$2\ GeH_2 \longrightarrow GeH_4 + Ge \qquad \ldots\ 31)$$

The other observed product was an unidentified black powder which may have been a mixture of sodium bromide and germanous hydride (GeH_2) or germanium. Its black appearance could be due to mercury adsorbed on the surface of the particles. The overall reaction, deduced from the amount of germane formed and the absence of other volatile products is represented by

$$2\ GeH_3Br + Na/Hg \longrightarrow 2\ NaBr + GeH_4 + GeH_2\ . \qquad \ldots\ 32)$$

There may have been some further decomposition of the GeH_2 into hydrogen and GeH or germanium, but very little hydrogen was found.

THERMAL DECOMPOSITION OF DIMETHYLDIGERMYLSILANE

The attempted pyrolysis of dimethyldigermylsilane at 85° showed that it was stable at that temperature. At 200° it decomposed into dimethylsilane, germane, hydrogen, and a germanium mirror. From the amounts of products obtained, the equation representing the stoichiometry of the decomposition is:

$$2(CH_3)_2Si(GeH_3)_2 \longrightarrow 2(CH_3)_2SiH_2 + H_2 + GeH_4 + 3GeH_{0.66}\ . \quad 33)$$

in which the germanium mirror is assumed to have the empirical formula $GeH_{0.66}$ in order to balance the equation. This is reasonable since in the pyrolysis of digermane at 195-222°, Emeléus and Jellinek (53) found a germanium mirror which had the formula $GeH_{0.3}$, and the pyrolysis of disilane produced a mirror with the formula $SiH_{0.7}$. The actual composition of the germanium mirror probably depends on the temperature and time of pyrolysis.

The formation of dimethylsilane rather than digermylsilane indicates that the Si-Ge bonds are weaker than the Si-C bonds in this compound, as expected. Although no kinetic data were obtained on the thermal decomposition of dimethyldigermylsilane, it is interesting to speculate on the mechanism of pyrolysis. Since the pyrolysis of digermane, disilane and most alkanes follow first order reaction kinetics, it is not unreasonable to assume that the thermal decomposition of dimethyldigermylsilane is unimolecular. One possible mode of decomposition involves the formation of dimethylsilane in four steps. In the first step one GeH_3 group splits off forming a substituted silyl radical which then combines with a hydrogen atom. Then the second GeH_3 group splits off forming another substituted silyl radical which combines with a second hydrogen atom to form dimethylsilane. These steps are represented in equations 34 to 37.

$$(CH_3)_2Si(GeH_3)_2 \longrightarrow (CH_3)_2(GeH_3)Si\cdot + \cdot GeH_3 \qquad \ldots 34)$$

$$(CH_3)_2(GeH_3)Si\cdot + H\cdot \longrightarrow (CH_3)_2(GeH_3)SiH \qquad \ldots 35)$$

$$(CH_3)_2(GeH_3)SiH \longrightarrow (CH_3)_2HSi\cdot \quad + \quad \cdot GeH_3 \qquad \ldots\ 36)$$

$$(CH_3)_2HSi\cdot \quad + H\cdot \longrightarrow (CH_3)_2SiH_2 \qquad \ldots\ 37)$$

The germyl radicals thus formed decompose further forming germane, hydrogen and a germanium mirror. Some of the hydrogen atoms react with the substituted silyl radicals formed according to equations 35 and 37 while the rest are recovered as molecular hydrogen. The germyl radicals can either decompose into GeH_2 and hydrogen (equation 38), or follow two other paths, both involving the formation of digermane by recombination. By one path, an excited molecule of digermane splits into germane and GeH_2 (equation 39). The GeH_2 may then decompose into germanium and hydrogen, disproportionate into germane and germanium, or polymerize (equations 40a, b, c).

$$\cdot GeH_3 \longrightarrow GeH_2^{\cdot} + H\cdot \qquad \ldots\ 38)$$

$$2\ \cdot GeH_3 \longrightarrow Ge_2H_6^* \longrightarrow GeH_4 + GeH_2 \qquad \ldots\ 39)$$

$$GeH_2 \longrightarrow Ge + 2\ H \qquad \ldots\ 40a)$$

$$2\ GeH_2 \longrightarrow GeH_4 + Ge \qquad \ldots\ 40b)$$

$$nGeH_2 \longrightarrow (GeH_2)_n \qquad \ldots\ 40c)$$

The other path involves the interaction of digermane with a third germyl radical to form a digermanyl radical which then splits into GeH_2 and another germyl radical (equations 41, 42). The GeH_2 then decomposes according to equations 40a, b or c.

$$\cdot GeH_3 + Ge_2H_6 \longrightarrow GeH_4 + \cdot Ge_2H_5 \qquad \ldots 41)$$

$$\cdot Ge_2H_5 \longrightarrow \cdot GeH_3 + GeH_2 \qquad \ldots 42)$$

Germane could also be formed by hydrogen atom abstraction from dimethyldigermylsilane by a germyl radical:

$$(CH_3)_2Si(GeH_3)_2 + \cdot GeH_3 \longrightarrow (CH_3)_2(GeH_3)SiGeH_2\cdot + GeH_4 \quad .. 43)$$

The resulting radical could then pick up a hydrogen atom formed by the decomposition of GeH_2 to reform dimethyldigermylsilane.

Although the composition of the germanium mirror is given as $GeH_{0.66}$, based on the amount of germane and hydrogen recovered, the mirror was not analysed and could in fact have a much lower hydrogen content.

From the observed decomposition products, it is clear that more than one simple mode of decomposition is necessary to explain the pyrolysis of dimethyldigermylsilane, and at least two of the proposed reaction paths must have similar probabilities.

PHYSICAL PROPERTIES OF COMPOUNDS $(CH_3)_nSi(GeH_3)_{4-n}$ (n=0 to 4) AND $(CH_3)_nGe(GeH_3)_{4-n}$ (n=4,3)

The physical constants of $(CH_3)_nSi(GeH_3)_{4-n}$ (n=0 to 4) and $(CH_3)_nGe(GeH_3)_{4-n}$ (n=4 or 3) are given in Table XII. None of these compounds has a high degree of association in the liquid phase as shown by the normal values of the Trouton Constant. This is expected because the molecules are probably only slightly polar, analogous to unsubstituted hydrocarbons. The increase in the heat of vapourization, ΔH_v, is associated mainly with the increase in molecular weight as a methyl group is replaced by a germyl group.

Melting Points

The melting points of the series of methylgermylsilanes decrease as the number of germyl groups increases, except for the symmetrical molecule, tetragermylsilane. The abnormally high melting point of tetragermylsilane is expected because of its high symmetry. The decrease in melting point with increasing molecular weight is contrary to that found for a series of homologous organic compounds. This may be explained by the fact that in an homologous hydrocarbon series an increase in molecular weight usually results from an increase in the carbon chain length as a proton is replaced by a methyl group,

TABLE XII

PHYSICAL CONSTANTS OF $(CH_3)_nSi(GeH\ )_{4-n}$ (n=0 to 4) AND $(CH_3)_nGe(GeH_3)_{4-n}$ (n=4,3)

Compound	m.p. °C	b.p. °C	ΔH_v cal./mole	Trouton's Constant	Chemical Shift ppm[1] τ (CH)	τ (GeH)
Me_4Si	- 95	23.5	-	-	10.49	-
Me_3SiGeH_3	- 77.4	73.6	7239.6	20.88	9.97	7.42
$Me_2Si(GeH_3)_2$	- 93.1	117.4	7694.6	19.7	9.67	7.00
$MeSi(GeH_3)_3$	-101.0	153.45	9578.09	22.45	9.43	6.69
$Si(GeH_3)_4$	- 53.3	-	-	-	-	6.36
Me_4Ge	- 88	43.5	-	-	9.87[2]	-
Me_3GeGeH_3	- 89.6	77.6	7529.5	21.46	9.75	7.07

1. Values for neat liquid in capillary tubes compared with dilute TMS in carbon tetrachloride, τ = 10.0 ppm.

2. Value for dilute solution in carbon tetrachloride (98)

which increases the possibility and extent of intermolecular bonding by van der Waals forces, thereby increasing the melting point. In a series of methylgermylsilanes, the replacement of a carbon atom by a much larger germanium atom does not alter the chain length but decreases the bonding due to van der Waals forces by decreasing the proton density around the molecule. In addition, when a methyl group is replaced by a germyl group, a carbon-silicon bond is replaced by a less polar germanium-silicon bond, and thus the overall polarity of the molecule is probably decreased. These changes could in part explain the decrease in melting point with the increasing number of germyl groups. However, since the melting point of a compound depends on a number of factors including crystal structure, bond type, dipole moment, and hydrogen bonding, the observed trends in the melting points cannot be completely accounted for in any simple way.

Boiling Points

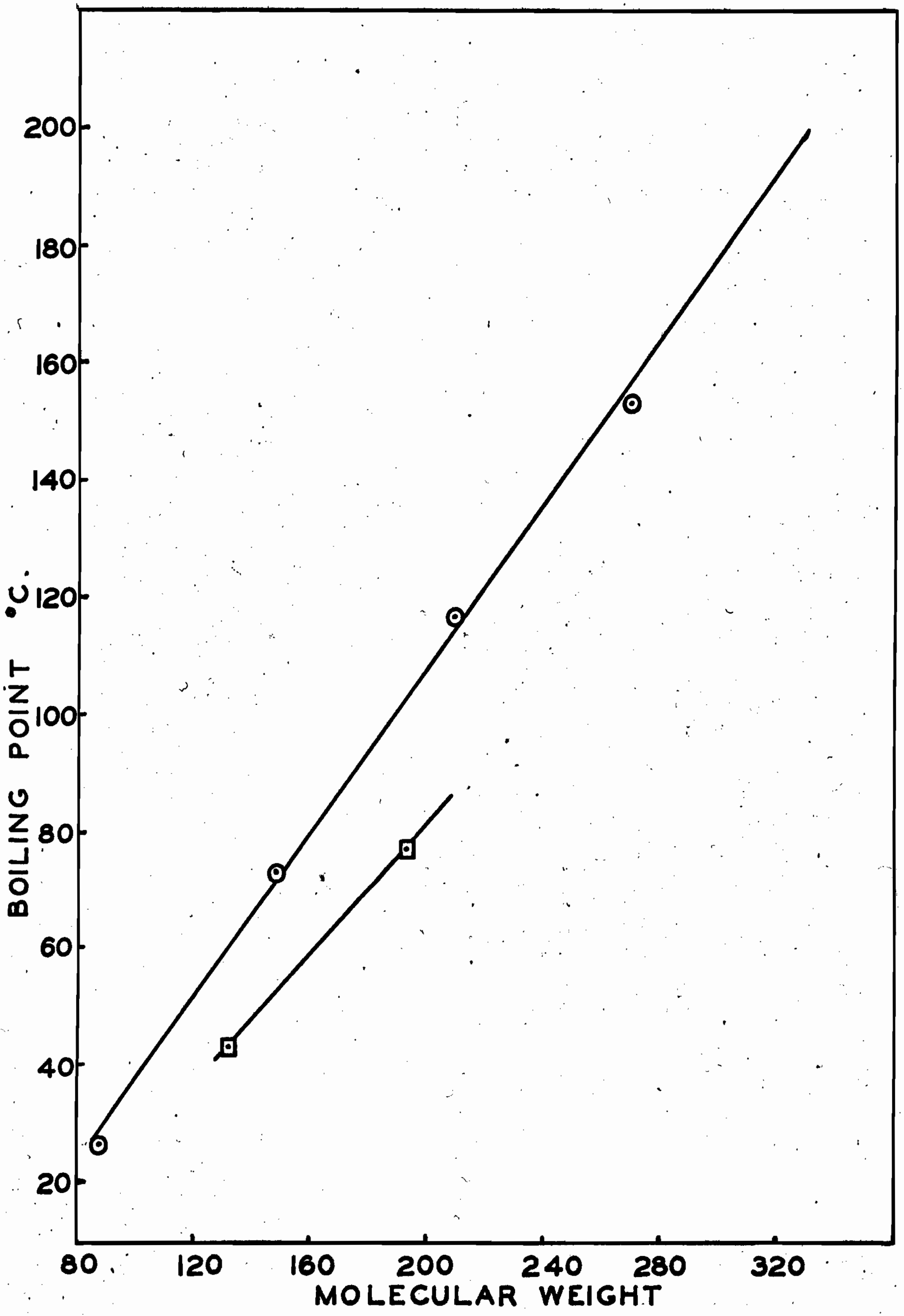
The boiling points of silane, germane and their methyl derivatives, like those of their carbon analogs, increase with increasing molecular weight. This is also true for the series of methylgermylsilanes, the boiling points of which increase linearly with molecular weight, as shown in

Figure 19

Variation in Boiling Point with Molecular Weight

⊙ $(CH_3)_nSi(GeH_3)_{4-n}$

⊡ $(CH_3)_nGe(GeH_3)_{4-n}$



BOILING POINT °C.
200
180
160
140
120
100
80
60
40
20
80
120
160
200
240
280
320
MOLECULAR WEIGHT

Figure 19. The boiling points of the first two members of the analogous germanium series, tetramethylgermane and 1,1,1-trimethyldigermane, fall slightly below the line (Figure 19) for the methylgermylsilanes. The linear increase for the methylgermylsilanes seems to indicate that the change in molecular weight when a methyl group is replaced by a germyl group is virtually the only factor influencing the boiling points of these compounds. The fact that the values for the germanium series are close to those of the methylgermylsilanes indicates that the small difference between the two series of compounds could probably be related to the increase in atomic weight accompanied by only a small change in covalent radius in going from silicon to germanium.

N.M.R. Spectra

Chemical shifts of both the methyl and germyl protons in the series of methylgermylsilanes, $(CH_3)_nSi(GeH_3)_{4-n}$ where n=0 to 4 are given in Table XIII and Figure 20. The proton chemical shifts of the neat liquids decrease monotonically as the methyl groups are replaced by germyl groups. A similar decrease is observed for the methyl protons in the series $(CH_3)_nMX_{4-n}$ where M = C, Si or Ge, and X = H or Cl, (Table XIV and Figure 21), as methyl groups are replaced by protons or chlorine atoms.

TABLE XIII

PROTON CHEMICAL SHIFT* OF $(CH_3)_nSi(GeH_3)_{4-n}$

n	CH	GeH
4	10.49 ppm	-
3	9.97	7.42 ppm
2	9.67	7.00
1	9.43	6.69
0	-	6.36

* Values for neat liquid relative to dilute TMS in CCl_4.

TABLE XIV

METHYL PROTON SHIFT IN $(CH_3)_nMX_{4-n}$

	M=C			M=Si			M=Ge
	X=Cl	X=H	X=H	X=Cl	X=H	X=H	X=H
n	(1)	(2)	(3)	(1)	(4)	(4)	(5)
4	9.037	4.0	9.06	10.00	0.0	- 7.6	10.14
3	8.404	4.1	9.11	9.578	- 4.5	-12.8	10.14
2	7.828	4.1	9.10	9.20	- 8.5	-17.3	10.14
1	7.257	4.1	9.12	8.85	-11.6	-21.0	10.18
Column	I	II	III	IV	V	VI	VII

(1) CCl_4 solution, ppm vs TMS = 10.0 (79).
(2) Neat liquids, ppm vs H_2O = 0 (80).
(3) Solutions, ppm vs TMS = 10.0 (81).
(4) Solutions, cps at 60 Mc vs TMS (82).
(5) Neat liquids, ppm vs 10% TMS in $CHCl_3$ (83).

<u>Figure 20</u>

Proton Chemical Shift of $(CH_3)_nM(GeH_3)_{4-n}$

Methyl Protons M = Si ⊙
M = Ge ⊡

Germyl Protons M = Si ◬
M = Ge ▽

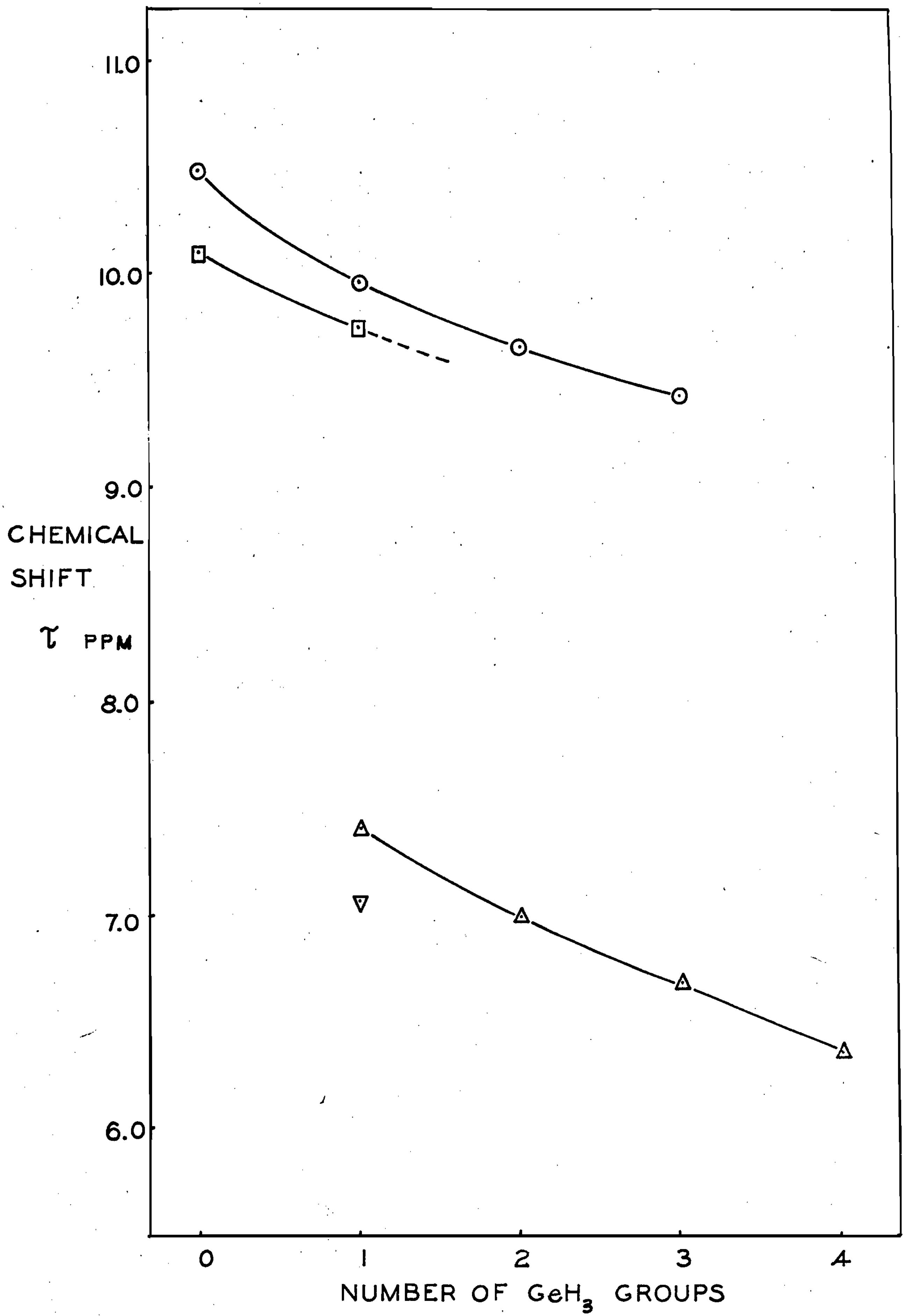
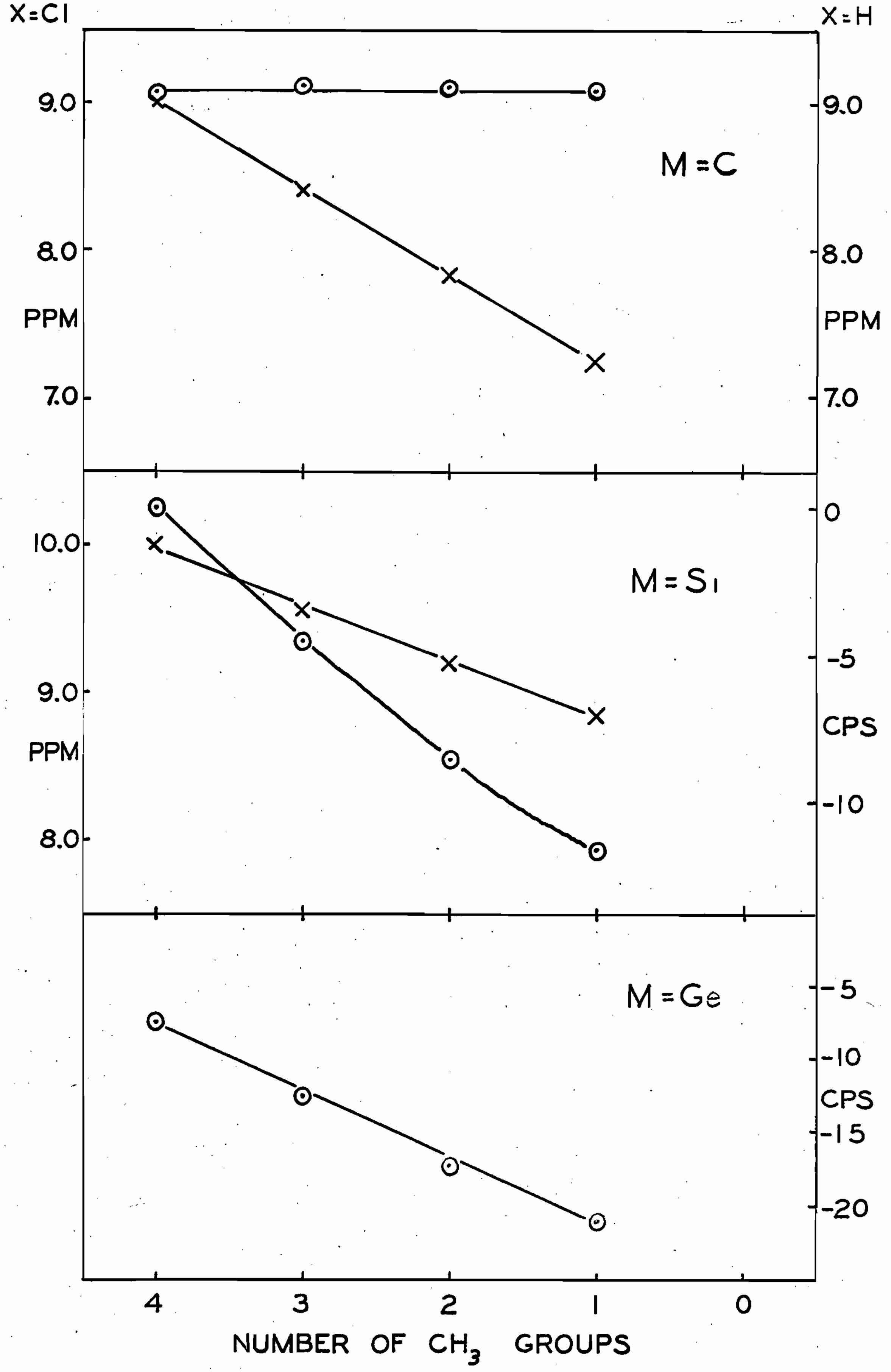

11.0
10.0
9.0
8.0
7.0
6.0
CHEMICAL
SHIFT
τ PPM
0
1
2
3
4
NUMBER OF GeH$_3$ GROUPS

Figure 21

Proton Chemical Shifts of $(CH_3)_nMX_{4-n}$

× X = Cl

⊙ X = H


X=Cl
X=H
9.0
8.0
PPM
7.0
M=C
10.0
9.0
PPM
8.0
0
-5
CPS
-10
M=Si
M=Ge
-5
-10
CPS
-15
-20
4
3
2
1
0
NUMBER OF CH_3 GROUPS

The values shown for the neat hydrocarbons (M=C, X=H, column II, Table XIV and the neat methylgermanes (M=Ge, X=H, column VII) do not change as n varies from 4 to 1. This is in contrast to the systematic decrease for the methylgermanes in solution (column VI). Although the values for hydrocarbons (column III) in solution show a very slight upward shift as n decreases, this may not be significant as it is within the limits of the experimental error.

TABLE XV

METHYL PROTON SHIFT IN SUBSTITUTED METHYLSILANES $(CH_3)_nSiX_{4-n}$

n	X=Cl (1)	X=H (2)	$X=GeH_3$ (3)
4	10.00 ppm	0.0 cps	10.49 ppm
3	9.578	- 4.5	9.97
2	9.20	- 8.5	9.67
1	8.858	-11.6	9.43

(1) CCl_4 solutions vs dilute TMS = 10.0 ppm (79).
(2) Solutions, cps at 60 Mc vs dilute TMS (82).
(3) Neat liquids, ppm vs dilute TMS = 10.0 (This work).

A concentration effect, in the case of the methylgermanes and hydrocarbons, thus completely masks any chemical shifts caused by intramolecular forces since the observed shifts for the neat liquids are constant. The concentration effect on going from infinite dilution in CCl_4 to the pure liquid is usually quite large and positive (e.g. +0.47 ppm for isopentane (84)). Although the data on the methylgermylsilanes in Tables XIII and XV are for neat liquids, a significant shift is still observed as the number of methyl groups varies. These observed shifts indicate that the concentration effect does not completely mask the intramolecular effects. Concentration effects are thus either 1) comparatively insignificant or 2) approximately constant. For the first member of the series, tetramethylsilane, there is a shift of +0.49 ppm on going from dilute solution in CCl_4 to the pure liquid, which indicates that the concentration effect is not small. Since the external shape of these molecules is roughly spherical, and the methylgermylsilanes are also roughly spherical, one would expect the concentration shift for the methylgermylsilanes to be approximately constant in the series. In this case, the same general trend would probably have been observed if the n.m.r. spectra had been obtained for the dilute solutions. An attempt was made to measure the chemical shift of dimethyldigermylsilane in a dilute solution of carbon tetrachloride, but on mixing a few drops of dimethyldigermylsilane with about 1 ml of carbon tetrachloride, a violent explosion occurred.

There was not a sufficient amount of sample available for further attempts with other solvents.

In the methylsilanes and -germanes, the decrease in chemical shift for the methyl protons with decreasing number of methyl groups has been explained in terms of the higher electronegativity of protons over methyl groups (83,85). This order of electronegativity does not at first seem reasonable, since the electronegativity of carbon is 2.5 while hydrogen is 2.1 (86). However, it has been pointed out that the group electronegativities are quite different from the electronegativities of the individual atoms, and the methyl group, with its three protons, is more electron releasing than a proton (63). An electronegativity of 1.57 for the methyl group has recently been calculated from bond dissociation data (87) compared with 2.1 for the proton on Pauling's scale. This simple explanation could also be applied to the methylchlorosilanes where methyl groups are replaced by more electronegative chlorine atoms.

For methyl halides (CH_3X) (84,88), ethyl halides (CH_3CH_2X) (89), silylhalides (SiH_3X) (90) and methylsilylhalides (CH_3SiH_2X) (91) chemical shifts of α protons vary inversely as the electronegativity of the substituent X, as would be expected for a pure inductive effect. An opposite effect occurs on the β protons of the ethyl halides (90), methylsilylhalides (91), isobutylhalides (Me_3CX) (92), and trimethylsilyl, -germyl, and -tin halides (Me_3MX) (93), contrary to that expected from inductive effects. Thus the chemical shift of the protons β to a substituent cannot be taken as a measure of the electronegativity of that substituent, and the proton chemical shift of the methylgermylsilanes cannot be explained solely in terms of the electronegativity of the substituents.

The shielding effect on β protons has been explained in terms of ionic resonance forms in which the substituent X assumes a negative charge, thus deshielding the α and β protons (92). Resonance forms would predominate when X has a large atomic number, and for the halides, as the atomic number of the halogen increases, so does the shielding.

An alternate explanation of the reverse shielding effect which would seem to be applicable to the methylgermylsilanes, is in terms of the difference in magnetic susceptibility with direction of a bond, an atom or a group of atoms.

This effect is called the magnetic anisotropy of the M-X bond, the substituent X, or even the M-M' bond (93,94). One factor contributing to the overall magnetic anisotropy in a given bond or molecule is the molecular dispersion effect (93,94) which can be qualitatively visualized as an expansion of the electronic orbitals which would increase as the number of electrons on the substituent X increases. This expansion would cause a decrease in the electron density and in the shielding of the proton, with a consequent shift to lower field.

A rough calculation of the shielding constant, σ, was made by applying McConnell's formula (95,96) for an axially symmetric group to methyltrigermylsilane and trimethylgermylsilane. The formula used was $\sigma_N^G = \frac{\Delta\chi^G}{3R^3}(1-3\cos^2\gamma)$ (96), where σ_N^G is the shielding constant of the axially symmetric group G at the proton N, $\Delta\chi^G$ is the magnetic anisotropy of the group G, and R is the distance from the electronic centre of the group G to the proton N, at an angle γ from the axis of symmetry of the group (Figure 22).

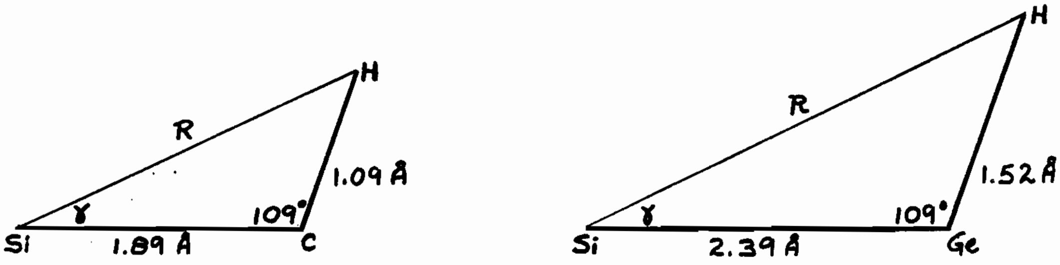


Figure 22

In applying this formula to the methylgermylsilanes, the following assumptions were made:

1) Bond lengths: All bonds were considered to be normal covalent, and the values used were: CH = 1.09Å as in CH_4 (97), GeH = 1.52Å as in GeH_3Cl (97), SiC = 1.89Å as in TMS (86), and SiGe = 2.39Å, the sum of the covalent radii (86).

2) Bond angles: All bond angles were considered to be tetrahedral, 109.47°, since the deviations reported for methyl and germyl compounds are small, and do not significantly affect the calculated values of R and γ , or the final result.

3) Centre of Anisotropy: The electronic centre of the anisotropic group, $Si(GeH_3)_3$ or $Si(CH_3)_3$, was taken as the Si atom for convenience. Although it is likely that the actual

centre is farther from the CH_3 or GeH_3 group than the silicon atom, the exact position would be very difficult to determine, and any deviation would only result in a small net decrease in the value of σ caused by the decrease in γ and increase in R. In addition, the $Si(GeH_3)_3$ or $Si(CH_3)_3$ groups were assumed to be axially symmetric about the Si-C or Si-Ge bonds respectively.

4) <u>Values of $\Delta\chi^G$:</u> The value of the magnetic anisotropy $\Delta\chi$ was taken to be 10×10^{-6} cm^3/mole, which is the value estimated by Reddy and Goldstein (96) for a C-C bond. They quote other values for the C-C bond, ranging from 1.3×10^{-6} to 5.6×10^{-6}. The high value of Reddy and Goldstein was chosen for these calculations because it is probably the best and it was also considered likely that the anisotropy of the Si-C and Si-Ge bonds would be greater rather than smaller than that of the C-C bond, since the former are bonds between dissimilar atoms, while the latter is a bond between two similar atoms.

Using these assumptions, the shielding factor calculated for the CH_3 protons in methyltrigermylsilane is -0.3 ppm. This means that on going from tetramethylsilane in which the silicon atom is spherically symmetric, to methyltrigermylsilane, the shielding of the methyl protons should decrease by 0.3 ppm. Experimentally, the decrease is 1.06 ppm, a factor of 3 greater than that calculated and in the same direction. The shielding factor for the GeH_3 protons in trimethylgermylsilane was calculated to be -0.1 ppm, indicating that in going from tetragermylsilane to trimethylgermylsilane, the shielding of the GeH_3 protons should decrease by that amount. Experimentally, there is an increase in the proton shielding of 1.06 ppm. In order for σ to have a positive value, either the term $(1-3\cos^2\gamma)$ in the equation $\sigma = \frac{\Delta\chi^G}{3R^3}(1-3\cos^2\gamma)$ must be positive or $\Delta\chi^G$ must be negative. For $(1-3\cos^2\gamma)$ to be positive, γ, the angle of the protons from the axis of symmetry at the centre of the anisotropic group (Figure 22), must be greater than 54.7°, and for trimethylgermylsilane, this would place the electronic centre of the anisotropic group only 0.5Å from the centre of the Ge atom on the Si-Ge bond. This is clearly not reasonable for an effect related to the anisotropy of the Si-Ge bond and the $Si(CH_3)_3$ group. A similar adjustment of the electronic centre would also have to be applied to methyltrigermylsilane for which calculations already agree with experiment. Alternatively a change in the sign of $\Delta\chi^G$ is more reasonable. The assumed value of 10×10^{-6} was for a cylindrical C-C bond, and the positive sign seems also to apply for the Si-C bond, which is ellipsoidal with the large end at the silicon atom. The Si-Ge bond on the other hand, is ellipsoidal with the smaller end at the silicon atom, and it would be reasonable to expect the magnetic anisotropy to change sign in this case as it does for chlorine. In the latter case, Reddy and Goldstein (96) report a value of 3.75×10^{-7} for σ, the shielding constant of chlorine, which implies a negative value of $\Delta\chi$, the magnetic anisotropy, the actual value depending on the geometry of the system.

Proton chemical shifts have also been explained by the dependence of CH chemical shift on M-C bond energies (98). It has been proposed (99) that the weaker the C-M bond, the more s character the carbon will employ in the C-H bonds, with a corresponding increase in the amount of p character in the C-M bond. Thus the increase in p character for larger elements results from decreasing strength of the C-M bond. Stronger C-H bonds form, and more effective overlap results as the amount of s character in the hybrid orbitals employed by carbon increases ($sp > sp^2 > sp^3$). Since the effective electronegativity of a carbon orbital depends on its hybridization (100) (the more s character, the more electronegative), the relative chemical shifts should be influenced by this effect. To apply this theory to the methylgermylsilanes, it is assumed that in tetramethylsilane, both carbon and silicon are sp^3 hybridized. In trimethylgermylsilane, since the Si-Ge bonds are weaker than the Si-C bonds, the weaker bonds are assumed to have an increased amount of p character, with a corresponding decrease in s character, while the Si-C bonds have increased s character and a decreased amount of p character.

An approximate orbital overlap integral calculation on the Si-C bond indicates that when the s character of the silicon hybrid orbitals is increased, the overlap integral increases only if the amount of s character in the carbon hybrid orbital is also increased. For this to be so, the p character of the CH bonds must decrease, the carbon will be effectively less electronegative, and the proton shielding should increase. However, experimentally, the proton shielding decreases, and therefore this theory does not explain the observed changes. Although Drago (98,99) relates bond strength with orbital hybridization, and proposes an increase in the amount of p character in the C-M bond as the size of M increases, it is more reasonable to assume that as the orbitals of M increase in size, more overlap will occur if the carbon orbitals have increased s character. Applying this idea to the methylgermylsilanes, it follows that as the substituents on the silicon change from methyl groups to germyl groups, the silicon will use orbitals with more s character in bonding with the larger germanium, and the Si-C bonds will have correspondingly more p character. An approximate orbital overlap integral calculation for the Si-C bond indicates that when the p character of the silicon is increased, the overlap integral increases only if the s character of the carbon orbitals to silicon increase. This would mean less s character in the C-H bonds, and consequently increased shielding of the protons, contrary to the observed trend.

Considering the experimental data, and the results obtained from attempts to apply magnetic anisotropy and electronegativity effects separately to explain these data, it seems likely that no simple effect is responsible for the observed shifts. These two effects, however, can qualitatively be used together to explain the chemical shift observed for the methylchlorosilanes, methylsilanes, and methylgermylsilanes (Table XV). For the methylchlorosilanes the inductive effect should cause a decrease in the proton shift as methyl groups are replaced by more electronegative chlorine atoms. The anisotropic effect should cause only a negligible change since the the size of the chlorine atom and the methyl groups are similar. This gives a net decrease in the chemical shift as the number of methyl groups decreases. For the methylsilanes, the anisotropic effect would be expected to cause an increase in the methyl proton shift as the methyl groups are replaced by much smaller protons. The small net decrease observed suggests that the inductive effect must cause a decrease in proton shift. This is supported by theoretical calculations which indicate that in some compounds a methyl group is more electron releasing than a proton (101), and in this respect, the proton can be considered more electronegative than the methyl group. This was also proposed to explain a similar effect in tin compounds (85).

For the methylgermylsilanes, it would be reasonable to assume the germyl groups to be less electronegative than the methyl groups, as indicated by the electronegativities of carbon (2.5) and germanium (1.7 to 1.9). Thus the inductive effect would cause a small increase in proton shift as methyl groups are replaced by germyl groups. The anisotropic effect, by comparison with the methylsilanes and methylchlorosilanes, should cause a decrease in the proton shift as the methyl groups are replaced by the much larger germyl groups. This is equivalent to assuming that the anisotropy of the Si-Ge bond, $\Delta\chi$, in McConnell's formula mentioned previously, becomes negative.

The proton chemical shift observed for the methylgermylsilanes can be explained in terms of the smaller electronegativity and larger size of the germyl group compared with the methyl group. In this explanation, it is necessary to assume that the magnetic anisotropic effect predominates, and that $\Delta\chi$ for Si-Ge bonds has a negative value.

Infrared Spectra

The frequency assignments of the fundamental vibrations of all the new compounds studied in this investigation are summarized in Table XVI and shown schematically on a correlation chart, Figure 23. These assignments are discussed briefly with particular emphasis on the characteristic frequencies associated with various groups. The following symbols and abbreviations are used: ν = valence stretching, δ = deformation, ρ = rocking,sym= symmetric,asym= asymmetric.

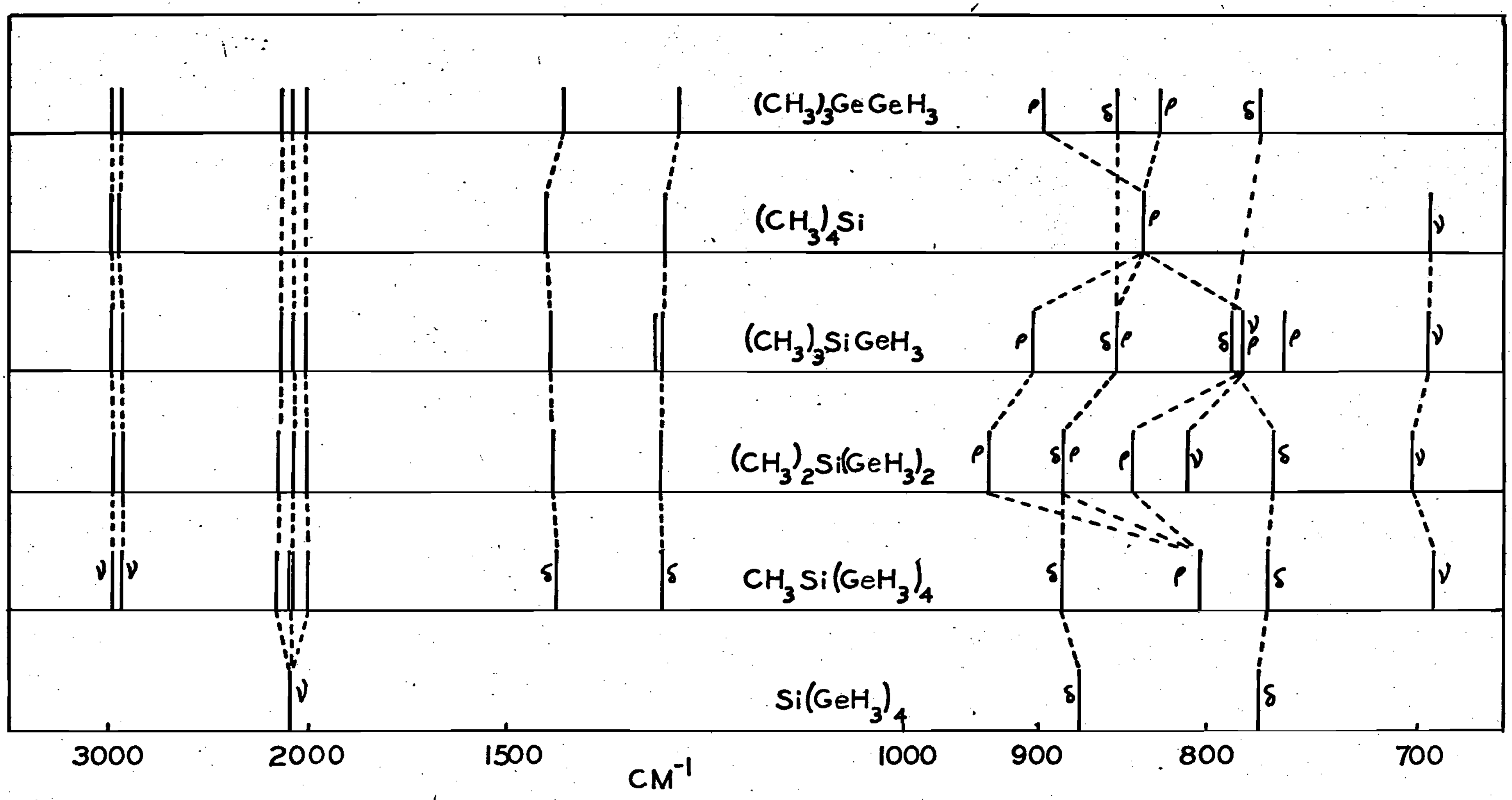
TABLE XVI

INFRARED ASSIGNMENTS

Vibration	$(GeH_3)_4Si$	$(GeH_3)_3Si(CH_3)$	$(GeH_3)_2Si(CH_3)_2$	$GeH_3Si(CH_3)_3$	$GeH_3Ge(CH_3)_3$
$\nu_{asym}CH_3$		2970	2970	2978	2980
$\nu_{sym}CH_3$		2912	2900	2910	2915
$\nu\ GeH_3$	2110 2072 2000	2115 2080 2065 2010	2120 2065 2015	2105 2060 2010	2100 2055 2010
$\delta_{asym}CH_3$		1410	1418	1412	1400
$\delta_{sym}CH_3$		1250	1258	1262 1254	1232
$\delta\ GeH_3$	872 772	885 768	883 765	786 850	850 772
$\rho\ CH_3$		802	935 883 840	903 850 781	898 824
$\nu_{asym}Si\text{-}C$			810	781	
$\nu_{Ge\text{-}C}$					<600
$\nu_{sym}Si\text{-}C$		693	702	695	

Figure 23

Infrared Correlation Chart


$(CH_3)_3GeGeH_3$
ρ
δ
ρ
δ
$(CH_3)_4Si$
ρ
ν
$(CH_3)_3SiGeH_3$
ρ
δ
ρ
δ
ν
ρ
ρ
ν
$(CH_3)_2Si(GeH_3)_2$
ρ
δ
ρ
ρ
ν
δ
ν
ν
ν
δ
δ
$CH_3Si(GeH_3)_4$
δ
ρ
δ
ν
ν
$Si(GeH_3)_4$
δ
δ
3000
2000
1500
1000
900
800
700
CM^{-1}

Trimethylgermylsilane

Trimethylgermylsilane should belong to the C_{3v} point group provided there is rotation about the symmetric position of the Si-C and Si-Ge bonds. For this model containing 17 atoms, there should be 45 fundamental vibrations, of which ten belong to the non-degenerate A_1 species, five are of the infrared inactive A_2 species, and the remaining thirty belong to the doubly degenerate E species. The symmetries of these vibrational modes given in Table XVII are based on those derived by Ball et al (60) for trimethylsilane.

The symmetric and asymmetric CH_3 stretching bands at 2910 and 2978 cm^{-1} respectively show a slightly larger separation of 68 cm^{-1} than the more symmetric tetramethylsilane for which the separation is 48 cm^{-1} (102). The frequency of the asymmetric stretching band for trimethylgermylsilane is higher than the corresponding band for tetramethylsilane. A comparison of these values (102) for tetramethylmethane (ν_{asym} = 2962 cm^{-1}), tetramethylsilane (ν_{asym} = 2967 cm^{-1}) and tetramethylgermane (ν_{asym} = 2982 cm^{-1}) reveals a linear increase in frequency with the mass attached to the methyl group, as shown in Figure 24. However the values for tetramethyltin (ν_{asym} = 2979 cm^{-1}) and tetramethyllead (ν_{asym} = 2999 cm^{-1}) fall below this line,

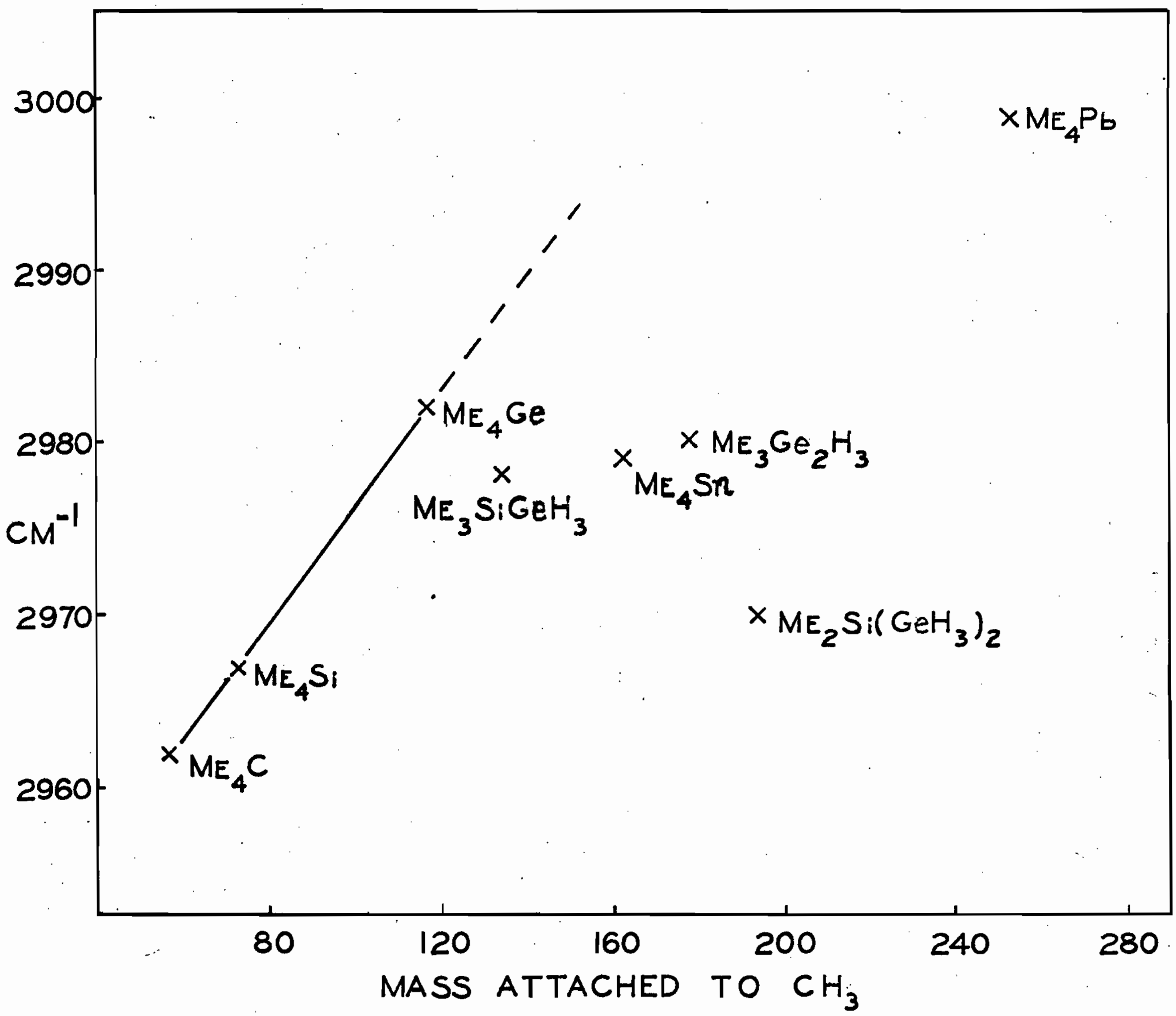
TABLE XVII

FUNDAMENTAL VIBRATIONS OF TRIMETHYLGERMYLSILANE
C_{3v} POINT GROUP

	A_1	A_2	E
ν CH asym	ν	ν	$\nu\nu$
ν CH sym	ν	-	ν
ν GeH asym	-	-	ν
ν GeH sym	ν	-	-
δ CH_3 asym	ν	ν	$\nu\nu$
δ CH_3 sym	ν	-	ν
δ GeH_3	ν	-	ν
ρ CH_3 + b Si-Ge	-	-	$\nu\nu$
ρ CH_3	ν	ν	-
ρ GeH_3	-	-	ν
ν SiC asym	-	-	ν
ν SiC sym	ν	-	-
δ SiC asym	-	-	ν
δ SiC sym	ν	-	-
τ CH_3	ν	-	-
τ GeH_3	-	ν	ν
Infrared Activity	+	-	+

Figure 24

Variation of $\nu_{asym}(CH_3)$ with Mass Attached to the Methyl Group


3000
2990
2980
2970
2960
CM^{-1}
80
120
160
200
240
280
MASS ATTACHED TO CH$_3$
ME$_4$Pb
ME$_4$Ge
ME$_3$SiGeH$_3$
ME$_4$Sn
ME$_3$Ge$_2$H$_3$
ME$_2$Si(GeH$_3$)$_2$
ME$_4$Si
ME$_4$C

indicating that the linearity of the first three members of the series is probably fortuitous, or that it is not applicable to molecules heavier than tetramethylgermane.

The weak absorption band at 2805 cm^{-1} is considered to be a combination of two of the CH_3 deformation vibrations which occur at about 1400 cm^{-1}. The GeH3 stretching vibrations give rise to a very strong band with a type C contour having a distinct PQR structure at 2105, 2060 and 2010 cm^{-1}. The sharpness and intensity of this absorption band is distinctive of germyl compounds, and it can be used to detect the presence of the GeH_3 or GeH_2 groups in a compound or a mixture.

The asymmetric CH_3 deformation band at 1412 cm^{-1} is at a lower frequency than a similar vibration of tetramethylsilane (δ_{asym} = 1430 cm^{-1}) while the symmetric band with its maximum at 1262 cm^{-1} is at a slightly higher frequency than in tetramethylsilane (δ_{sym} = 1254 cm^{-1}). The shoulder on the low frequency side of this band for trimethylgermylsilane is probably a partially resolved splitting of the symmetric vibration. The very weak band at 1074 cm^{-1} is due to the Si-O-Si absorption band of a trace impurity, probably hexamethyldisiloxane.

The absorption bands at 903, 850 and 781 cm^{-1} are all assigned to CH_3 rocking vibrations by comparison with Me_2GeCl_2 (ρCH_3 = 773, 849 cm^{-1}) and $MeSiH_2Cl$ (ρCH_3 = 873, 900 cm^{-1}). The single band of tetramethylsilane at 869 cm^{-1} splits into 3 bands as the symmetry of the molecule decreases. The asymmetric GeH_3 deformation vibration should occur in the 840-860 cm^{-1} region (cf. 842 cm^{-1} for CH_3GeH_3) (111) and it is probably masked by the CH_3 rocking band at 850 cm^{-1}. The symmetric GeH_3 deformation vibration is assigned to the band at 786 cm^{-1} mainly from intensity considerations and by comparison with the two similar fundamentals in digermane. The symmetric deformation vibration should have a much greater intensity than the asymmetric vibration, and the absorption band at 760 cm^{-1} in the spectrum of trimethylgermylsilane is much too weak to be due to symmetric GeH_3 deformation vibrations, even though its frequency compares well with one of the similar fundamentals in digermane ($\delta_{sym}GeH_3$ = 755 cm^{-1}). The band at 760 cm^{-1} might be due to a CH_3 rocking vibration.

The symmetric Si-C stretching vibration is assigned to the band at 695 cm^{-1}, virtually the same frequency as in tetramethylsilane (ν_{sym}Si-C = 696 cm^{-1}). The corresponding asymmetric vibration is probably masked by the strong bands at 781 and 786 cm^{-1}.

1,1,1-Trimethyldigermane

This molecule, like trimethylgermylsilane, should belong to the C_{3v} point group, and there should be 45 fundamental vibrations. The symmetries of these vibrations are the same as those of trimethylgermylsilane given in Table XVII when Si is replaced by Ge.

The CH_3 stretching vibrations at 2980 and 2915 cm^{-1} observed for 1,1,1-trimethyldigermane are both only 2 cm^{-1} lower than the corresponding asymmetric and symmetric vibrations of tetramethylsilane (ν_{asym} = 2982 cm^{-1}; ν_{sym} = 2917 cm^{-1}) respectively. When the value of the asymmetric stretching frequency is plotted against the mass attached to the methyl group (Figure 24), the point falls below the line which passes through the values for the tetramethyl carbon, silicon, and germanium compounds, further indicating that the linearity is probably fortuitous. The weak band at 3080 cm^{-1} could be the R branch of the asymmetric CH_3 stretching vibration, while the corresponding P branch might be hidden by the strong symmetric CH_3 stretching band at 2915 cm^{-1}. Similarly, the weak band at

2810 cm^{-1} could be the P branch of the symmetric stretching vibration, as well as a combination of two of the CH_3 deformation frequencies at about 1400 cm^{-1}. The R branch of this band would be hidden by the strong CH_3 asymmetric stretching Q branch at 2980 cm^{-1}.

The very strong, sharp band consisting of a Q branch at 2055 cm^{-1} and P and R branches at 2100 and 2010 cm^{-1} is characteristic of the GeH_3 stretching vibrations. The asymmetric CH_3 deformation vibration, assigned to the band at 1400 cm^{-1} is as expected, weaker than the absorption band at 1232 cm^{-1}, due to the symmetric CH_3 deformation vibration. The CH_3 rocking vibrations were assigned to the absorption bands at 898 and 824 cm^{-1}, from the splitting of the corresponding band in tetramethylgermane into two bands, one at higher, and one at lower frequency. The asymmetric GeH_3 deformation vibration which gives rise to the band at 850 cm^{-1} is much weaker than the absorption band at 772 cm^{-1} which from its position and intensity, can only be assigned to the symmetric GeH_3 deformation vibration. The weak shoulder at 660 cm^{-1} might be due to a Ge-C asymmetric stretching vibration, although it is at a higher frequency than that of tetramethylgermane (ν_{asym}Ge-C = 590 cm^{-1}) or dimethyldichlorogermane (ν_{asym}Ge-C = 634 cm^{-1}) (104). It would be more reasonable to assign the stronger band which is cut off at about 600 cm^{-1} to the asymmetric Ge-C stretching vibration.

Dimethyldigermylsilane

The molecular symmetry of dimethyldigermylsilane is such that it belongs to the C_{2v} point group. There are 45 fundamental vibrations for this molecule of 17 atoms, with only the A_2 species being infrared inactive. A partial list of these fundamental modes, with their symmetries, is given in Table XVIII, obtained by comparison with dimethylsilane (60).

The symmetric and asymmetric CH_3 stretching vibrations at 2970 and 2900 cm^{-1} respectively are both 10 cm^{-1} lower than the corresponding bands in trimethylgermylsilane. In addition, these absorption bands due to CH_3 are much less intense in the spectrum of dimethyldigermylsilane than they are in that of trimethylgermylsilane at the same pressure, indicating the decrease in the number of CH_3 groups. The weak band at 2800 cm^{-1} is probably a combination of two of the CH_3 deformation vibrations which occur at about 1400 cm^{-1}.

The GeH_3 stretching vibrations which give rise to the characteristic P, Q, R bands are at 2120, 2065 and 2015 cm^{-1}.

TABLE XVIII

FUNDAMENTAL VIBRATIONS OF DIMETHYLDIGERMYLSILANE
C_{2v} POINT GROUP

	A_1	A_2	B_1	B_2
ν CH asym	✓	✓	✓	✓
ν CH sym	✓	-	✓	-
ν GeH asym	✓	✓	✓	✓
ν GeH sym	✓	-	✓	-
δ GeH asym	✓	✓	✓	✓
δ GeH sym	✓	-	✓	-
δ CH asym	✓	✓	✓	✓
δ CH sym	✓	-	✓	-
ρ CH_3	✓	✓	✓	✓
ρ GeH_3	✓	✓	✓	✓
ν Si-C asym	-	-	✓	-
ν Si-C sym	✓	-	-	-
ν Si-Ge asym	-	-	✓	-
ν Si-Ge sym	✓	-	-	-
b $Si-C_2$	✓	-	-	-
b $Si-Ge_2$	✓	-	-	-
τ CH_3	-	✓	-	✓
τ GeH_3	-	✓	-	✓
Infrared Activity	+	-	+	+

These bands shift to higher frequencies as the mass attached to the germyl group increases. This effect is also found in methylgermane and methyl-d_3-germane in which the fundamental frequency increases from 2084.8 to 2090.1 cm^{-1} as the mass attached to the germyl group increases (103). The difference in frequencies of the GeH_3 bands for methylgermane and dimethyldigermylsilane (2084.8 and 2065 cm^{-1}, respectively) are probably due to differences in the Ge-H bond strength which masks out the mass effect.

The absorption bands at 1418 and 1258 cm^{-1} are assigned to the asymmetric and symmetric CH_3 deformation vibrations respectively, although they have shifted to slightly lower frequencies than in trimethylgermylsilane. The weak absorption band at 1037 cm^{-1} may be due to a combination of two of the GeH_3 rocking frequencies which would be expected to occur in the 500 cm^{-1} region (103). The CH_3 rocking vibrations are assigned to the bands at 935, 883 and 840 cm^{-1} which have all decreased in intensity compared to the corresponding bands in the spectrum of trimethylgermylsilane. This is expected from the decrease in the number of methyl groups contributing to the absorption bands.

The weak, asymmetric GeH_3 deformation vibration which is expected in the region between 880 and 900 cm^{-1} (cf. 899 cm^{-1} in Ge_2H_6 (59); 885 cm^{-1} in GeH_3SiH_3 (22); 880 cm^{-1} in GeH_3OCOCH_3 (105); 900 cm^{-1} in CH_3GeH_3 (103)) is probably masked by the CH_3 rocking band at 883 cm^{-1} or might be responsible for the weak shoulder at 840 cm^{-1}. The much stronger symmetric GeH_3 deformation is assigned to the intense band at 765 cm^{-1} by comparison with the similar band at 755 cm^{-1} in digermane (59). The strong absorption band at 810 cm^{-1} is assigned to the Si-C asymmetric stretching vibration by comparison with dimethyldichlorosilane (ν_{asym}Si-C = 805 cm^{-1}) (106), and the much weaker band at 702 cm^{-1} is assigned to the symmetric Si-C stretching vibration.

Methyltrigermylsilane

This molecule, like trimethylgermylsilane, belongs to the C_{3v} point group, and has a total of 45 fundamental vibrations. Ten of these vibrations are of the non-degenerate A_1 species, five are of the infrared inactive A_2 species, and thirty are of the doubly degenerate E species. The symmetries of these vibrations, obtained by comparison with trimethylsilane (60), are given in Table XIX.

The absorption bands due to the CH_3 stretching

TABLE XIX

FUNDAMENTAL VIBRATIONS OF METHYLTRIGERMYLSILANE

C_{3v} POINT GROUP

	A_1	A_2	E
νCH asym	-	-	✓
νCH sym	✓	-	-
νGeH asym	✓	✓	✓✓
νGeH sym	✓	-	✓
δ CH_3	✓	-	✓
δ GeH_3 asym	✓	✓	✓
δ GeH_3 sym	✓	-	✓
ρ GeH_3 + b Si-C	-	-	✓✓
ρ GeH_3	✓	✓	-
ρ CH_3	-	-	✓
ν Si-Ge asym	-	-	✓
ν Si-Ge sym	✓	-	-
δ SiGe asym	-	-	✓
δ SiGe sym	✓	-	-
ν Si-C	✓	-	-
τ CH_3	-	✓	✓
τ GeH_3	-	✓	✓
Infrared Activity	+	-	+

vibrations are much weaker in the spectrum of methyltrigermylsilane than those of any of the other methylgermylsilanes, which have a larger number of methyl groups. As expected, the asymmetric band at 2970 cm^{-1} is stronger than the symmetric absorption band at 2912 cm^{-1}. The very strong, sharp band, at 2065 cm^{-1} with a shoulder at 2080 cm^{-1} and P and R branches at 2115 cm^{-1} and 2010 cm^{-1} is assigned to the GeH_3 stretching vibrations. The occurrence of a shoulder on the high frequency side of the Q branch is unusual, and may be due to the unresolved splitting of the symmetric and asymmetric vibrations. The CH_3 deformation vibrations produce only very weak bands, with the asymmetric deformation giving a broad, diffuse band centred at about 1410 cm^{-1} while the band assigned to the symmetric deformation is very much stronger, and sharper at 1250 cm^{-1}.

The absorption band at 885 cm^{-1} is assigned to the GeH_3 asymmetric deformation vibration, at a higher frequency than the single CH_3 rocking vibration which is assigned to the sharp band of medium intensity at 802 cm^{-1}. The much stronger band at 768 cm^{-1} is assigned to the symmetric GeH_3 deformation because of its position and high intensity. The sharp absorption band at 818 cm^{-1} is not readily assigned, but may be due to the out-of-phase GeH_3 deformation vibration. It seems to be too strong to be due to an impurity and there are no other unassigned bands present in the spectrum. The remaining weak absorption band at 693 cm^{-1} is ascribed to the Si-C stretching vibration because of its position and the weakness of the absorption caused by only a single methyl group in the molecule, compared with the other methylgermylsilanes.

Tetragermylsilane

This molecule, like tetramethylsilane, has tetrahedral symmetry and belongs to the T_d point group. Because of symmetry considerations, the 45 fundamental vibrations for this molecule of 17 atoms are reduced to only nineteen, and the irreproducible form of the representation matrix is: $\Gamma = 3A_1 + A_2 + 4E + 4F_1 + 7F_2$ (107). The normal modes and their symmetries are given in Table XX (102). According to the selection rules, the wholly symmetric A_1 and doubly degenerate E vibrations are Raman active only. The triply degenerate F_2 vibrations are active in both infrared and Raman, while the A_2 and F_1 vibrations are inactive. Thus, seven fundamental frequencies should be observed in the infrared. Of these, the GeH_3 rocking vibration ν_{17}, and the triply degenerate skeletal vibrations, ν_{18} and ν_{19}, would have frequencies below 600 cm^{-1}. Of the four

TABLE XX

FUNDAMENTAL VIBRATIONS OF TETRAGERMYLSILANE

T_d POINT GROUP

	A_1	A_2	E	F_1	F_2
νGeH_3 asym	ν_1	-	ν_5	ν_9	ν_{13}
νGeH_3 sym	-	-	-	-	ν_{14}
δGeH_3 asym	-	-	ν_6	ν_{10}	ν_{15}
δGeH_3 sym	ν_2	-	-	-	ν_{16}
ρGeH_3	-	-	ν_7	ν_{11}	ν_{17}
Skeletal, non-degenerate	ν_3	-	-	-	-
Skeletal, doubly degenerate	-	-	ν_8	-	-
Skeletal, triply degenerate	-	-	-	-	ν_{18}
Skeletal, triply degenerate	-	-	-	-	ν_{19}
τGeH_3	ν_4	-	-	ν_{12}	-
Infrared Activity	-	-	-	-	+

remaining infrared active vibrations, the sharp band at 2072 cm^{-1} with weak P and R branches at 2110 and 2000 cm^{-1} is assigned to the asymmetric and symmetric GeH_3 stretching vibrations, ν_{13} and ν_{14}. The strong absorption band at 772 cm^{-1} is assigned to the symmetric GeH_3 deformation vibration, ν_{16}, because of its position and intensity. The corresponding GeH_3 asymmetric deformation vibration, ν_{15}, is expected to be much weaker, and is assigned to the very weak diffuse band centred at about 872 cm^{-1}. The very weak diffuse absorption band centred at about 1390 cm^{-1} must be a combination band, possibly the sum of the infrared active vibration ν_{16} and the Raman active ν_3 vibration, producing a combination band of the infrared active F_2 species (107).

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. Digermane was prepared in 6.8 per cent yield by the reaction of equimolar amounts of bromogermane with ammonia-free germyl sodium. The use of organic solvents such as diglyme, tetrahydrofuran and benzene actually decreased the yield, no digermane was recovered and germane was the only volatile product.

2. Bromogermane does not react with metallic sodium, but the reaction with sodium amalgam completely destroys the bromogermane and gives germane as the only volatile product.

3. A large excess of chlorine reacted explosively with ammonia-free germyl sodium, producing hydrogen chloride and germanium tetrachloride as volatile products.

4. Trimethylgermylsilane was prepared in 42 per cent yield by the reaction of trimethylchlorosilane with germyl sodium. Its vapour pressure-temperature relationship in the range 15.0 to 41.4° is expressed by the equation

$$\log P_{mm} = 3.03018 - 0.00114T + 1.75 \log T - 1455.88/T.$$

The constants calculated from this equation are: boiling point, 73.6°, heat of vaporization, -7.24 kcal./mole and Trouton's Constant, 20.88 calories degree^{-1} mole^{-1}. The melting point is -77.4±0.2°. There were two sharp peaks in the proton n.m.r. spectrum at τ = 9.97 ppm and 7.42 ppm.

5. Germyl sodium and dimethyldichlorosilane reacted to form dimethyldigermylsilane in 26.8 per cent yield. Vapour pressures in the range 23.8 to 119.5° are given by the equation:

$$\log P_{mm} = 5.27705 - 0.004334T + 1.75 \log T - 2046.05/T$$

which was used to calculate the following constants: boiling point, 117.4°; heat of vaporization, -7.69 kcal./mole; and Trouton's Constant, 19.7 calories degree^{-1} mole^{-1}. The melting point was -93.1±0.1° and the two equal peaks in the proton n.m.r. spectrum occurred at τ = 9.67 ppm and 7.00 ppm.

6. Dimethyldigermylsilane was stable at 85° and decomposed at 200° into dimethylsilane, germane, hydrogen and a germanium mirror which had the empirical formula $GeH_{0.66}$.

7. A 34.4 per cent yield of methyltrigermylsilane was obtained when an excess of methyltrichlorosilane was condensed on ammonia-free germyl sodium. The vapour pressure of this

compound in the range from 27.9 to 105.1° is given by the equation

$$\log P_{mm} = 2.65334 - 0.00266\,T + 1.75 \log T - 1817.73/T.$$

The following constants were calculated from this equation: boiling point, 153.5°, heat of vaporization, -9.58 kcal./mole and Trouton's Constant, 22.45 calories degree^{-1} mole^{-1}. The melting point was -101.0±0.1°. The proton n.m.r. spectrum consisted of two peaks at $\tau = 9.43$ ppm and 6.69 ppm.

8. Germyl sodium and silicon tetrachloride reacted to give very small quantities of tetragermylsilane which was identified by its infrared and proton n.m.r. spectra. The latter consisted of only a single sharp peak at $\tau = 6.36$ ppm. The melting point was -53.3±0.4°.

9. When silicon tetrafluoride was bubbled through a solution of germyl sodium in liquid ammonia, germane was produced, but no tetragermylsilane. Silicon tetrafluoride in the gas phase did not react with ammonia-free germyl sodium to produce tetragermylsilane.

10. The interaction of bromosilane and germyl sodium produced a 7.8 per cent yield of germylsilane which had recently been

prepared by other methods.

11. Trimethylbromogermane reacted with ammonia-free germyl sodium to give an 8.5 per cent yield of 1,1,1-trimethyldigermane, and it was also produced in 36.4 per cent yield by the action of trimethylfluorogermane on an excess of ammonia-free germyl sodium. In the range from 0.0 to 54.0°, the vapour pressure of this compound is given by the equation:

$$\log P_{mm} = 8.1394 - 0.00824\,T + 1.75 \log T - 2393.04/T.$$

Constants calculated from this equation are: boiling point, 77.6°, heat of vaporization, -7.53 kcal./mole, and Trouton's Constant, 21.46 calories degree^{-1} mole^{-1}. The melting point was $-89.6 \pm 0.2°$. The proton n.m.r. spectrum consisted of two peaks at τ = 7.07 ppm and 9.75 ppm.

12. An explanation is given for the decrease in melting point with increase in molecular weight in the series of methylgermylsilanes. Although this decrease is apparently opposite that found for an homologous carbon series, it is attributed to decreased van der Waals bonding in the solid, due to decreased proton density around the germanium atoms which replace the carbon atoms.

13. The boiling points of the series of methylgermylsilanes were shown to increase linearly with molecular weight, and the first two members of the analogous germanium series show a similar increase. This is taken to indicate that there is little difference between silicon and germanium in these two series.

14. Proton n.m.r. data showed that the replacement of a methyl group by a germyl group decreased the proton shielding in the series of methylgermylsilanes. This shift was explained in terms of the smaller electronegativity and large size of the germyl group compared with the methyl group, assuming that the effect of magnetic anisotropy predominates.

15. The infrared spectra of five new compounds were determined in the gas phase, and frequency assignments were made for absorption bands in the region 4000 to 650 cm^{-1}.

COMPOUNDS CONTAINING THE GERMYL (GeH_3) GROUP

Compound	Melting Point °C	Boiling Point °C	Method of Preparation	Reference
GeH_4	-165	-88.5		1,2,3,4, 33,61
Ge_2H_6	-109	29	By-product of GeH_4 Gas Discharge	29 5
Ge_3H_8	-	-	By-product of GeH_4	5
Ge_4H_{10}	-	176.9	HCl on Mg_2Ge	62
Ge_5H_{12}	-	234	" " "	62
Ge_6H_{14} to Ge_9H_{20}	-	-	Gas Discharge	5
GeH_3CH_3	-	-	GeH_3Na	10,36
	-158	-35.1/760 mm	$LiAlH_4$	35
	-	-23.5/745 mm	LiH	34
$CH_2{=}CHGeH_3$	-	- 3.5	$LiAlH_4$	13
$CH_2{=}CHCH_2GeH_3$	-	37/752.7 mm	$LiAlH_4$	12
$C_2H_5GeH_3$	-	-	GeH_3Na	10,36
	-	11.5/743.5 mm	LiH	34
i-Amyl GeH_3	-	-	$GeH_3Na(NH_3)$	36

Compound	Melting Point °C	Boiling Point °C	Method of Preparation	Reference
n-$C_3H_7GeH_3$	-	-	$GeH_3Na(NH_3)$	10
	-	30/760 mm	$LiAlH_4$	37
n-$C_4H_9GeH_3$	-	74	"	11
n-$C_5H_{11}GeH_3$	-	104-5	"	11
n-$C_6H_{13}GeH_3$	-	128.9	"	11
n-$C_7H_{15}GeH_3$	-	85/74 mm	"	11
n-$C_8H_{17}GeH_3$	-	80/31 mm	"	11
$CF_3CH_2CH_2GeH_3$	-	46/750.5 mm	LiH	12
GeH_3F	-22	15.6	$GeH_3Br+AgF$	39
GeH_3Cl	-52	28	$GeH_4+HCl(AlCl_3)$	15
GeH_3Br	-32	52	$GeH_4+HBr(AlBr_3)$	15
			GeH_4+Br_2	16
GeH_3I	-	-	-	38
GeH_3GeH_2I	-17	-	$Ge_2H_6+I_2$(-63°C)	14
GeH_3GeH_2Cl	-	-	$GeH_3GeH_2I+AgCl$	14
GeH_3CN	-	-	$GeH_3Cl+AgCN$	16

Compound	Melting Point °C	Boiling Point °C	Method of Preparation	Reference
GeH_3NCO	-44.0	71.5	$GeH_3Cl+AgNCO$	16
GeH_3NCS	18.6	150	$GeH_3Br+AgNCS$	16
GeH_3OCOCH_3	12.6	82.4	$GeH_3Br+AgOCOCH_3$	16
GeH_3OCH_3	-	-	$GeH_3Cl+NaOCH_3$ (-50°C)	18
GeH_3OGeH_3	-	0/66 mm	$(GeH_3)_2S+HgO_{(red)}$ (-40°C)	20
GeH_3SGeH_3	-	0/5 mm	GeH_3I+HgS	20
GeH_3Na	-	-	$GeH_4+Na(NH_3)$	10
GeH_3K	-	-	$GeH_4+K(NH_3)$	10
$GeH_3Li \cdot 2NH_3$	-	-	$GeH_4+Li(NH_3)$	21
AsH_2GeH_3	-	-	Gas Discharge	43
	-	-	CaGe /Ca_3As_2+HCl	25
PH_2GeH_3	-	-	Gas Discharge	43
	-	-	CaGe /Ca_3P_2+HCl	25
GeH_3GePH_4	-	-	Gas Discharge	43
$GeH_3P_2H_3$ (?)	-	-	" "	43
GeH_3NH_2	-	-	CaGe /Ca_3N_2	25

Compound	Melting Point °C	Boiling Point °C	Method of Preparation	Reference
GeH_3SiH_3	-119.7	7.0	Gas Discharge	22
	-	-	$GeH_3Cl+SiH_3K$	24
	-	-	$SiH_3Br+GeH_3Br$	This work
	-	-	Ca(Ge,Si)+HCl	23
	-	-	Mg(Ge,Si)+HCl	26
Si_2GeH_8 to Si_5GeH_{14}	-	-	"	26
$SiGe_2H_8$ to $SiGe_3H_{10}$	-	-	"	26
$Si_3Ge_2H_{12}$	-	-	"	26
$Si_2Ge_3H_{14}$	-	-	"	26
$GeH_3Si(CH_3)_3$	-77.4	73.6	$GeH_3Na+ClSi(CH_3)_3$	This work
$(GeH_3)_2Si(CH_3)_2$	-93.1	117.4	" $+Cl_2Si(CH_3)_2$	"
$(GeH_3)_3SiCH_3$	-101.0	153.5	" $+Cl_3SiCH_3$	"
$(GeH_3)_4Si$	-53.3	-	" $+SiCl_4$	"
$GeH_3Ge(CH_3)_3$	-89.6	77.6	" $+FGe(CH_3)_3$	"

APPENDIX II

COMPUTER CALCULATION OF VAPOUR PRESSURE EQUATION BY THE METHOD OF LEAST SQUARES

The coefficients of an expression are calculated by the "Method of Least Squares" by minimizing the sum of the squares of the difference between the calculated and observed values by partial differentiation with respect to each coefficient. For the vapour pressure - temperature relationship,

$$\log P = A - BT + C \log T - D/T \text{ ,} \qquad \ldots 1)$$

if we let $\log P = y$ and $A - BT + C \log T - D/T = f(x_i)$, then $y = f(x_i)$.

Let $V_i = f(x_i) - y_i$ and then S, the sum of the errors squared is $S = \sum_1^n V_i^2 = \sum_1^n \left[f(x_i) - y_i\right]^2$

$$\text{or} \quad S = \sum_1^n \left[A - BT_i + C \log T_i - D/T_i - \log P_i\right] \qquad \ldots 2)$$

where n is the number of experimental data.

Conditions for the best fit by the "Method of Least Squares" are:

$$\frac{\partial S}{\partial A} = 0 \qquad \ldots 3)$$

$$\frac{\partial S}{\partial B} = 0 \qquad \ldots 4)$$

$$\frac{\partial S}{\partial C} = 0 \qquad \text{... 5)}$$

$$\frac{\partial S}{\partial D} = 0 \qquad \text{... 6)}$$

On differentiation of equation 2 according to equations 3, 4, 5 and 6, four simultaneous equations are obtained:

$$nA - B\sum T_i + C\sum \log T_i - D\sum \frac{1}{T} = \sum \log P_i \qquad \text{... 7)}$$

$$A\sum T_i - B\sum {T_i}^2 + C\sum T_i \log T_i - nD = \sum T_i \log P_i \qquad \text{... 8)}$$

$$A\sum \log T_i - B\sum T_i \log T_i + C\sum(\log T_i)^2 - D\sum \frac{\log T_i}{T_i}$$

$$= \sum(\log P_i/\log T_i) \qquad \text{... 9)}$$

$$A\sum 1/T_i - nB + C\sum \log T_i/T_i - D\sum 1/{T_i}^2 = \sum \log P_i/T_i \qquad \text{..10)}$$

The solution of these four simultaneous equations gives values of A, B, C and D. The computer program on the following four pages written in Fortran IV for an IBM 7040 computer does this computation for all four variables and also for C fixed at 1.75, the value used in the standard Nernst equation (108). The print-out from this program gives the name of the compound, the final equation, a list of all the experimental data with the corresponding calculated pressures, the difference, V_i, and for convenience in plotting, the values of $1/T_i$. The sum of the errors squared, S, is given so that a comparison can be made of the fit of the two equations. The boiling point is calculated by increasing the temperature from 0°C in 5° steps until the calculated pressure is greater than 760 mm. The value of T_i is then decreased by 1° steps until P_i is less than 760 mm and finally T_i is increased by 0.05° steps until P_i is again greater than 760 mm. This value of the boiling point is then printed out.

The heat of vaporization, ΔH is calculated by differentiation of equation 1 with respect to T at the previously calculated boiling point. This value is also printed out, Trouton's Constant is calculated from the value of the heat of vaporization divided by the boiling point and printed out.

```
      PRESSURE TEMPERATURE LEAST SQUARES FIT ROUTINE
      DIMENSIONP(50),T(50),TC(50),ALGT(50),ALGP(50),PC(50),ER(50),RT(50)
     1 ,GAS(12)
      READ 1000, GAS
      PRINT 2001, GAS
      READ 1001, N
      READ1002,(TC(I),P(I), I =1,N)
      SUMT = 0.0
      SUMLT = 0.0
      SINVT = 0.0
      SUMLP =0.0
      SUMT2 = 0.0
      SUMTLT =0.0
      SUMTLP =0.0
      SUMLT2 = 0.0
      SIVTLT = 0.0
      SIVTLP = 0.0
      SLPLT = 0.0
      SINVT2 = 0.0
      SER2 = 0.0
      DO 10  I = 1, N
      T(I)= TC(I)+273.16
      ALGT(I) = ALOG10(T(I))
      ALGP(I) = ALOG10(P(I))
      SUMT = SUMT + T(I)
      SUMLT = SUMLT +ALGT(I)
      SINVT = SINVT + 1.0/T(I)
      SUMLP = SUMLP + ALGP(I)
      SUMT2 = SUMT2 + T(I)*T(I)
      SUMTLT = SUMTLT +T(I)*ALGT(I)
      SUMTLP = SUMTLP+T(I)* ALGP(I)
      SUMLT2 = SUMLT2 + ALGT(I)*ALGT(I)
      SIVTLT = SIVTLT +ALGT(I)/T(I)
      SIVTLP = SIVTLP +ALGP(I)/T(I)
      SLPLT = SLPLT + ALGP(I) * ALGT(I)
   10 SINVT2 = SINVT2 + 1.0/(T(I)*T(I))
      PRINT 2002, SUMT, SUMLP
      AN = N
      E1 = AN * SUMT2 - SUMT*SUMT
      E2 = SUMT * SUMLT - AN * SUMTLT
      E3 = AN * AN - SINVT * SUMT
      E4 = SUMT * SUMLP - AN * SUMTLP
      E5 = SUMTLT * SUMT - SUMT2 * SUMLT
      E6 = SUMTLT * SUMLT - SUMLT2 * SUMT
      E7 = SIVTLT * SUMT - AN * SUMLT
      E8 = SUMTLP * SUMLT - SLPLT * SUMT
      E9 = AN * SUMLT - SUMTLT * SINVT
      E10 = SUMLT2*SINVT - SIVTLT * SUMLT
      E11 = SINVT2 * SUMLT - SIVTLT * SINVT
      E12 = SLPLT * SINVT - SIVTLP * SUMLT
      F1 = E2 * E5 - E6 * E1
      F2 = E3 * E5 - E7 * E1
      F3 = E4 * E5 - E8 * E1
      F4 = E6*E9 - E10 * E5
```

```
      F5 = E7 * E9 - E11 * E5
      F6 = E8 * E9 - E12 * E5
      D = (F3 * F4 - F6 * F1 )/(F2 * F4 - F5 * F1)
      C = (F6 - F5 * D)/F4
      B = (E12 - E11 * D - E10 * C )/E9
      A = (B*SUMT - C*SUMLT + D*SINVT +SUMLP)/AN
      PRINT 2000, A, B, C, D
      PRINT 2006
      L = 0
      DO 30   I = 1, N
      PC(I) = 10.0 ** (A-B*T(I) + C*ALGT (I) - D/T(I))
      ER(I) = P (I) - PC(I)
      RT(I) = 1.0/T(I)
      SER2 = SER2 +ER(I)*ER(I)
      PRINT  2005 , TC(I), P(I), PC(I), ER(I), RT(I)
      IF (L.LT.45) GO TO 30
      PRINT 2007
      L = 0
   30 L = L+2
      PRINT 2003, SER2
C     BOILING POINT DETERMINATION
      TEMPC = 0.00
      DO 60 I=1,50
      TEMP = TEMPC + 273.16
      RTK = 1.0/TEMP
      BLGT = ALOG10(TEMP)
      PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
      PRINT 2008, TEMPC, PCAL, RTK
      IF (L.LT.45) GO TO 50
      PRINT 2007
      L = 0
   50 L=L+1
      IF(PCAL .GT. 760.00) GO TO 80
   60 TEMPC = TEMPC + 5.00
   80 DO 61 I=1,6
      TEMP = TEMPC + 273.16
      RTK = 1.0/TEMP
      BLGT = ALOG10(TEMP)
      PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
      PRINT 2008, TEMPC, PCAL, RTK
      IF ( L.LT. 45) GO TO 51
      PRINT 2007
      L = 0
   51 L=L+1
      IF (PCAL.LT. 760.00) GO TO 81
   61 TEMPC = TEMPC - 1.00
   81 DO 62 I=1,20
      TEMP = TEMPC + 273.16
      RTK = 1.0/TEMP
      BLGT = ALOG10(TEMP)
      PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
      PRINT 2008, TEMPC, PCAL, RTK
      IF ( L.LT.45) GO TO 52
      PRINT 2007
      L = 0
```

```
   52 L= L+1
      IF (PCAL.GT. 760.00) GO TO 82
   62 TEMPC = TEMPC + 0.05
   82 PRINT 2009, TEMPC
      HVAP = (B*TEMP*TEMP - 0.43429*C*TEMP - D)*2.30258*1.987
      TROUT =- HVAP*RTK
      PRINT 2011,HVAP
      PRINT 2012, TROUT
C     PRESSURE TEMPERATURE LEAST SQUARES FIT ROUTINE  C=1.75
      PRINT 2001, GAS
      SER2 = 0.0
      E1 =AN*SUMT2 - SUMT*SUMT
      E2 =(SUMLT*SUMT - AN*SUMTLT)*1.75
      E3 = AN*AN-SUMT*SINVT
      E4 = SUMT* SUMLP - AN* SUMTLP
      E5 = AN *SUMT - SUMT2 * SINVT
      E6 =(SUMTLT * SINVT - SUMT * SIVTLT)* 1.75
      E7 = SUMT * SINVT2- AN* SINVT
      E8 = SUMTLP * SINVT - SIVTLP * SUMT
      D = (E5*(E4-E2)-E1*(E8-E6))/(E3*E5-E7*E1)
      C = 1.75
      B = (E4-E2-E3*D)/E1
      A = (B*SUMT - C*SUMLT +D*SINVT +SUMLP)/AN
      PRINT 2000,A,B,C,D
      PRINT 2006
      L = 0
      DO 40 I =1,N
      PC(I) = 10.0**(A-B*T(I) +C*ALGT(I) - D/T(I))
      ER(I) = P(I) - PC(I)
      RT(I) = 1.0/T(I)
      SER2 = SER2 + ER(I)* ER(I)
      PRINT 2005,TC(I),P(I),PC(I),ER(I),RT(I)
      IF (L.LT.45) GO TO 40
      PRINT 2007
      L = 0
   40 L=L+2
      PRINT 2003, SER2
C     BOILING POINT DETERMINATION
      TEMPC = 0.00
      DO 70 I= 1,50
      TEMP = TEMPC + 273.16
      RTK = 1.0/TEMP
      BLGT = ALOG10(TEMP)
      PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
      PRINT 2008, TEMPC, PCAL, RTK
      IF (L.LT. 45) GO TO 55
      PRINT 2007
      L = 0
   55 L=L+1
      IF (PCAL.GT.760.00) GO TO 90
   70 TEMPC = TEMPC + 5.00
   90 DO 71 I=1,6
      TEMP = TEMPC + 273.16
      RTK = 1.0/TEMP
      BLGT = ALOG10(TEMP)
```

```
     PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
     PRINT 2008, TEMPC, PCAL, RTK
     IF (L.LT.45) GO TO 56
     PRINT 2007
     L = 0
  56 L=L+1
     IF (PCAL .LT. 760.00) GO TO 91
  71 TEMPC = TEMPC - 1.00
  91 DO 72 I= 1,20
     TEMP = TEMPC + 273.16
     RTK = 1.0/TEMP
     BLGT = ALOG10(TEMP)
     PCAL = 10.0**(A - B*TEMP + C*BLGT - D/TEMP)
     PRINT 2008, TEMPC, PCAL, RTK
     IF (L.LT.45) GO TO 57
     PRINT 2007
     L = 0
  57 L=L+1
     IF (PCAL.GT.760.00) GO TO 92
  72 TEMPC = TEMPC + 0.05
  92 PRINT 2009, TEMPC
     HVAP = (B*TEMP*TEMP - 0.43429*C*TEMP - D)*2.30258*1.987
     TROUT =- HVAP*RTK
     PRINT 2011,HVAP
     PRINT 2012, TROUT
1000 FORMAT (12A6)
1001 FORMAT (I2)
1002 FORMAT (F5.1,F8.2)
2000 FORMAT(8H0LOG P = F10.6,3H - F10.6,4HT + F10.5,9H LOG T - F11.6,2H/T)
    1/T)
2001 FORMAT (36H1 NERNST VAPOR PRESSURE EQUATION FOR 12A6)
2002 FORMAT (9H0 SUMT = F10.3,12HSUM LOG P = F10.3)
2003 FORMAT(27H0 SUM OF ERRORS SQUARED IS   ,F8.4)
2005 FORMAT (1H0,F22.2,F15.2,F17.2,F14.2,F15.6)
2006 FORMAT (86H0               TEMP, C.    P, MM.,  EXP.      P,MM.,
    1CALC.     ERROR         1/T                )
2007 FORMAT (86H1               TEMP, C.    P, MM.,  EXP.      P,MM.,
    1CALC.     ERROR         1/T                )
2008 FORMAT (1H , F22.2,F32.2,F19.6)
2009 FORMAT (23H0 THE BOILING POINT IS   F6.2)
2011 FORMAT (27H0 HEAT OF VAPORIZATION IS  ,F10.2, 14HCALORIES/MOLE  )
2012 FORMAT(23H0 TROUTON'S CONSTANT IS  , F8.2)
     STOP
     END
```

BIBLIOGRAPHY

1. Voegelen, E. Z. anorg. Chem. 30, 325 (1902).
2. Müller, J.H. and Smith, N.H. J. Am. Chem. Soc. 44, 1909 (1922).
3. Paneth, F. and Schmidt-Hebbel, E. Chem. Ber. 55, 2615 (1922).
4. Schenck, R. Rec. Trav. Chim. 41, 569 (1922).
5. Drake, J.E. and Jolly, W.L. J. Chem. Soc. 2807 (1962).
6. Johnson, O.H. Chem. Revs. 48, 259 (1951).
7. Rijkens, F. "Organogermanium Compounds", Germanium Research Committee, Utrecht, November, 1960.
8. Quane, D. and Bottei, R.S. Chem. Revs. 63, 403 (1963).
9. Borer, K. and Phillips, C.S.G. Proc. Chem. Soc. 189 (1959).
10. Teal, G.K. and Kraus, C.A. J. Am. Chem. Soc. 72, 4706 (1950).
11. Satgé, J. Ann. Chim. (Paris) 6, 519 (1961).
12. Ponomarenko, V.A., Zueva, G.Ya., and Andreev, N.S. Izv. Akad. Nauk SSSR, Otdel Khim. Nauk, 1358 (1961) English Trans. 1639. Chem. Abstracts 58, 3904 e
13. Brinckman, F.E. and Stone, F.G.A. J. Inorg. and Nuclear Chem. 11, 24 (1959).
14. MacKay, K.M. and Roebuck, P.J. J. Chem. Soc. 1195 (1964).
15. Dennis, L.M. and Judy, P.R. J. Am. Chem. Soc. 51, 2321 (1929).

16. Srivastava, T.N., Griffiths, J.E. and Onyszchuk, M. Can. J. Chem. 40, 739 (1962).

17. Seyferth, D. and Kahlen, N. J. Org. Chem. 25, 809 (1960).

18. Griffiths, J.E. Thesis, McGill University, 1958.

19. van Dyke, C.H. Private Communication, March 1965.

20. Goldfarb, T.D. and Sujishi, S. J. Am. Chem. Soc. 86, 1679 (1964).

21. Amberger, E. and Boeters, H.D. Angew. Chem. 75, 860 (1963).

22. Spanier, E.J. and MacDiarmid, A.G. Inorg. Chem. 2, 215 (1963).

23. Royen, P. and Rocktäschel, C. Angew. Chem. (Int'l Ed) 3, 314 (1964).

24. Varma, R. and Cox, A.P. Angew. Chem. (Int'l Ed) 3, 586 (1964).

25. Royen, P., Rocktäschel, C. and Mosch, W. Angew. Chem. (Int'l Ed) 3, 703 (1964).

26. Timms, P.L., Simpson, C.C. and Phillips, C.G.S. J. Chem. Soc. 1467 (1964).

27. Sujishi, S. and Keith, J.N. J. Am. Chem. Soc. 80, 4138 (1958).

28. Macklen, E.D. J. Chem. Soc. 1989 (1959).

29. Dennis, L.M., Corey, R.B. and Moore, R.W. J. Am. Chem. Soc. 46, 657 (1924).

30. Jolly, W.L. J. Am. Chem. Soc. 83, 335 (1961).

31. Féher, F. and Cramer, J. Z. Anorg. Chem. 297, 14 (1958).

32. Faktor, M.M. J. Phys. Chem. 66, 1003 (1962).

33. Piper, T.S. and Wilson, M.K. J. Inorg. and Nuclear Chem. 4, 22 (1957).

34. Ponomarenko, V.A., Vzenkova, G.Ya. and Egorov, Yu. P. Doklady Akad. Nauk SSSR, 122, 405 (1958). Eng. Trans., 703. Chem. Abstracts 53, 112 e.

35. Amberger, E. and Boeters, H. Angew. Chem. 73, 114 (1961).

36. Glarum, S.N. and Kraus, C.A. J. Am. Chem. Soc. 72, 5398 (1950).

37. Johnson, O.H. and Jones, L.V. J. Org. Chem. 17, 1172 (1952).

38. Sujishi, S. Abstract of XVII International Congress of Pure and Applied Chemistry, Munich 1959. Lecture A 225, p.53.

39. Srivastava, T.N. and Onyszchuk, M. Proc. Chem. Soc. 205 (1961).

40. MacDiarmid, A.G. Quart. Rev. (London). 208 (1956).

41. Kraus, C.A. and Carney, E.S. J. Am. Chem. Soc. 56, 765 (1934).

42. Emeléus, H.J. and MacKay, K.M. J. Chem. Soc. 2676 (1961).

43. Drake, J.E. and Jolly, W.L. Chem. and Ind. (London) 1470 (1962).

44. Jolly, W.L. "Synthetic Inorganic Chemistry" Prentice-Hall, Englewood-Cliffs, N.J., 1960.

45. Dodd, R.E. and Robinson, P.L. "Experimental Inorganic Chemistry" Elsevier Publishing Co., London, 1954.

46. Dushman, S. "Scientific Foundations of Vacuum Technique" John Wiley and Sons, Inc. New York, 1949.

47. Stock, A. "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y., 1933.

48. Laubengayer, A.W. and Corey, R.B. J. Phys. Chem. 30, 1043 (1926).

49. LeRoy, D.J. Can. J. Res. 28B, 492 (1950).

50. Cady, G.H. and Siegwarth, D.P. Anal. Chem. 31, 618 (1959).

51. Finholt, A.E., Bond, A.C. Jr., Wilzbach, K.E. and Schlesinger, H.I. J. Am. Chem. Soc. 69, 2692 (1947).

52. Emeléus, H.J. and Gardner, E.R. J. Chem. Soc., 1900 (1938).

53. Emeléus, H.J. and Jellinek, H.H.G. Trans. Faraday Soc. 40, 93 (1944).

54. Brown, M.P. and Fowles, G.W.A. J. Chem. Soc. 2811 (1958).

55. Kraus, C.A. and Flood, E.A. J. Am. Chem. Soc. 54, 1635 (1932).

56. Johnson, O.H. and Harris, D.M. J. Am. Chem. Soc. 72, 5564 (1950).

57. Johnson, O.H. and Nebergall, W.H. J. Am. Chem. Soc. 70, 1706 (1948).

58. Shackelford, J.M., De Schmertzing, H., Heuther, C.H. and Podall, H. J. Org. Chem. 28, 1700 (1963).

59. Dows, D.A. and Hexter, R.M. J. Chem. Phys., 24, 1029 (1956).

60. Ball, D.F., Goggin, P.L., McKean, D.C. and Woodward, L.A. Spectrochim. Acta 16, 1358 (1960).

61. Corey, R.B., Laubengayer, A.W. and Dennis, L.M. J. Am. Chem. Soc. 47, 112 (1925).

62. Amberger, E. Angew. Chem. 71, 372 (1959).

63. Rochow, E.G., Hurd, D.T. and Lewis, R.N. "The Chemistry of Organometallic Compounds", John Wiley and Son. Inc., N.Y. 1957.

64. Kraus, C.A. Chem. Revs. 8, 251 (1931).

65. Kraus, C.A. and Foster, L.S. J. Am. Chem. Soc. 49, 457 (1927).

66. Kraus, C.A. and Nutting, H.S. J. Am. Chem. Soc. 54, 1622 (1932).

67. Kraus, C.A. and Sherman, C.S. J. Am. Chem. Soc. 55, 4694 (1933).

68. Gilman, H. and Gerow, C.W. J. Am. Chem. Soc. 79, 342 (1957).

69. Gilman, H. and Gerow, C.W. J. Org. Chem. 22, 334 (1957).

70. George, M.V., Peterson, D.J. and Gilman, H. J. Am. Chem. Soc. 82, 403 (1960).

71. Gilman, H. and Gerow, C.W. J. Am. Chem. Soc. 78, 5435 (1956).

72. Kraus, C.A. and Neal, A.M. J. Am. Chem. Soc. 52, 695 (1930).

73. Smith, F.B. and Kraus, C.A. J. Am. Chem. Soc. 74, 1418 (1952).

74. Gilman, H. and Gerow, C.W. J. Am. Chem. Soc. 78, 5823 (1956).

75. Milligan, J.G. and Kraus, C.A. J. Am. Chem. Soc. 72 5297 (1950).

76. Gilman, H. and Smith, C.L. J. Am. Chem. Soc. 86, 1454 (1964).

77. Kraus, C.A. and Neal, A.M. J. Am. Chem. Soc. 52, 4426 (1930).

78. Cottrell, T.L. "The Strengths of Chemical Bonds" Ed. 2 Butterworths, London, 1958.

79. Brown, M.P. and Webster, D.E. J. Phys. Chem. 64, 698 (1960).

80. Pople, J.A., Schneider, W.G. and Bernstein, H.J. "High Resolution Nuclear Magnetic Resonance" McGraw Hill, N.Y., 1959.

81. Jackman, L.M. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", International Series of Monographs on Organic Chemistry, Vol.5, London, 1959.

82. Schmidbaur, H. Chem. Ber. 97, 1639 (1964).

83. Van der Kelen, G.P., Verdonck, L. and Van der Vondel, D. Bull. Chem. Soc. Belgium 73, 733 (1964).

84. Allred, A.L. and Rochow, E.G. J. Am. Chem. Soc. 79, 5361 (1957).

85. Amberger, E., Fritz, H.P., Kreiter, C.G. and Kula, M-R. Chem. Ber. 96, 3270 (1963).

86. Pauling, L. "The Nature of the Chemical Bond" Cornell Univ. Press, Ithaca, N.Y. 1939.

87. Constantinides, E. Proc. Chem. Soc. 290 (1964).

88. McCoy, C.R. and Allred, A.L. J. Inorg. and Nuclear Chem. 25, 1219 (1963).

89. Dailey, B.P. and Shoolery, J.N. J. Am. Chem. Soc. 77, 3977 (1955).

90. Ebsworth, E.A.V. and Turner, J.J. J. Phys. Chem. 67, 805 (1963).

91. Ebsworth, E.A.V. and Frankiss, S.G. Trans. Faraday Soc. 59, 1518 (1963).

92. Bothner-By, A.A. and Naar-Colin, C. J. Am. Chem. Soc. 80, 1728 (1958).

93. Schmidbaur, H. and Ruidisch, I. Inorg. Chem. 3, 599 (1964).

94. Schaefer, T., Reynolds, W.F. and Yonemoto, T. Can. J. Chem. 41, 2969 (1963).

95. McConnell, H.M. J. Chem. Phys. 27, 226 (1957).

96. Reddy, G.S. and Goldstein, J.H. J. Chem. Phys. 38, 2736 (1963).

97. "Handbook of Chemistry and Physics" 44th Ed. The Chemical Rubber Publishing Co., Cleveland, 1963.

98. Drago, R.S. and Matwiyoff, N.A. J. Organometal. Chem. 3, 62 (1965).

99. Drago, R.S. J. Inorg. and Nuclear Chem. 15, 237 (1960).

100. Coulson, C.A. "Valence" 2nd Ed. Oxford University Press, 1961.

101. Whitehead, M.A., Baird, N.C. and Kaplansky, M. Theoret. Chim. Acta In Press, 1965.

102. Young, C.W., Koehler, J.S. and McKinney, D.S. J. Am. Chem. Soc. 69, 1410 (1947).

103. Griffiths, J.E. J. Chem. Phys. 38, 2879 (1963).

104. Griffiths, J.E. Spectrochim.Acta 20, 1335 (1964).

105. Srivastava, T.N. and Onyszchuk, M. Can. J. Chem. 41, 1244 (1963).

106. Smith, A.L. J. Chem. Phys. 21, 1997 (1953).

107. Kovalev, I.F. Optics and Spectroscopy 6, 387 (1959).

108. Griffiths, J.E. Inorg. Chem. 2, 375 (1963).