THE PREPARATION AND PROPERTIES OF DERIVATIVES OF GERMANE

by

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INTRODUCTION

The chemistry of carbon and to a lesser extent that of silicon has been extensively studied and recent rapid progress in organosilicon chemistry has prompted renewed interest in the properties of tetracovalent germanium compounds. Much of the work has centred on compounds of the type, $R_{4-n}GeX_n$ where n = 0 to 4, R is alkyl or aryl and X is a uni- or divalent atom. Since comprehensive reviews on the chemistry of inorganic and organic germanium compounds are available (56, 57), only a brief outline of the more relevant literature will be given here to facilitate discussion of the reactions and new compounds reported in this thesis.

Nomenclature

Although considerable interest was focussed on germanium compounds from about 1920 to 1936, renewed activity in this field during the past decade has resulted in a gradual change in the nomenclature of organogermanium compounds. Therefore, the following tentative rules for the naming of these compounds, concordant with modern usage, are given:

1) The names "germane", "digermane" and "trigermane" are now generally accepted for the first three alkane type hydrides of germanium. Their derivatives are structurally analogous to those of the first three members of the alkane series and the rules accepted for the nomenclature of organic compounds (109) should be followed as closely as possible in the naming of germanium analogues.

2) If organic nomenclature is ambiguous or inapplicable, the recommend-

ations of the Committee on Nomenclature, Spelling and Pronunciation of the American Chemical Society for the naming of silicon compounds (21) should be followed for the naming of analogous germanium compounds.

3) Inorganic nomenclature is recommended in accordance with present organic usage if such naming is simpler and more specific. Thus, GeH_3Br becomes germyl bromide, but bromogermane is equally correct.

The combining term "sil-" rather than "silic-" is recommended for silicon (21) and the analogous shorter form "germ-" instead of "german-" for germanium is less confusing. Thus the GeH_3 group becomes "germyl" and GeH_3O- is called "germoxy" corresponding to "silyl" and "siloxy" in silicon compounds. The GeH_2 group becomes "germylene" and Ge_2H_5 the "digermanyl" radical. Similarly, $(GeH_3)_2O$ is called digermoxane instead of bis-digermanyl oxide. Use of the shorter term "germ" renders the nomenclature of germanium compounds more consistent with respect to the parent germane and with the well established nomenclature of organosilicon compounds. Therefore, the preceding rules have been adopted in the naming of germanium compounds encountered in this thesis.

Inorganic Hydrides of Germanium

Only three volatile binary hydrides of germanium have been isolated, namely mono-, di- and tri-germane (22, 27). Their physical properties are summarized in the following table.

Hydride	B.P. (°C)	M.P. (°C)	Density (gm/cc)
GeH_4	-90	-165	1.532 (-142°)
Ge_2H_6	29	-109	1.98 (-109°)
Ge_3H_8	110.5	-105.6	2.2

Monogermane has been prepared in small yields by (a) the treatment of a zinc- or magnesium-germanium alloy with aqueous hydrochloric acid (87, 108), and (b) the electrolytic reduction of germanium dioxide in concentrated sulphuric acid using lead electrodes (86). Dennis and his co-workers (22, 27) prepared and characterized mono-, di- and trigermane recovered from the reaction of magnesium germanide with excess acid in which the overall conversion of germanium was only about 22%. The relative amounts of each hydride (73.6% GeH_4, 22% Ge_2H_6, 1% Ge_3H_8) did not correspond with that obtained for the silanes (40% SiH_4, 30% Si_2H_6, 15% Si_3H_8, 10% Si_4H_{10}) in the analogous reaction of magnesium silicide with excess acid. Kraus and Carney (63) obtained only germane in about 70% yield by treating magnesium germanide with ammonium bromide in liquid ammonia.

A more general method for the preparation of hydrides involves the reduction of the corresponding halogen derivative with lithium aluminum hydride, as represented by the equation.

$$4\ MX_n + nLiAlH_4 \longrightarrow 4MH_n + nLiX + nAlX_3$$

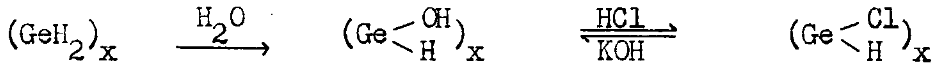
where X = halogen and M = B, Al, Si, Ge, Sn, As, Sb (79). However, the yield of monogermane prepared in this way does not exceed 30% (45). During the course of this investigation, Piper and Wilson (89) reported the preparation of germane in 75% yield by the reduction of an acidic solution of germanium dioxide with sodium borohydride.

Although the chemistries of germanium and silicon hydrides show marked similarities, there are, however, two important differences. Silane is spontaneously inflammable in air or moisture whereas germane is stable in air and can be formed in aqueous solution without simultaneous decomposition. Also, germane reacts quantitatively with sodium in liquid ammonia (63) according to the equation,

$$GeH_4 + Na \longrightarrow GeH_3Na + 1/2\ H_2$$

but silane does not.

Two lower and non-volatile hydrides, germylene, $(GeH_2)_x$, and germanoacetylene, $(GeH)_x$, have been prepared. Germylene results from the treatment of calcium germanide with hydrochloric acid (98, 99, 100). Alternately, germylene is produced in quantitative yield by the reaction of germyl sodium with phenyl bromide (50). The insolubility of germylene in organic solvents, its low volatility and failure to react with halogens or hydroxyl ions in stoichiometric ratios suggest that germylene is a long chain polymer. By reaction with water it forms a red compound which is labile to hydrochloric acid.



$$(GeH_2)_x \xrightarrow{H_2O} \left(Ge\begin{smallmatrix}<OH\\<H\end{smallmatrix}\right)_x \underset{KOH}{\overset{HCl}{\rightleftharpoons}} \left(Ge\begin{smallmatrix}<Cl\\<H\end{smallmatrix}\right)_x$$

Germylene is stable in liquid ammonia (50) but, on warming or removal of ammonia, disproportionation occurs.

$$3(GeH_2)_x \longrightarrow x\ GeH_4 + 2(GeH)_x$$

Germanoacetylene, $(GeH)_x$, is a strong reducing agent and explodes on contact with air. It has been prepared by the interaction of sodium germanide with either cold water (33) or ammonium bromide in liquid ammonia (63).

Tetraalkylgermanes and Organogermanium Hydrides

The preparation and properties of only methyl and ethyl derivatives of germane will be considered here, since they are of particular interest in this investigation.

The first organogermanium compound, tetraethylgermane, was prepared in 1899 by the alkylation of germanium tetrachloride with diethylzinc (131). Later, tetramethyl- and tetraethyl-germane were prepared by the reaction of Grignard reagents (30, 65, 122) or zinc dimethyl (70, 29) with germanium tetrachloride. Both are liquids at room temperature and are comparatively unreactive.

Partially substituted alkylgermanes such as, CH_3GeH_3, $C_2H_5GeH_3$ and $C_3H_7GeH_3$, have been prepared by the reaction of germyl sodium with alkyl halides (123).

$$GeH_3Na + RX \longrightarrow RGeH_3 + NaX$$

Similarly, ethylisoamyl- and diethylisoamylgermane have been prepared from ethylgermane (50).

$$C_2H_5GeH_3 + Na \longrightarrow C_2H_5GeH_2Na + 1/2\ H_2$$

$$C_2H_5GeH_2Na + i\text{-}C_5H_{11}Br \longrightarrow C_2H_5(i\text{-}C_5H_{11})GeH_2 + NaBr$$

Dimethylgermane was formed by the reduction of dimethylgermanium sulphide with zinc and hydrochloric acid (128) but the yield was only about 6%.

Kraus and Flood (65) obtained triethylgermane by the ammonolysis of triethylgermyl lithium. The preparation of trimethylgermane is not reported in the literature.

The reduction of organohalogermanes with lithium aluminum hydride which proceeds according to the general equation,

$$4R_{4-n}GeCl_n + nLiAlH_4 \longrightarrow 4R_{4-n}GeH_n + nLiCl + nAlCl_3$$

where $n \leqslant 4$, affords another method by which alkyl, aryl or cycloalkylgermanes can be prepared (59, 60, 61, 127). Although methyl and ethyl substituted germanes have not been made by this method, there is no doubt they could be obtained in this way.

Germyl Compounds

Only six volatile derivatives of germane containing the GeH_3 group are reported in the literature. Their physical properties are recorded in the following table.

Compound	B.P. (°C)	M.P. (°C)
$H-GeH_3$	-90	-165
CH_3-GeH_3	-23	-158
$C_2H_5-GeH_3$	9.2	-183
$C_3H_7-GeH_3$	30	-
$Cl-GeH_3$	28.0	- 52
$Br-GeH_3$	52.0	- 32

Germyl chloride and bromide have been prepared by the reaction of germane with hydrogen chloride and hydrogen bromide respectively using the corresponding aluminum trihalide as catalyst (31). Small amounts of the corresponding dihalides are also produced either by disproportionation or by further substitution. Iodination of germane probably yields germyl iodide which is too unstable to be isolated (31). Germyl halides appear to be much less stable thermally than the corresponding silyl halides. In sharp contrast with the halosilanes, analogous halogermanes do not react with water to form digermoxane, nor can the hydrolysis of Ge-H bonds with aqueous alkali be adapted for the quantitative estimation of hydrogen. Unlike the reaction of chlorosilane with ammonia which yields trisilylamine, chlorogermane and ammonia react to form ammonium chloride and germylene which subsequently disproportionates into germanoacetylene and germane (34).

Derivatives of Tetraalkylgermanes and Organogermanium Hydrides

Among the trimethyl- and triethyl-halogermanes only trimethylfluorgermane has not been prepared. Rochow prepared trimethylchlorogermane by the reaction of methyl magnesium chloride with dimethyldichlorogermane (92). Trimethylbromogermane was obtained by Dennis and Patnode from the reaction of tetramethylgermane with hydrogen bromide in the presence of aluminum tribromide as catalyst (32). Cleavage of a methyl group from tetramethylgermane with iodine gives trimethyliodogermane (71). The same compound also results from the reaction of methyl magnesium iodide with dimethyldimethoxygermane according to the equation (129),

$$(CH_3)_2Ge(OCH_3)_2 + CH_3MgI \longrightarrow (CH_3)_3GeI + (CH_3O)MgI$$

The mixed ether, trimethylmethoxygermane, has been prepared by the reaction of trimethyliodogermane with sodium in methanol (129). In the methoxy series, $(CH_3)_{4-n}Ge(OCH_3)_n$ where n = 0 to 4, boiling points increase with increasing methoxy substitution. This is in marked contrast with the analogous chloro series, $(CH_3)_{4-n}GeCl_n$, in which the boiling points increase with increasing chloro substitution passing through a maximum at dimethyldichlorogermane. Rockow attributed this to a self-stabilization of dimethyldichlorogermane without further clarification (92).

Hydrolysis of trimethylchloro- and trimethylbromo-germanes has been reported to yield an unidentified volatile product (32, 92). Likewise, ammonolysis of trimethylbromogermane, dissolved in benzene, gave an unidentified oil (32).

Kraus and Flood (65) found that the reaction of bromine with tetraethylgermane,

$$(C_2H_5)_4Ge + Br_2 \longrightarrow (C_2H_5)_3GeBr + C_2H_5Br$$

yielded triethylbromogermane which was easily converted to hexaethyldigermoxane by hydrolysis,

$$(C_2H_5)_3GeBr + HOH \longrightarrow ((C_2H_5)_3Ge)_2O + 2HBr$$

Cleavage of the digermoxane with hydrogen fluoride, chloride or iodide gave the corresponding triethylgermyl halide.

$$((C_2H_5)_3Ge)_2O + 2HX \longrightarrow 2(C_2H_5)_3GeX + H_2O$$

Hexaethyldigermthian*, $((C_2H_5)_3Ge)_2S$, was obtained when triethylbromogermane was heated with alcoholic sodium sulphide (13).

Triethylchlorogermane and ammonia form a weak 1:1 adduct which undergoes reversible ammonolysis in excess liquid ammonia (65). Under identical conditions triethylchlorosilane reacts with ammonia to form hexaethyldisilazine, $((C_2H_5)_3Si)_2NH$, (9, 105, 106) and trimethylchlorostannane yields a stable 1:1 adduct (64). If the reaction of triethylchlorogermane with ammonia is conducted in the presence of sodium, ammonolysis is irreversible and hexaethyldigermazine, $((C_2H_5)_3Ge)_2NH$, is formed (65). In the analogous reaction with lithium and ethylamine, which is a weaker ammonolyzing agent than ammonia, hexaethyldigermane, $(C_2H_5)_6Ge_2$, results in low yield. This digermane is formed in high yield by the reaction of triethylbromogermane with sodium in the absence of a solvent (65).

On the basis of the preparation of a series of alkylgermyl derivatives including trialkylgermyl formate, acetate, propionate, cyanate, cyanide, isothiocyanate, haloacetate, halopropionate among others (1, 2, 3, 4, 5, 6, 7), Anderson has proposed the following conversion series in which any derivative can be converted to any other on its right by reaction with the appropriate silver salt, $\equiv Ge{-}I \longrightarrow S \longrightarrow Br \longrightarrow CN \longrightarrow CNS$ and $\longrightarrow Cl \longrightarrow NCO \longrightarrow O$ and $OCOR \longrightarrow F$.

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*For nomenclature see Compt. rend. XVth Conference, Int. Union Pure Appl. Chem. (Amsterdam), 1949, p. 127

Similar silver salt conversion series have been suggested by MacDiarmid (78) and Eaborn (39) for silyl and trialkylsilyl derivatives respectively.

Theoretical Aspects of Germanium Chemistry

Electronegativity: The scale of electronegativity devised by Pauling (88) indicated that the electronegativity of the Group IVB elements decreased in the following order:

Element	C	Si	Ge	Sn
Electronegativity	2.5	1.8	1.7	1.7

Sanderson noticed, however, that the chemical behaviour of some germanium compounds was not compatible with this trend (102, 103, 104) and, in fact, germanium appeared to have a higher electronegativity than silicon, as indicated in the following new scale of electronegativity: C (2.47), Si (1.74), Ge (2.31), Sn (2.03), Pb (2.37).

On the basis of physical evidence, Allred and Rochow proposed another scale of electronegativities compatible with the observed chemical anomalies and Pauling's original definition of electronegativity. Values obtained by Allred and Rochow are compared with those of Pauling and of Sanderson in the following table (94, 95).

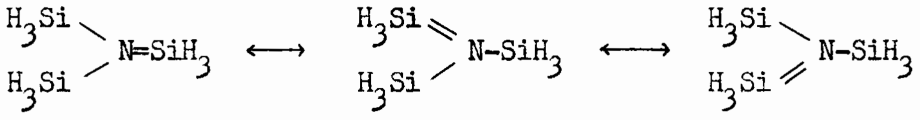
Electronegativities of Group IVB Elements

Element	C	Si	Ge	Sn	Pb
Pauling	2.5	1.8	1.7	1.7	-
Sanderson	2.47	1.74	2.31	2.03	2.37
Allred and Rochow	2.60	1.90	2.00	1.93	2.45

$d_\pi - p_\pi$ Bonding: Group IVB elements other than carbon can expand their covalency from four to a theoretical maximum of nine by utilizing vacant d-orbitals in their outermost electronic shell. However, the most common expanded covalency number is six as found, for example in the following ions:

$SiF_6^{=}$, $GeF_6^{=}$, $GeCl_6^{=}$, $SnCl_6^{=}$, $SnBr_6^{=}$, $SnI_6^{=}$ and $PbCl_6^{=}$.

The electron donor activity of Group V, VI and VII elements is reduced when bonded to silicon. When compared with trimethylamine, trisilylamine, $(SiH_3)_3N$, forms a much weaker addition compound with electron deficient boron trifluoride (16, 17, 18). Also, trimethylamine forms a 1:1 adduct with boron trimethyl (15), which is a weaker electron acceptor than the trifluoride, but trisilylamine does not (17). Structural studies of trisilylamine indicated a planar molecule instead of the expected pyramidal structure (55). This substantiated the earlier suggestion that the electron pair on nitrogen was back co-ordinated to the silicon atom forming a d_π-p_π bond as represented in the following scheme.



The physical and chemical behaviour of compounds containing Si-N, Si-O, Si-S and Si-X (halogen) bonds are not incompatible with the concept of d_π-p_π back co-ordination bonding (42, 43, 120, 121). It should be emphasized that a back co-ordination bond is not merely the result of an inductive effect but rather represents a region in which atomic orbitals of different atoms overlap with the formation of a chemical bond. In the case of silicon, the d-orbital is originally empty and the electrons are donated from the p_π-orbital of the more electronegative atom. Theoretical calculations by

Craig et al. (23, 24) have indicated that the d_π-p_π bond will be stronger when the electronegativity difference between the two atoms is greater.

Further evidence for π-type bonding was obtained by Chatt and Williams who studied the ionization constants of the p-$CH_3M\ C_6H_4COOH$ acids, where M = C, Si, Ge and Sn (20). They concluded that an interaction, independent of the principal quantum number of the metal atom, occurred between the localized orbitals of the benzene ring and the outer d-orbitals of silicon, germanium and tin.

Outline of the Research Problem

The purpose of this investigation was to explore the chemistry of volatile compounds of germanium with a view to obtaining information for a further comparison with the chemistry of volatile silicon compounds.

The lack of germyl derivatives, when compared with the abundance of silyl compounds, prompted an attempt to prepare more compounds of this type. Since silyl iodide was readily converted into its derivatives with a variety of silver salts, it was hoped that similar reactions would be applicable for the preparation of germyl compounds.

The effects arising from the substitution of methyl groups for hydrogen atoms in the germyl group was also of interest. Accordingly, the preparation and reactions of methylbromogermane and trimethylbromogermane were studied. It was of particular interest to prepare compounds containing Ge-O bonds which would be suitable for a study of the donor activity of oxygen bonded to germanium.

A further purpose of this work was to complete the characterization of several previously prepared germanium compounds which are not fully described in the literature.

EXPERIMENTAL

Introduction

Since most of the compounds used and prepared in this investigation were quite volatile and in some cases unstable in air and moisture, it was necessary to use high vacuum techniques for their manipulation. A detailed description of the experimental methods is not necessary since comprehensive reviews are available (35, 37, 44, 101, 115). However, the more important operations will be briefly outlined.

The use of high vacuum techniques has the following advantages: a) reactants and products of sufficient volatility may be transferred quantitatively by distillation, b) reactions may be done with such small amounts as 5 c.c. (S.T.P.) of gas, c) compounds can be confined in glass containers in the absence of air and moisture, and d) highly toxic compounds can be handled in comparative safety. Some of the disadvantages are: a) non-volatile substances and compounds whose boiling points exceed about 200° cannot be conveniently transferred by distillation at room temperature without using special techniques, b) the complete separation by fractional distillation of compounds whose boiling points differ by less than 20° is difficult, and c) large scale preparations are impractical. These disadvantages, however, did not seriously affect the preparation and manipulation of compounds encountered in this investigation.

Apparatus

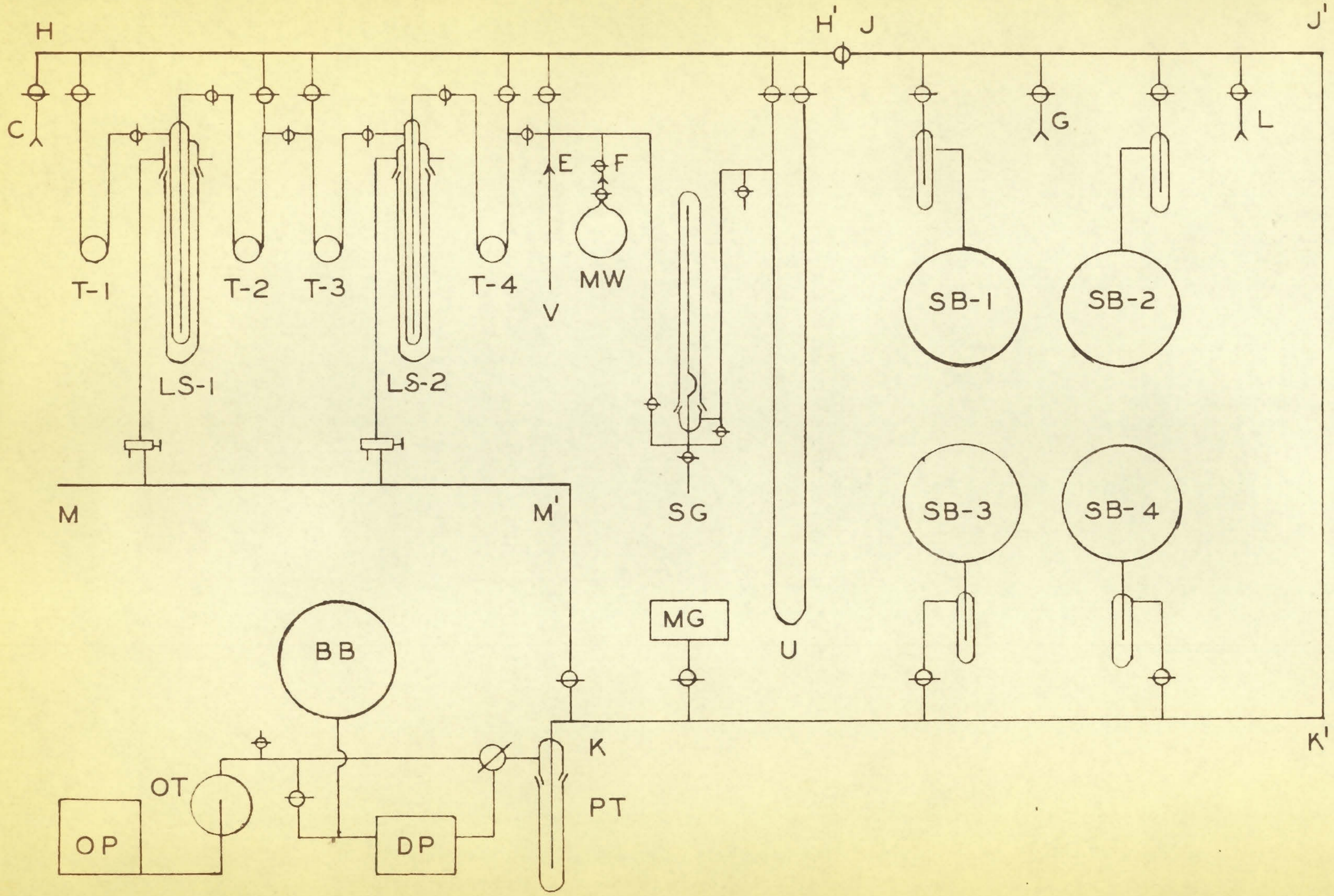
The apparatus, represented diagrammatically in Figure 1, was constructed of pyrex glass and consisted of four main sections; a) a pumping system, b) storage vessels, c) a fractionation line for the purification of volatile compounds, and d) an apparatus for the measurement of physical properties. These sections are described and their particular functions are briefly discussed under separate headings. Stopcocks and ground glass joints were lubricated with Apiezon "N" vacuum grease except where specifically noted.

Pumping System: Evacuation of the apparatus was effected with a mercury diffusion pump, DP, backed by a rotary oil pump, OP. A ballast bulb, BB, was incorporated into the system in order that the apparatus could be maintained at low pressure with the diffusion pump and without the simultaneous use of the rotary oil pump. The pumps were protected from contamination with condensable vapours by a removable pump trap, PT, which was cooled with liquid air. The oil trap, OT, prevented oil from being forced back into the apparatus in the event of a power failure. The apparatus was evacuated before use to a pressure of less than 1 micron, measured with a tilting McLeod gauge, MG.

Storage of Materials: Volatile materials were stored in 5 litre bulbs, SB-1, 2, 3 and 4, connected through condensation traps and stopcocks the vacuum line JJ'KK'. The volumes of these bulbs were determined by expanding a known amount of air from a calibrated volume into each and measuring the resultant pressure. Application of the ideal gas equation gave the required volume. Germane, methylgermane, ammonia, hydrogen chloride and

FIGURE 1

Schematic Diagram of Apparatus


H
H'
J
J'
C
G
L
E
F
T-1
T-2
T-3
T-4
MW
V
LS-1
LS-2
M
M'
SG
SB-1
SB-2
SB-3
SB-4
MG
U
BB
K
K'
OT
PT
OP
DP

hydrogen bromide were stored in these bulbs for long periods without decomposition. Unstable and very volatile compounds were sealed in small bulbs equipped with glass "break-offs" for storage at liquid air temperature, while more stable and less volatile compounds were sealed in glass vials for storage at room temperature.

Fractionation Line: Stopcocks and ground glass joints, C, E, F, G and L, on the vacuum line HH' and JJ', served as convenient points for the introduction of gases into the line and for the attachment of auxiliary apparatus. The purification of volatile materials was done by distillation using either "Stock" traps, T-1, 2, 3 and 4 each of about 50 c.c. capacity, cooled with appropriate slush baths, or low temperature distillation columns, LS-1 and 2, similar to that described by LeRoy (73). The outer jackets of the "LeRoy stills", which were immersed in liquid air during operation, could be evacuated through the auxiliary vacuum line MM'. The use of a "LeRoy still" for fractional distillation was a decided improvement over the conventional "slush" bath technique because any particular temperature between 0 and -196° could be conveniently maintained by the application of a suitable potential drop across the heater of the distillation column.

A unit for the determination of vapour pressure and molecular weight was also attached to the main vacuum line HH'.

Analytical System: Molecular weights were determined in an apparatus consisting of a cold finger, V, a thin walled molecular weight bulb, MW, of low weight and accurately known volume, 438.8 c.c., and a spoon gauge, SG, used as a null point indicator. The pressure of air required to balance the pressure of gas within the glass spoon was read accurately on the adjacent manometer, U.

Temperature Measurements: Temperatures below 0° were measured with an accuracy of ± 0.1° by means of copper-constantan thermocouples in conjunction with a sensitive potentiometer. This method was preferred for its simplicity over the vapour pressure thermometer technique (35, 115). Temperatures greater than 0° were measured with an accurate mercury in glass thermometer.

Pressure Measurements: Pressure measurements were made with a soft glass spoon gauge in order to prevent gas-mercury vapour interaction. The spoon gauge, SG, was sufficiently sensitive to detect a pressure of 0.2 mm. and strong enough to withstand a pressure differential of at least 70 mm. When the pressure differential across the spoon was zero, the null point was indicated by the fine pointer surmounting the spoon being collinear with two sight marks in front and behind the outer jacket.

Measurements of vapour pressures at different temperatures were made in four ways depending on the amount of material available, the temperature range required and the nature of the compound. If a sufficiently large sample was available and the temperature range extended below -160°, the "LeRoy still", LS-1, was used. The temperature of the distillation column was adjusted to the desired values and the corresponding vapour pressures were measured with the spoon gauge. For vapour pressure measurements in the range -160° to 20°, it was more convenient to condense the compound into the cold finger, V, which could be surrounded with appropriate slush baths in order to obtain the required temperatures. Vapour pressure measurements above room temperature were made while the cold finger and spoon gauge apparatus was immersed in a variable temperature thermostat. Under these conditions it was necessary to use Dow-Corning high vacuum silicone grease as a stopcock lubricant.

When only very small samples of gas (10-15 c.c. at S.T.P.) were available or, when reaction with the tap grease was suspected, vapour pressures were determined in a detachable all-glass spoon gauge unit of small volume ($\backsim$5 c.c.) fitted with a glass "break-off" to facilitate recovery of the sample. After condensation of a gas into the cold finger, the unit was sealed in vacuum and vapour pressure - temperature measurements were made in the usual way.

Determination of Molecular Weight and Purity: The molecular weight of a compound was determined by obtaining the weight of vapour at a measured pressure and temperature in a bulb of known volume, (438.8 c.c.). Application of the ideal gas equation gave the molecular weight with an error usually less than 1%.

The purity of a compound was determined by measuring the vapour pressure at constant temperature of successive small samples. If these were practically constant, the sample was considered to be tensiometrically pure. When the vapour pressure - temperature relationship of a compound was available in the literature, a comparison was made with the values obtained in this work.

Determination of Melting Point: The magnetic plunger technique, described by Stock (115), was used for the determination of melting points. A plunger, consisting of a soft iron rod encased in glass and attached to a slender glass rod terminating in a glass cross, fitted into the cold finger, V, shown in Figure 1. It was raised magnetically about two inches so that the cross rested on a ring of condensed compound where a thermocouple was attached. The temperature of the cold finger was raised (0.5°/min) and the temperature at which the plunger fell was taken as the melting point.

Measurement of Infrared Spectra: A Perkin Elmer Model 21 double beam infrared spectrophotometer with sodium chloride optics was used for obtaining infrared spectra. The gas cell (10 cm. long x 5 cm. diameter) had 5 mm. sodium chloride windows held in position with silicone grease and Apiezon "Q" wax. The windows were repolished periodically using an alcoholic suspension of aluminum oxide and a rotating wheel.

Spectra were obtained at pressures sufficient to record weak absorption bands and successive determinations at lower pressures were done until the strongest bands had been resolved. The spectrum of a compound having a low vapour pressure at room temperature was determined at the highest pressure possible without risking condensation of the compound on the cell windows.

Characterization of Compounds: Germanium containing compounds were characterized by the measurement of the following physical properties:

1) Molecular weight in the vapour state
2) Vapour pressure-temperature relationship
3) Latent Heat of Vapourization
4) Trouton's Constant
5) Boiling point at 760 mm. (extrapolated)
6) Melting point

7) Infrared spectrum.

In general, the nature of the preparation of a particular compound limited the possible products which could be produced and each of these would differ appreciably with respect to molecular weight. Therefore, it was considered that molecular weight determinations in conjunction with a normal Trouton constant and infrared spectral analysis were sufficient for establishing the identity of a compound and hence chemical analyses were not done.

Preparation of Materials

Germane: The reduction of germanium tetrachloride with excess lithium aluminum hydride in ether solution (45) according to the equation,

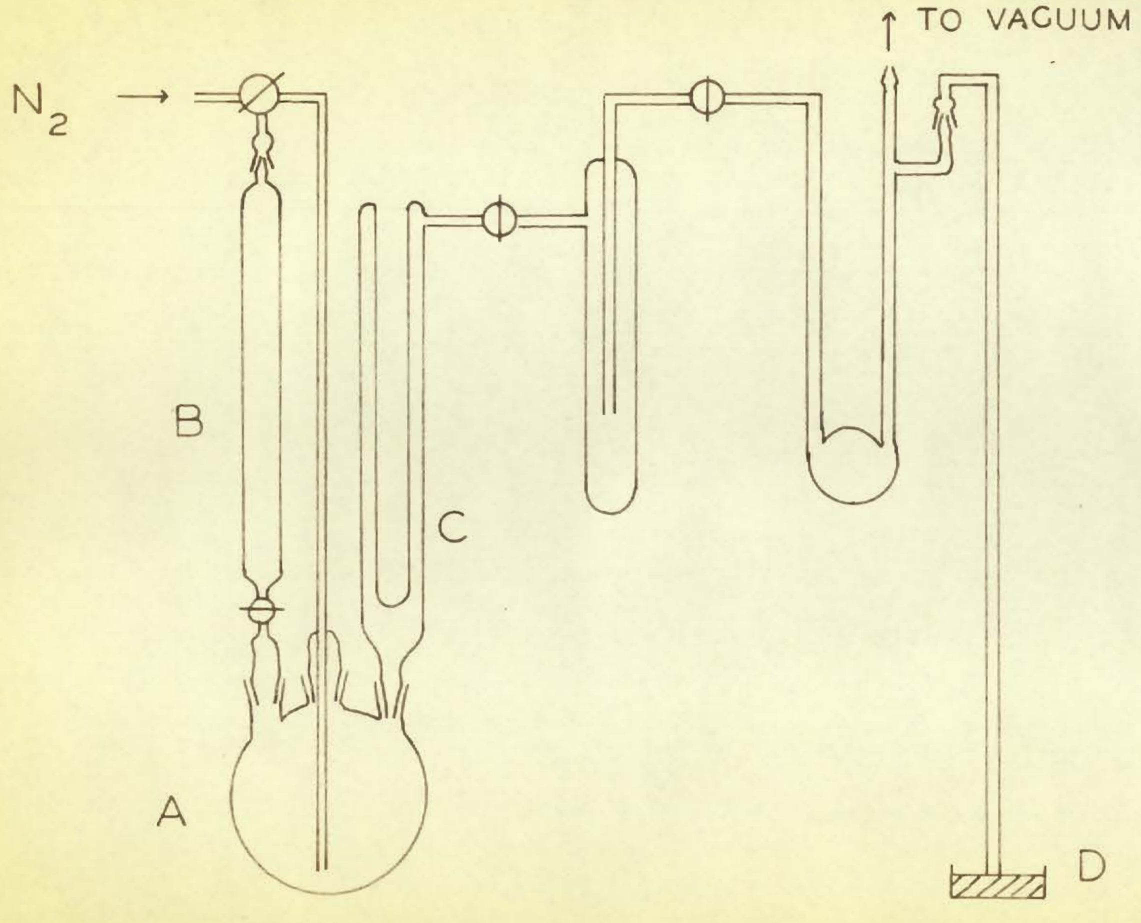
$$GeCl_4 + LiAlH_4 \longrightarrow GeH_4 + LiCl + AlCl_3$$

proceeds smoothly at room temperature to form germane in 28% yield. This method was selected over others (27, 63, 80, 85, 86, 87, 108, 126) because of the availability of the starting materials, the relatively good yield and the simplicity of the purification of the resulting germane.

The reaction was done in an apparatus shown diagrammatically in Figure 2. A one litre three-necked flask, A, was equipped with a dropping funnel, B, a magnetic stirring bar, a reflux condenser, C, and a nitrogen inlet which extended almost to the bottom of the flask. The condenser, C, was maintained at -80° in order to retain the bulk of the solvent and was attached to two traps leading to the vacuum manifold. A mercury "blow-off", D, served to allow hydrogen produced in the reaction and nitrogen to escape without the simultaneous admission of air and moisture.

FIGURE 2

Reduction Apparatus


N2
TO VACUUM
B
C
A
D

In a typical preparation, germanium tetrachloride (25 gm.) dissolved in dry ether (40 ml.) was admitted slowly over a period of ninety minutes from the dropping funnel to a magnetically stirred lithium aluminum hydride (16 gm.) - ether (100 ml.) slurry. Dry nitrogen was bubbled through the solution and germane was condensed along with some ether in the traps cooled with liquid air. After the complete addition of germanium tetrachloride solution, the mixture was stirred at room temperature for one hour to ensure complete removal of germane.

The products, condensed in the traps, were separated by distillation at -120° into ether and germane fractions. Germane was further purified by three distillations at -155° (Found: M, 76.4; Yield: 20%. Required for GeH_4: M, 76.6). Vapour pressure - temperature measurements agreed with those determined by Corey, Laubengayer and Dennis (22).

During the course of this investigation, a new preparation of germane in 60-75% yield, by the reduction of an aqueous acidic solution of germanium dioxide with sodium borohydride, was published (89). The only impurity reported was digermane which could be readily separated from germane by low temperature distillation.

Using the apparatus shown in Figure 2, a sample of germanium dioxide (2.00 gm.) was dissolved in boiling 1 M hydrobromic acid (250 ml.). Sodium borohydride (16 gm.) in water (150 ml.) was dropped slowly into the germanium dioxide solution, which was maintained at 35° instead of at 0° as indicated by Piper and Wilson (89). The mixture was stirred magnetically for thirty minutes after the final addition of borohydride solution.

The product mixture was passed through a trap cooled to -80°, which retained the solvent, while the more volatile digermane and germane passed through. Germane (Found: M, 76.0; Yield: 96%. Required for GeH_4: M, 76.6) was separated from digermane (Found: M, 151.7; Yield: 0.9%. Required for Ge_2H_6: M, 151.2) by distillation at -136°.

Tetramethylgermane: Although tetramethylgermane can easily be prepared by the action of methylmagnesium chloride on germanium tetrachloride, special techniques are required to separate the product from the solvent (30). Therefore, the reaction of dimethylzinc with germanium tetrachloride, which was reported to proceed quantitatively (70), was used.

Germanium tetrachloride (0.044 moles) and dimethylzinc (0.04 moles) were allowed to react at room temperature for one week in a 400 ml. flask. A white matrix of zinc chloride appeared in the flask. The product mixture was cooled in liquid air and the methane formed was pumped away. Excess germanium tetrachloride was separated by distillation through a trap maintained at -64° in which it was retained. The volatile fraction at -64° was impure tetramethylgermane (Found: M, 136.6; v.p. at 0°: 130.2 mm. Required for $Ge(CH_3)_4$: M, 132.6; v.p. at 0° (ref.30): 139.3 mm.). This sample was treated with distilled water in order to destroy germanium tetrachloride which was probably the only impurity. Water was retained in the flask immersed in a bath held at -64° while the more volatile components were condensed in a trap cooled with liquid air. By subsequent distillation at -80 and at -130°, hydrogen chloride (v.p. at -130°: 19 mm.) was separated from tetramethylgermane which remained in the trap held at -130°. Tetramethylgermane was purified by redistillation at -80° (Found:

M, 132.4; v.p. at 0°: 139.1 mm.; Yield: 67%. Required for $Ge(CH_3)_4$: 132.6; v.p. at 0° (ref.30): 139.3 mm.).

A sample was taken for an infrared spectrum determination in the gas phase at pressures of 70, 28.3 and 11.6 mm. The principal peaks and their frequency assignments, in the range 4000 to 650 $cm.^{-1}$, are listed in Table I and a copy of the spectrogram is shown in Figure 3. These agreed with the spectra reported in the literature (62, 76).

Germyl Chloride: The halogenation of germane was effected by reaction with hydrogen chloride in the presence of anhydrous aluminum trichloride as catalyst (31, 77). The apparatus consisted of a 500 ml. flask equipped with a ground glass joint and a side arm trap in which reactants and products could be condensed. The flask was attached to the vacuum apparatus with a ground glass joint and the contents isolated by means of a stopcock. The reaction temperature was controlled by placing the flask in an oven with the neck protruding from the side to protect the stopcock lubricant at higher temperatures.

Aluminum trichloride (1.8 gm.) was placed in the flask and sublimed onto the walls by heating in vacuo at 110° for twelve hours. Germane and hydrogen chloride, in a 1:1 mole ratio, were allowed to react at 60° for one hour. Hydrogen formed in the reaction was pumped away through a trap immersed in liquid air, which retained the condensable products as well as unconsumed reactants. Germane and hydrogen chloride were separated from the product mixture by distillation at -132° and the fraction involatile at this temperature was found by molecular weight (Found: M, 118.2. Required for GeH_3Cl: M, 111.1), vapour pressure (Found: v.p. at -23.6°:

TABLE I

Vibration Frequencies of Tetramethylgermane*

Frequency (cm.$^{-1}$)	Intensity	Vibration	Assignment
3180	w.	13 + 19	combination
3065	m.	1 + 19	"
2990	v.s.	13	CH_3 stretch
2920	v.s.	14	CH_3 stretch
2820	s.sh.	2(6)	overtone
2475	w.	2(2)	"
2080	v.w.	2 + 7	combination
1847	w.	2 + 18	"
1803	w.	2(7) + 8	"
1548	w.sh.	2, 18 + 19	CH_3 deformation
1530	m.		
1512	w.sh.		
1445	s.	15	CH_3 deformation
1410	s.		
1252	s.sh.	16	CH_3 deformation
1245	v.s.		
1238	s.sh.		
1067	w.	14-7	combination
1030	w.		
825	v.s.	17	CH_3 rock

* For a complete assignment of the 19 fundamental frequencies, see ref. 62 and 76.

v. = very, s. = strong, m. = medium, w. = weak, sh. = shoulder

---

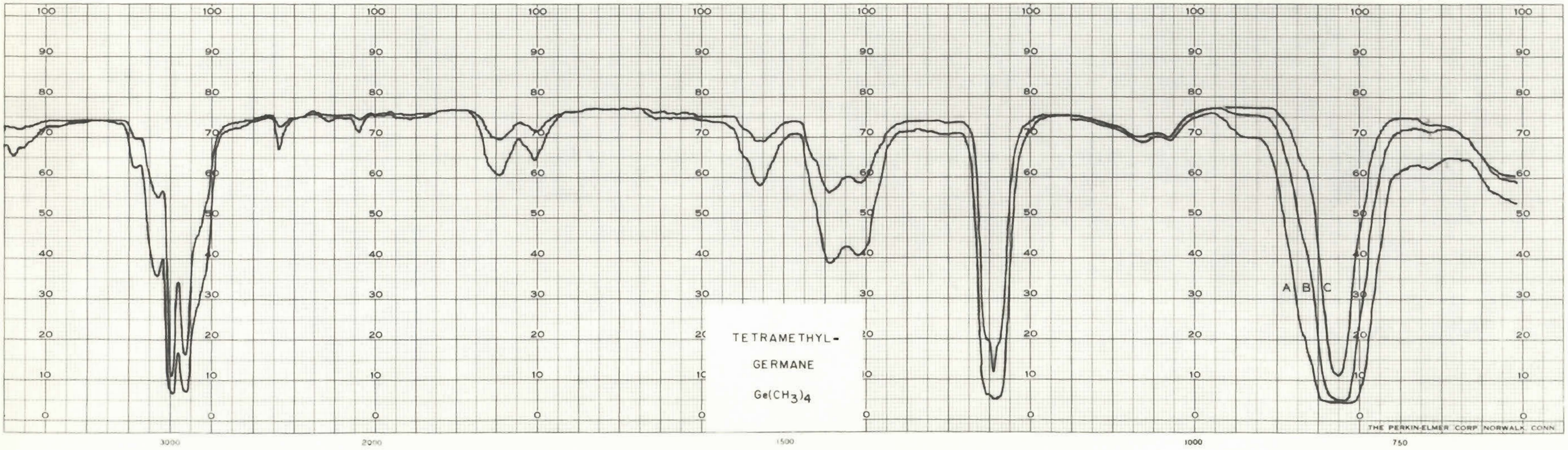
FIGURE 3

Infrared Spectrum of Tetramethylgermane

Pressure: A, 70.0 mm.

B, 28.3 mm.

C, 11.6 mm.



TETRAMETHYL-
GERMANE
$Ge(CH_3)_4$

69.7 mm. Required for GeH_3Cl: v.p. at -23.6°: 71.3 mm.) and an infrared spectrum determination (77) to be germyl chloride contaminated with a small amount of germylene chloride. Tensiometrically pure germyl chloride was obtained after five distillations at -96° (Found: M, 110.5. Required for GeH_3Cl: M, 111.1). The infrared spectrum, shown in Figure 4, was found to be the same as that reported by Lord and Steese (77). Principal absorption peaks and their frequency assignments are listed in Table II.

The yield of germyl chloride was usually about 20% as compared with 48% reported by Dennis and Judy (31) and 5% by Lord and Steese (77).

TABLE II

Vibration Frequencies of Germyl Chloride

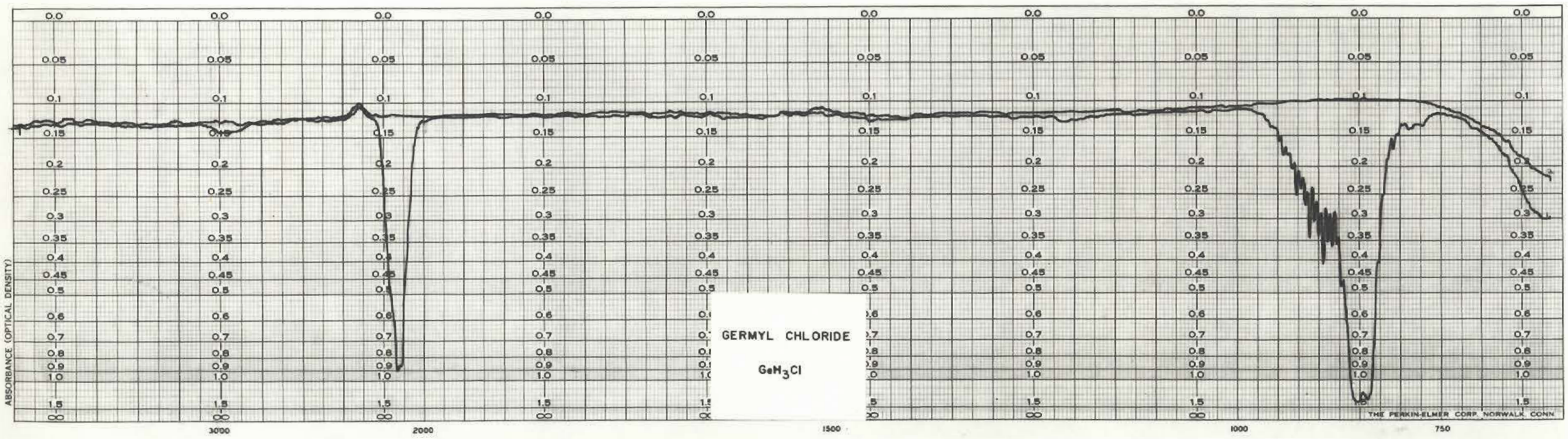
Frequency cm.$^{-1}$		Intensity	Vibration	Assignment
This work	Lord and Steese			
2114	2121.2	v.s.	ν_1	sym. Ge-H stretch
847	847.7	v.s.	ν_2	sym. Ge-H deformation
-	422.6	-	ν_3	Ge-Cl stretch
2130	2129.4	v.s.	ν_4	asym. Ge-H stretch
878	874.6	s.	ν_5	asym. Ge-H deformation
-	604.1	-	ν_6	GeH_3-Cl stretch

v. = very, s. = strong, sym. = symmetric, asym. = asymmetric

FIGURE 4

Infrared Spectrum of Germyl Chloride

Pressure: 15.0 mm.


GERMYL CHLORIDE

GeH_3Cl

Miscellaneous Materials: Commercially available samples of HCl, HBr, H_2S, NH_3, BF_3, CH_3OH and CH_3SH were purified by low temperature distillation and the molecular weight and vapour pressure of each compound were checked before use.

Samples of Ag_2O, Ag_2CO_3, AgCN, AgCNO and HgS were obtained commercially and used without further purification.

Reagent grade methyl iodide was used after two bulb to bulb distillations, the middle fraction being retained (Found: M, 138.2. Required for CH_3I: M, 141.9).

RESULTS

Reactions of Germyl Chloride

Attempted Preparations of Compounds Containing Ge-O-Ge, Ge-S-Ge, Ge-O-C and Ge-S-C Bonds:

The formation of compounds containing Si-O-Si bonds by hydrolysis of halosilanes (105, 114, 116) as well as by reaction of a halosilane with silver carbonate (39), silver oxide or mercuric oxide (38) suggested that digermoxane, $(GeH_3)_2O$, might be prepared in similar ways. Dennis and Judy (31) hydrolysed germyl chloride but did not obtain digermoxane, nor was the hydrolysis satisfactory for the quantitative estimation of hydrogen bonded to germanium. Consequently, attempts were made to prepare digermoxane by the reactions of germyl chloride with silver oxide and with silver carbonate.

Disilthian, $(SiH_3)_2S$, has been prepared by passing the vapours of iodosilane over solid mercuric sulfide (42). Hence, the formation of digermthian, $(GeH_3)_2S$, was attempted by passing germyl chloride alone and in a mixture with hydrogen sulfide over mercuric sulfide.

Some alkylalkoxygermanes, $R_nGe(OCH_3)_{4-n}$ where $n = 0$ to 3, have been obtained by refluxing the appropriate halogermane in methanol or in sodium methylate - methanol solutions (129). Since this is not practical with germyl chloride, which is thermally unstable, the reactions of germyl chloride with methanol and with methanethiol were done in the vapour phase at room temperature.

Reaction of Germyl Chloride with Silver Oxide

A short length of glass tube, loosely packed with silver oxide and ground glass wool, was connected to two traps, one at each end, and to the vacuum manifold. Germyl chloride (2.18 mmoles) was passed twelve times through the silver oxide plug. There was no noticeable change and hydrogen was not produced. Distillation of the condensable material at -146° yielded a distillate (0.02 mmoles) too small to be identified while the residue (2.07 mmoles) was chlorogermane (Found: M, 109. Required for GeH_3Cl: M, 111.1). Since the recovery of germyl chloride was 95% of the amount used initially, it was concluded that a reaction had not occurred.

Reaction of Germyl Chloride with Silver Carbonate

Germyl chloride (1.91 mmoles) was passed six times through a silver carbonate - glass wool plug which changed gradually from greenish-yellow to black. The product mixture was condensed at -196° leaving only a trace of hydrogen which was pumped off. Carbon dioxide (0.28 mmoles) was distilled from the mixture at -130° (Found: M, 44.3. Required for CO_2: M, 44.0), leaving as residue 1.43 mmoles of germyl chloride contaminated with a small amount of carbon dioxide (Found: M, 106.9. Required for GeH_3Cl: M, 111.1; for CO_2: M, 44.0). The recovery of germyl chloride was about 75% of the amount used initially. After removal of the volatile material from the reaction trap, a pale yellow solid, characteristic of the decomposition of germyl chloride, remained. One quarter of the germyl chloride decomposed in the presence of silver carbonate forming some carbon dioxide but no digermoxane was found.

Reaction of Germyl Chloride with Methanol

Germyl chloride (1.92 mmoles) and spectro-grade methanol (5.40 mmoles) were expanded in the apparatus, containing a silver oxide - glass wool plug. In addition to the formation of hydrogen (0.65 mmoles), a yellow solid gradually appeared on the walls of the apparatus and on the surface of the silver oxide. By distillation of the products at -80°, a mixture of germyl chloride and methanol was recovered (0.18 mmoles. Found: M, 69.7. Required for GeH_3Cl: M, 111.1; for CH_3OH: M, 32.0). The residue (5.37 mmoles) was methanol (Found: M, 33.2. Required for CH_3OH: M, 32.0) slightly contaminated with germyl chloride. Under the experimental conditions used, germyl chloride decomposed almost completely without the formation of methoxygermane.

Reaction of Germyl Chloride with Mercuric Sulfide

An attempt to prepare digermthian, $(GeH_3)_2S$, was made by repeatedly passing germyl chloride (0.66 mmoles) through a charge of mercuric sulfide (1.6 gm.). Hydrogen was not produced and all of the germyl chloride was recovered unchanged.

Reaction of Germyl Chloride with Hydrogen Sulfide

A further attempt to prepare digermthian, $(GeH_3)_2S$, was made by passing a mixture of germyl chloride (0.66 mmoles) and hydrogen sulfide (1.77 mmoles) repeatedly through a mercuric sulfide - glass wool plug. Unchanged hydrogen sulfide (1.75 mmoles) and germyl chloride (0.66 mmoles) were separated by distillation at -143°.

Reaction of Methanethiol with Germyl Chloride

The preparation of methylthiogermane, CH_3SGeH_3, was attempted by slowly passing a mixture of germyl chloride (0.66 mmoles) and methanethiol (0.83 mmoles) repeatedly through a charge of mercuric sulfide. Hydrogen was not produced. The reaction mixture was distilled at -126° giving 0.38 mmoles of methanethiol (Found: M, 46.0. Required for CH_3SH: M, 48.0) while, in the range -120 to -101°, a mixture (0.49 mmoles) of methanethiol and germyl chloride passed through the distillation column. (Found: M, 65.9. Required for CH_3SH: M, 48.0; for GeH_3Cl: M, 111.1). The residue (0.53 mmoles) was germyl chloride slightly contaminated with methanethiol (Found: M, 109.8. Required for GeH_3Cl: M, 111.1; for CH_3SH: M, 48.0). Germyl chloride and methanethiol were recovered unchanged.

Reaction of Germyl Chloride with Silver Cyanide

Germyl chloride (1.50 mmoles) was passed four times through a silver cyanide - glass wool plug which changed from white to brown. Hydrogen was not produced and distillation of the resultant mixture in the range -98 to -91° gave successive fractions having molecular weights of about 80 (Required for GeH_3Cl: M, 111.1; for GeH_3CN: M, 101.6; for HCN: M, 27.0). This indicated that appreciable decomposition had already occurred. To ensure the complete consumption of germyl chloride, the product mixture was distilled at -90° and the volatile fraction (v.p. of GeH_3Cl at -90°: 2.4 mm) was recycled four times through the cyanide plug. The product mixture was subsequently distilled through a trap maintained at -80°. The fraction, volatile at this temperature (0.78 mmoles) was found to have a molecular weight of 49.2 which indicated a mixture of hydrogen cyanide (M, 27.0) and germyl cyanide (M, 101.6). The residue (0.615 mmoles) of almost pure germyl cyanide (Found: M, 100.1. Required for GeH_3CN: M, 101.6) had a vapour pressure at -80° which was not constant but increased gradually. On standing overnight at room temperature, its molecular weight decreased to 48.4.

The combined samples of impure germyl cyanide were stored at room temperature during which the apparent molecular weight decreased from 58.7 to 46.5 and the vapour pressure was slightly higher than that of hydrogen cyanide (Found: v.p. at -45.2°, 28.5 mm.; at -22.9°, 89.1 mm. Required for HCN (ref. 46): v.p. at -45.2°, 21.6 mm.; at -22.9°, 85.2 mm.).

Germyl cyanide was produced according to the equation,

$$GeH_3Cl + AgCN \longrightarrow GeH_3CN + AgCl$$

and decomposed rapidly.

By distillation of impure germyl cyanide at -153°, a volatile fraction (0.122 mmoles) too small to be identified by molecular weight or vapour pressure but which was undoubtedly germane, was recovered (v.p. of GeH_4 at -153°: 3.5 mm.). The sample of impure germyl cyanide was heated at 70° for one hour. The fraction volatile at room temperature was taken for a determination of its infrared spectrum at pressures of 127.5 and 43.5 mm. Germyl cyanide, germane and hydrogen cyanide were identified as components of this sample. The principal peaks and frequency assignments are listed in Table III and a copy of the spectrogram is shown in Figure 5(a). A comparison of the spectra, shown in Figures 5(a) and 5(b), shows that the germane content, as indicated by the strong absorption peak at 819 cm.$^{-1}$, was substantially increased after storage of the sample at room temperature for two weeks.

TABLE III

Vibration Frequencies of Impure Germyl Cyanide

Frequency (cm.$^{-1}$)	Intensity	Assignment
3320	s.	C-H stretch in HCN
2120	v.s.	Ge-H stretch
2059	s.	C≡N stretch in GeH_3CN
1430 1380	m.	C-H bend (overtone) in HCN
883	s.	Asymmetric GeH_3 deformation
844	v.s.	Symmetric GeH_3 deformation
816	s.	Ge-H deformation in GeH_4
743	s.	Ge-C stretch in GeH_3CN
712	s.	H-C bend in HCN

v. = very, s. = strong, m. = medium, w. = weak.

Reaction of Germyl Chloride with Silver Cyanate

Germyl chloride (2.1 mmoles) was slowly passed ten times through a dry silver carbonate plug. There was no visible change and the recovery of germyl chloride (Found: M, 109.2. Required for GeH_3Cl: M, 111.1) was

FIGURE 5(a)

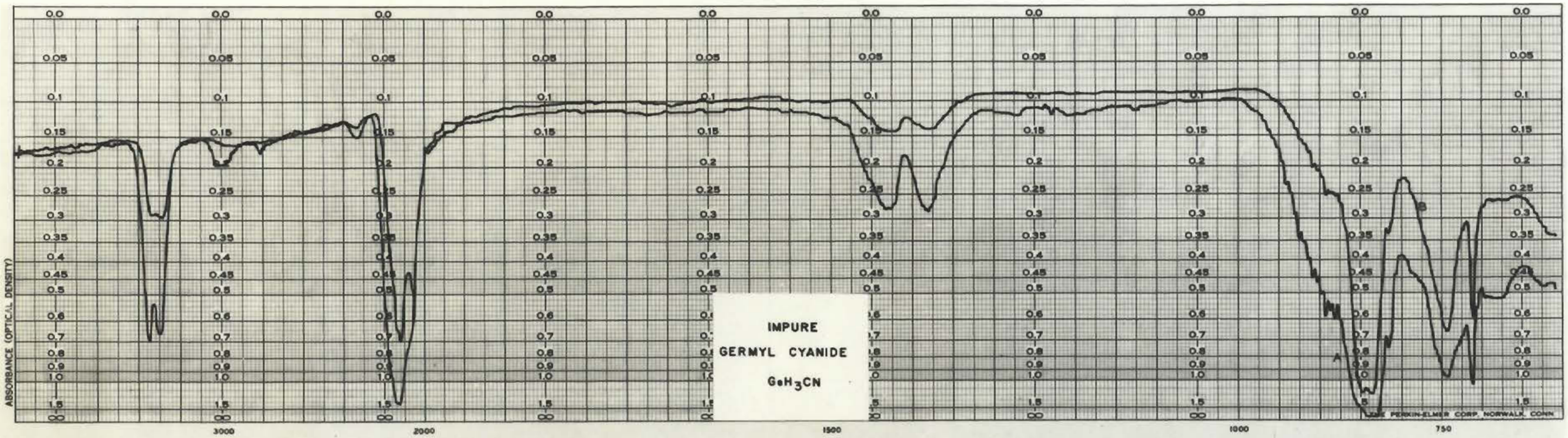
Infrared Spectrum of Impure Germyl Cyanide

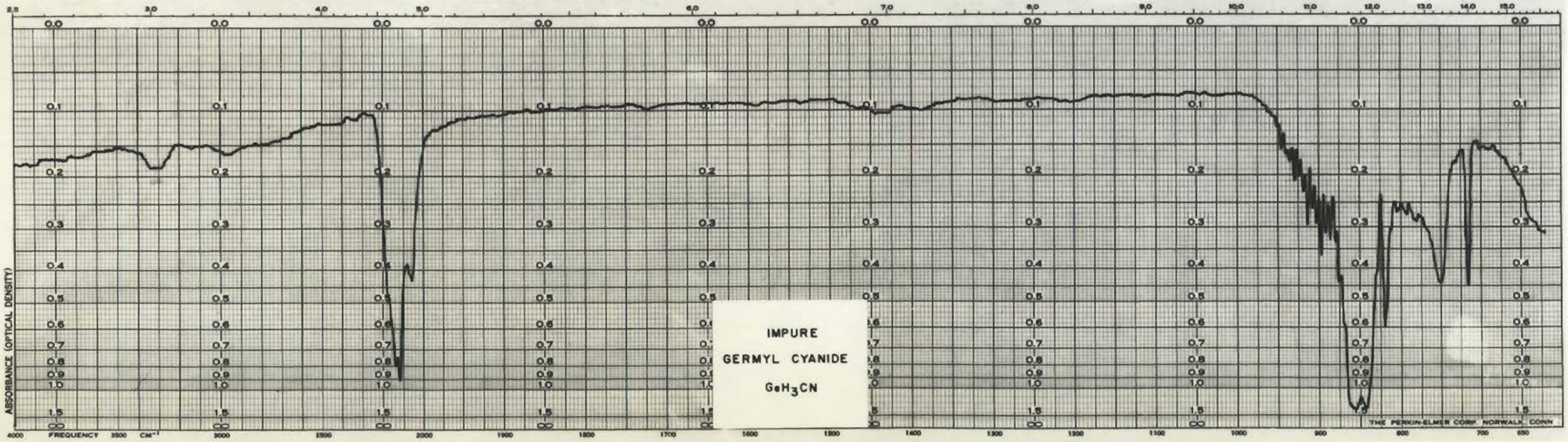
Pressure: A, 127.5 mm.
B, 43.5 mm.

FIGURE 5(b)

Infrared Spectrum of Impure Germyl Cyanide

Pressure: 25. mm.


IMPURE
GERMYL CYANIDE
GeH_3CN


IMPURE
GERMYL CYANIDE
GeH_3CN

quantitative.

Reaction of Germyl Chloride with Sodium Methylate

The reaction of liquid germyl chloride (2.24 mmoles, m.p. of GeH_3Cl: -52°) with dry sodium methylate was allowed to proceed at -50° for thirty minutes. Hydrogen was not produced in the reaction. A sample of the reaction products was taken for an infrared spectrum determination in the gas phase at a pressure of 43.5 mm. Principal peaks are listed in Table IV and a copy of the spectrogram is shown in Figure 6. The absorption band at 3695 $cm.^{-1}$, due to an O-H stretching vibration, indicated the presence of methanol, either as an impurity or as a decomposition product.

Fractionation of the products by distillation at -155° gave a small amount of germane (0.057 mmoles) and unreacted germyl chloride (0.037 mmoles) was recovered by distillation at -96°. At -70°, the distillate (0.52 mmoles) was methoxygermane contaminated with methanol (Found: M, 95.4. Required for CH_3OGeH_3: M, 106.6; for CH_3OH: M, 32.0) and the same components were present in the residue, which had a molecular weight of 75.8. Since methanol and methoxygermane appeared to have similar vapour pressures, it was impossible to separate them by fractional distillation in the LeRoy apparatus. Moreover, methanol could not be removed by chemical means.

TABLE IV

Vibration Frequencies of Impure Methoxygermane

Frequency ($cm.^{-1}$)	Intensity	Assignment
3695*	m.	O-H stretching
2960 2827	s.	C-H stretching
2375 2270	m.	unidentified
2128	v.s.	Ge-H stretch
2090*	s.sh.	unidentified
1500	w.b.	CH_3 deformation
1250	w.b.	" "
1083	s.	unidentified
1063	v.s.	CH_3-O rocking
1033	s.	C-O stretch
1010	s.	" "
855	v.s.b.	GeH_3 deformation
790	m.	unidentified
760	s.	"
748	s.	"
650	s.b.	GeH_3 rocking

v. = very, s. = strong, m. = medium, w. = weak,

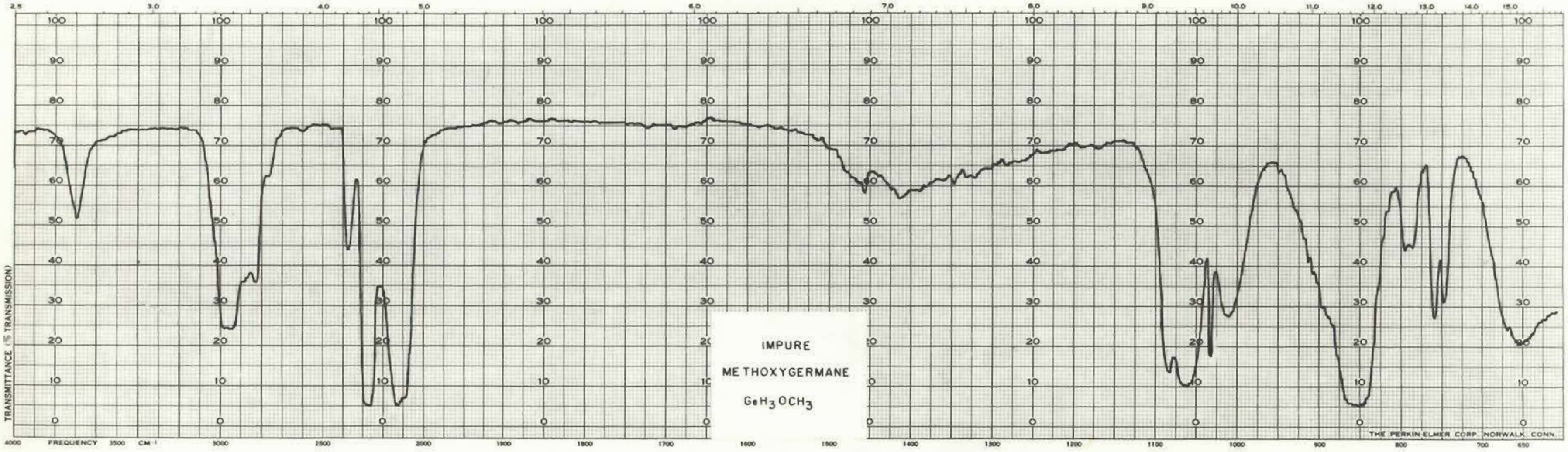
b. = broad, sh. = shoulder

*CH_3OH impurity

FIGURE 6

Infrared Spectrum of Impure Methoxygermane

Pressure: 43.5 mm.



IMPURE

METHOXYGERMANE

GeH_3OCH_3

Derivatives of Methylgermane

The results of preceding experiments indicated that germyl chloride was not sufficiently reactive to be used as an efficient germylating agent. This may be attributed, in part, to the marked thermal instability of germyl chloride. The substitution of alkyl groups for hydrogen in germane enhanced the stability of trialkylgermyl derivatives (1, 32, 65, 92). Therefore, it was of particular interest to determine the usefulness of methylhalogermanes in the preparation of such compounds as 1,1'-dimethyldigermoxane, $(CH_3GeH_2)_2O$, and methylmethoxygermane, $CH_3GeH_2OCH_3$.

Preparation of Methylgermane

Germyl sodium was formed by the reaction of germane (0.96 mmoles) with freshly cut sodium (0.105 gm.) in liquid ammonia (6.42 mmoles), as represented by the equation,

$$GeH_4 + Na \longrightarrow GeH_3Na + 1/2\ H_2$$

After the removal of hydrogen from the frozen mixture, methyl iodide (1.63 mmoles) was reacted with germyl sodium for one hour at -50 to -60° to form methylgermane,

$$GeH_3Na + CH_3I \longrightarrow CH_3GeH_3 + NaI$$

Subsequent fractional distillation of the reaction mixture is summarized in the following table.

Purification of Methylgermane by Distillation

Fraction	Temp. (°C)	Yield (mmoles)	M.W.	Inferred Component(s)
1	-155	0.03	-	GeH_4
2	-151	-	-	-
3	-136.7	0.42	71.0	CH_3GeH_3 + NH_3
4	-134.3	0.93	52.9	CH_3GeH_3 + NH_3
5	-130.3	1.25	37.7	CH_3GeH_3 + NH_3
6	-124.2	1.10	17.9	NH_3
7	-122.0	1.04	17.5	NH_3
8	-119.5	0.96	17.7	NH_3
9	-115.0	0.69	17.7	NH_3
10	-106.0	0.20	17.7	NH_3
11	-106.0	Balance	pumped	away
12	Residue	0.06	-	CH_3I

Ammonia, contained in Fractions 3, 4 and 5 was converted to solid ammonium chloride by reaction with anhydrous hydrogen chloride (2.62 mmoles) while methylgermane and excess hydrogen chloride remained in the gas phase. Hydrogen chloride (0.66 mmoles) was separated from methylgermane (Found: M, 90.9, 90.3; Yield, 67%. Required for CH_3GeH_3: M, 90.6) by distillation at -157°.

Although the above preparation resulted in a high yield of methylgermane, this condensation method was not readily adaptable for producing larger quantities. Therefore, the flow technique, originally devised by

Teal and Kraus (123), was used with only slight modification.

In a typical preparation, germane (9.28 mmoles) was carried in a stream of dry nitrogen through a solution of sodium in liquid ammonia kept at about -70°. The effluent gas, containing ammonia, nitrogen, hydrogen and unreacted germane, passed through a solution of concentrated phosphoric acid, which removed most of the ammonia, and finally through two traps cooled in liquid air where germane was retained, while nitrogen and hydrogen escaped through a mercury bubbler. Excess methyl iodide was dropped slowly with stirring on the liquid ammonia solution and was allowed to react with dissolved germyl sodium for about one hour.

Unreacted germane (5.92 mmoles) was recovered from the contents of the cold traps by distillation at -157° while methylgermane (1.7 mmoles) was volatile at -129° (Found: M, 90.0; Yield, 50.6%. Required for CH_3GeH_3: M, 90.6). The last trace of ammonia was removed by reaction with anhydrous hydrogen chloride.

Characterization of Methylgermane

Methylgermane has been characterized by its boiling point, melting point and by analysis (123) but its vapour pressure - temperature relationship and infrared spectrum have not been reported. Accordingly, vapour pressure - temperature measurements were made and the results in the range -114.4 to -37.8° are tabulated in Table V. A plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 7 from which the following values were calculated.

Vapour pressure equation in the range -114.4 to -37.8°:

$$\log_{10} p_{mm} = \frac{-861}{T} + 6.321$$

Boiling point at 760 mm. (extrapolated) = -23.0 ± 0.2°

Teal and Kraus (123) = -23°

Latent Heat of Vapourization: 3965 cals./mole

Trouton's Constant: 15.9

There was no decomposition and vapour pressures were determined with decreasing as well as increasing temperature to ensure that equilibrium conditions had been attained.

The average of three melting point determinations, -153.8, -153.5, -154.0 was -153.7 ± 0.3°. Teal and Kraus (123) reported a value of -158°.

A sample was taken for a determination of its infrared spectrum at pressures of 40.8, 23.0 and 7.8 mm. The frequencies of the principal peaks and their assignments are listed in Table VI; and a copy of the spectrogram is shown in Figure 8.

TABLE V

Vapour Pressures of Methylgermane

Temperature (°C)	Vapour Pressure (mm. Hg)
-114.4	9.1
- 99.7	24.5
- 90.0	44.6
- 85.3	56.0
- 73.0	102.8
- 61.7	173.0
- 59.0	192.0
- 54.0	249.1
- 51.0	269.2
- 50.6	282.7
- 46.2	334.5
- 43.0	371.4
- 40.0	408.4
- 37.8	437.0
- 57.0	211.9
- 65.0	153.5

FIGURE 7

Vapour Pressure plot of Methylgermane

$\log_{10}p(\text{mm})$ vs. $1/T$

(-114.4 to -37.8°)

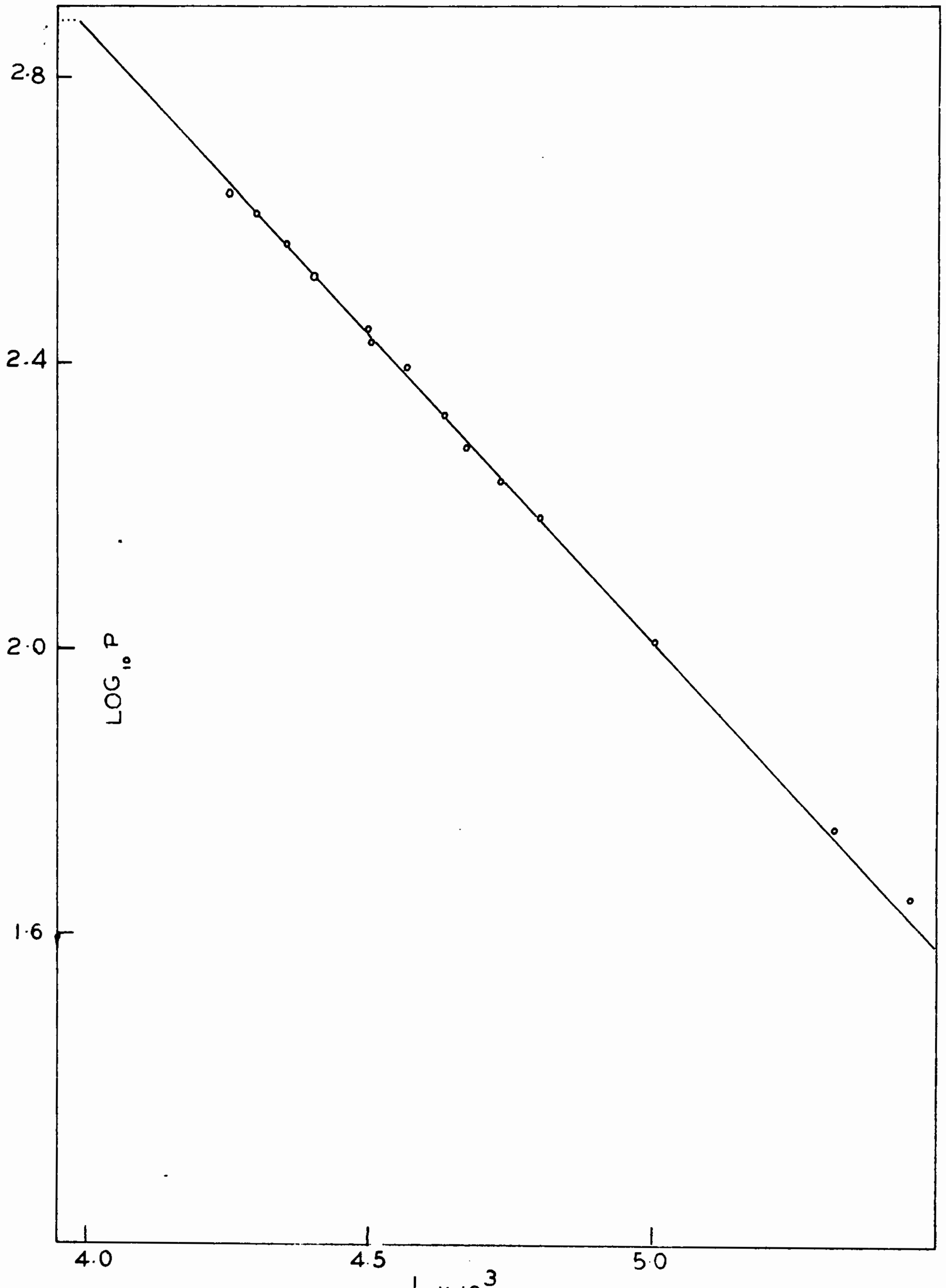

2·8
2·4
2·0
1·6
$\mathrm{LOG}_{10}\,P$
4·0
4·5
5·0
$\frac{1}{T} \times 10^3$

TABLE VI

Vibrational Frequencies of Methylgermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3008	m.	C-H stretch (sym.) and (asym.)
2960	m.	
2860	v.w.	
2100	v.s.	Ge-H stretch (sym.) and (asym.)
1440	v.w.	CH_3 deformation (asym.)
1266 1256 1247	w.	CH_3 deformation (sym.)
845	v.s.	GeH_3 deformation
712	m.	Ge-C stretch

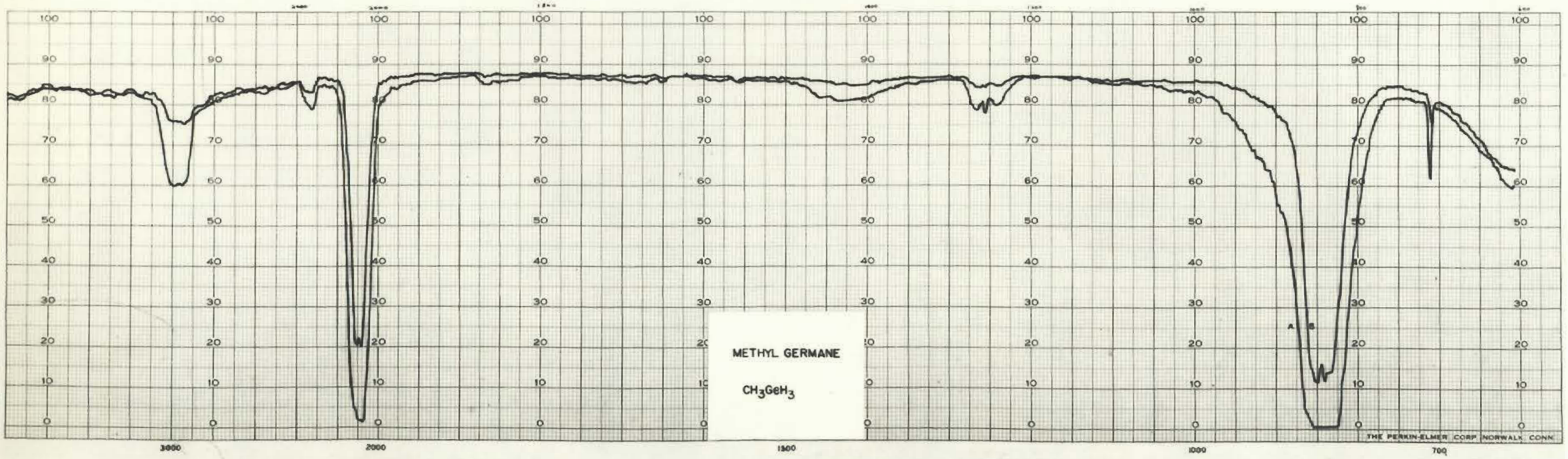
s. = strong, m. = medium, w. = weak, v. = very

sym. = symmetric, asym. = asymmetric

FIGURE 8

Infrared Spectrum of Methylgermane

Pressure: A, 23. mm.
B, 7.8 mm.



METHYL GERMANE

CH_3GeH_3

Preparation of Methyldichlorogermane

Methylgermane (1.46 mmoles) and hydrogen chloride (1.12 mmoles) were reacted in the presence of aluminum trichloride at 100°. The reaction was stopped after four hours because the aluminum trichloride turned pale yellow, indicating that some decomposition had occurred. After pumping away the hydrogen, formed in the reaction, through a trap maintained at -196°, unreacted methylgermane and hydrogen chloride were removed together (0.04 mmoles) by distillation in the range -130 to -92°. The residue, contained only methyldichlorogermane (Found: M, 162.3. Required for CH_3GeHCl_2: M, 159.6), which passed through a trap held at -45.2° yielding a tensiometrically pure product (v.p. at 20°: 25.8 mm.).

Characterization of Methyldichlorogermane

The vapour pressure - temperature relationship of a tensiometrically pure sample of methyldichlorogermane (v.p. at 20°: 25.4 mm.) was measured in an all glass spoon gauge. The data are listed in Table VII and a plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 9. The following values were calculated from the linear portion of this plot.

Vapour pressure equation in the range 7.9 to 73.0°:

$$\log_{10}p_{mm.} = \frac{-1800}{T} + 7.553$$

Boiling point at 760 mm. (extrapolated): 112.4°

Latent Heat of Vapourization: 8290 cals./mole

Trouton's Constant: 21.5

TABLE VII

Vapour Pressures of Methyldichlorogermane

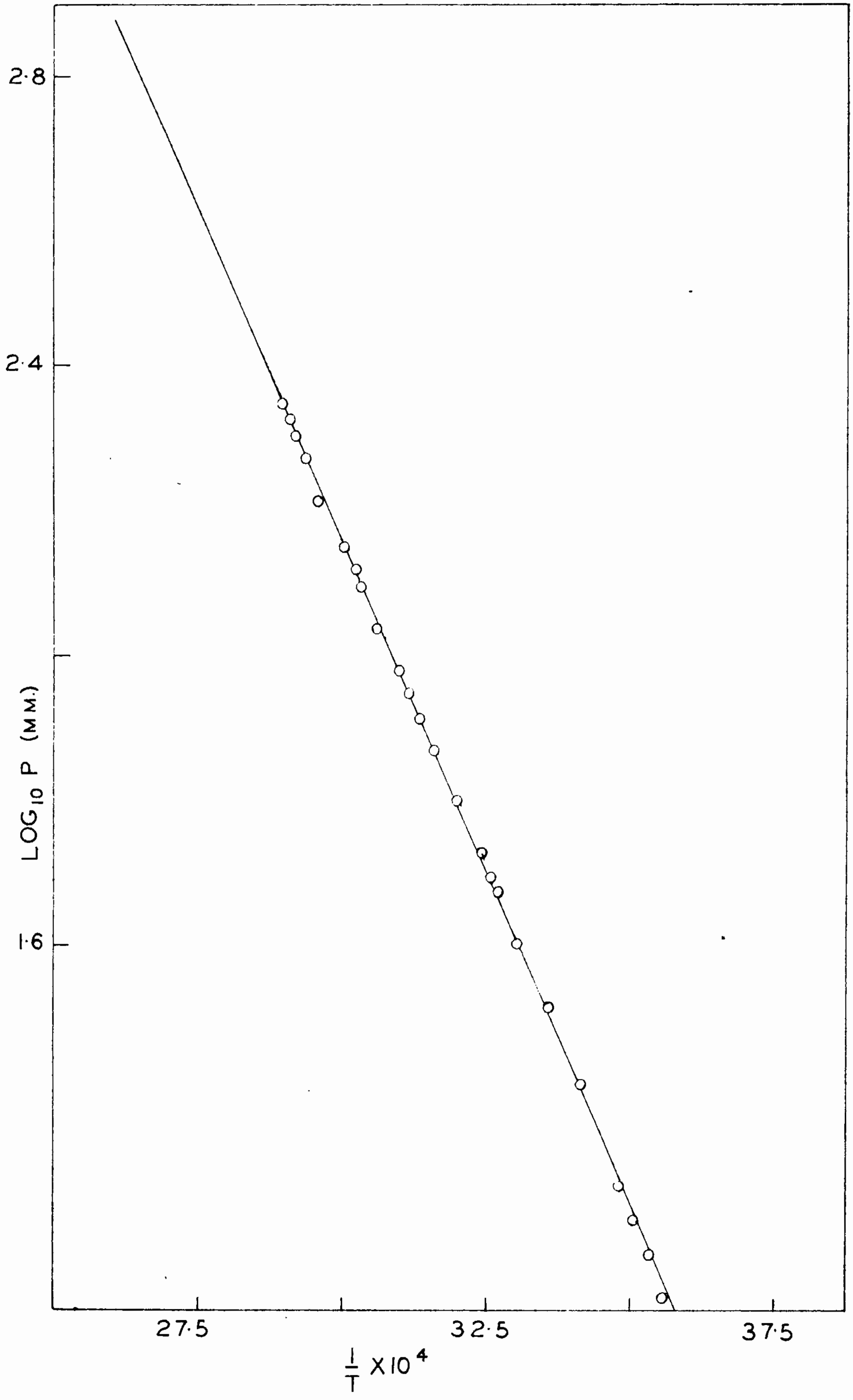
Temp. (°C)	v.p. (mm.)	Temp. (°C)	v.p. (mm.)
7.9	13.0	53.5	109.1
10.1	14.8	57.0	124.5
12.3	16.6	60.3	141.1
13.9	18.4	64.5	163.7
20.0	25.4	69.9	200.8
24.7	32.3	73.0	223.6
29.4	40.0	70.7	210.8
32.8	47.1	68.8	197.7
34.0	49.2	67.2	186.8
36.0	53.3	58.0	131.8
40.0	63.1	47.7	89.3
43.6	74.0	39.3	63.2
46.2	82.0	23.4	30.3
50.0	95.5		

FIGURE 9

Vapour Pressure plot of Methyldichlorogermane

$\log_{10} p(\text{mm})$ vs. $1/T$

(7.9 to 73.0°)


2·8
2·4
1·6
LOG$_{10}$ P (MM.)
27·5
32·5
37·5
$\frac{1}{T}$ X10^4

Vapour pressure at 20° (calculated): 25.9 mm.

Vapour pressure at 20° (observed): 25.4 mm.

At higher temperatures, the liquid became pale yellow, indicating that slight decomposition had occurred. However, vapour pressures, measured with decreasing and increasing temperature, agreed, indicating that decomposition was negligible and equilibrium conditions had been attained for all measurements.

The average value of three melting point determinations, -63.0, -63.2 and -63.1° was -63.1 ± 0.1°.

A sample was taken for a determination of its infrared spectrum at pressures of 17.0 and 10.8 mm. The principal peaks and their frequency assignments are listed in Table VIII. A copy of the spectrogram is shown in Figure 10.

TABLE VIII

Vibration Frequencies of Methyldichlorogermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
2995 2905	w.	C-H stretching (sym.) and (asym.)
2120	v.s.	Ge-H stretching
1412	m.	CH_3 deformation (asym.)
1258	m.	CH_3 deformation (sym.)
853	s.	Ge-H bending
827	v.s.	Ge-CH_3 rocking
783	m.	$GeCl_2$ wagging
707	m.	Ge-C stretch
666	m.	unidentified

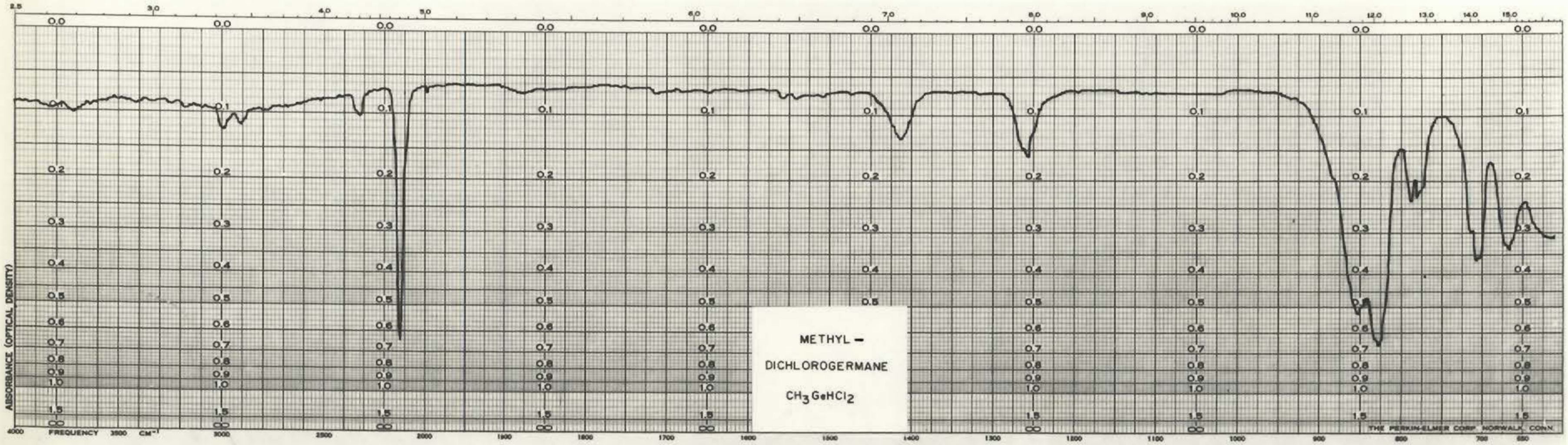
v. = very, s. = strong, m. = medium, w. = weak

sym. = symmetric asym. = asymmetric

FIGURE 10

Infrared Spectrum of Methyldichlorogermane

Pressure: 16.0 mm.


METHYL –
DICHLOROGERMANE
CH_3GeHCl_2
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
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
∞
ABSORBANCE (OPTICAL DENSITY)
4000
FREQUENCY 3500 CM⁻¹
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
650
THE PERKIN-ELMER CORP. NORWALK, CONN.

Preparation of Methylbromogermane

Methylgermane (3.08 mmoles) and hydrogen bromide (3.08 mmoles), in the presence of aluminum tribromide, were reacted at 100° for four hours. Hydrogen, formed in the reaction, was pumped away through a trap held at -196°, which retained the condensable gases. Unreacted methylgermane and hydrogen bromide were removed together by distillation at -96°, leaving a residue of tensiometrically pure methylbromogermane (Found: M, 169.7; v.p. at 0°: 26.8 mm.; Yield: 53%. Required for CH_3GeH_2Br: M, 169.5).

Characterization of Methylbromogermane

Vapour pressures of a tensiometrically pure sample of methylbromogermane (v.p. at 0°: 27.1 mm.) were determined at temperatures in the range 0 to 60°. These are recorded in Table IX and a plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 11. The following data were calculated from this plot.

Vapour pressure equation in the range 0 to 60°:

$$\log_{10}p_{mm.} = \frac{-1740}{T} + 7.804$$

Boiling point at 760 mm. (extrapolated): 80.3°

Latent Heat of Vapourization: 7960 cals./mole

Trouton's Constant: 22.6

Vapour pressure at 0° (calculated): 27.1 mm.

Vapour pressure at 0° (observed): 27.2 mm.

TABLE IX

Vapour Pressures of Methylbromogermane

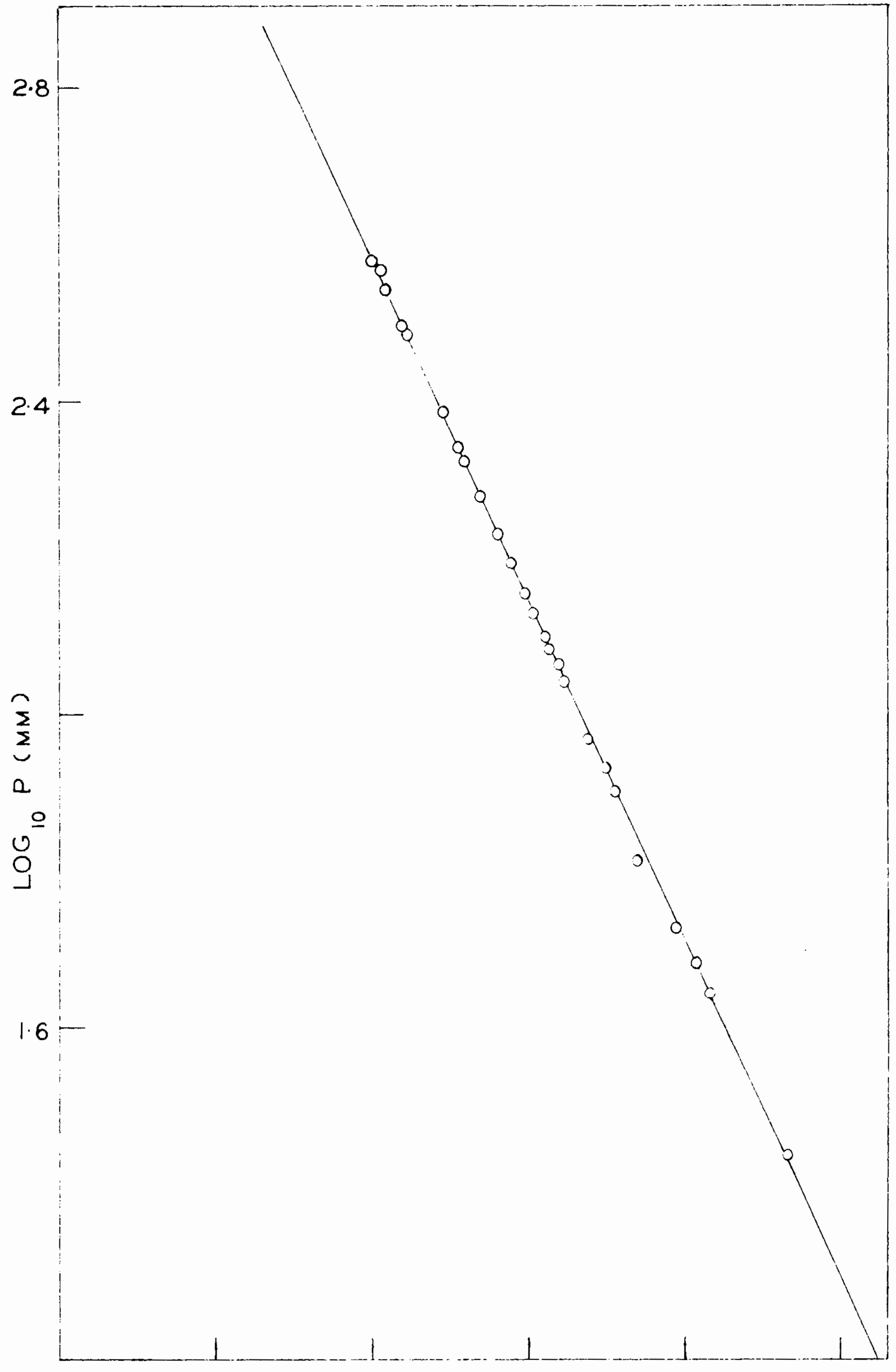
Temp. (°C)	v.p. (mm.)	Temp. (°C)	v.p. (mm.)
0.0	27.1	38.9	169.5
9.5	44.2	42.2	189.8
11.5	48.0	44.3	210.2
14.1	53.3	48.0	241.8
18.9	65.0	54.6	312.3
23.4	85.4	57.6	347.7
25.4	93.0	60.0	378.0
29.0	110.0	59.0	369.7
31.0	121.0	53.6	306.0
32.0	125.8	45.0	220.0
33.4	134.0	30.3	116.0
35.0	143.5	22.5	79.8
36.9	156.0		

FIGURE 11

Vapour Pressure plot of Methylbromogermane

$\log_{10} p(\mathrm{mm})$ vs. $1/T$

(0 to 60°)


2·8
2·4
1·6
LOG$_{10}$ P (MM)
27·5
32·5
37·5
$\frac{1}{T}$ X 10^4

Vapour pressures, measured with increasing and decreasing temperature, indicated that no decomposition had occurred and that equilibrium conditions had been attained.

The melting point of a pure sample was -89.2 ± 0.2°C.

The infrared spectrum of methylbromogermane, determined in the gas phase at pressures of 68.5 and 14.5 mm., is shown in Figure 12. The principal peaks and an assignment of frequencies to particular vibrations are listed in Table X.

Reaction of Methylbromogermane with Silver Carbonate

Methylbromogermane (1.42 mmoles) was passed slowly through a silver carbonate (2.0 gm.) - glass wool plug which turned black during the process. Hydrogen ($\sim$0.3 mmoles), formed in the reaction, was pumped away through a trap cooled in liquid air which retained condensable vapours. These were distilled at -96° to separate carbon dioxide (2.15 mmoles. Found: M, 47.5. Required for CO_2: M, 44.0) from the residue, which was recycled several times through the silver carbonate plug. Traces of carbon dioxide were removed by further distillation at -96°, while the non-volatile fraction was passed through a trap held at -45.2°. The fraction, volatile at this temperature (0.14 mmoles), was mainly unreacted methylbromogermane (Found: M, 155.5. Required for CH_3GeH Br: M, 169.5) contaminated with a small amount of lower molecular weight material.

A clear viscous liquid of undetectable vapour pressure at room temperature remained on the walls of the apparatus and probably on the surface

TABLE X

Vibrational Frequencies of Methylbromogermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3010	m.	C-H stretch
2940	m.	
2100	v.s.	Ge-H stretch
1420	m.	CH_3 deformation (asym.)
1260	m.	CH_3 deformation (sym.)
1248	m.	
878	v.s.sh.	GeH_2 bending
860	v.s.sh.	GeH_2 wagging
838	v.s.	Ge-CH_3 rock
708	v.s.	Ge-C stretch
700	v.s.	Ge-C stretch

v. = very, s. = strong, m. = medium, sh. = shoulder

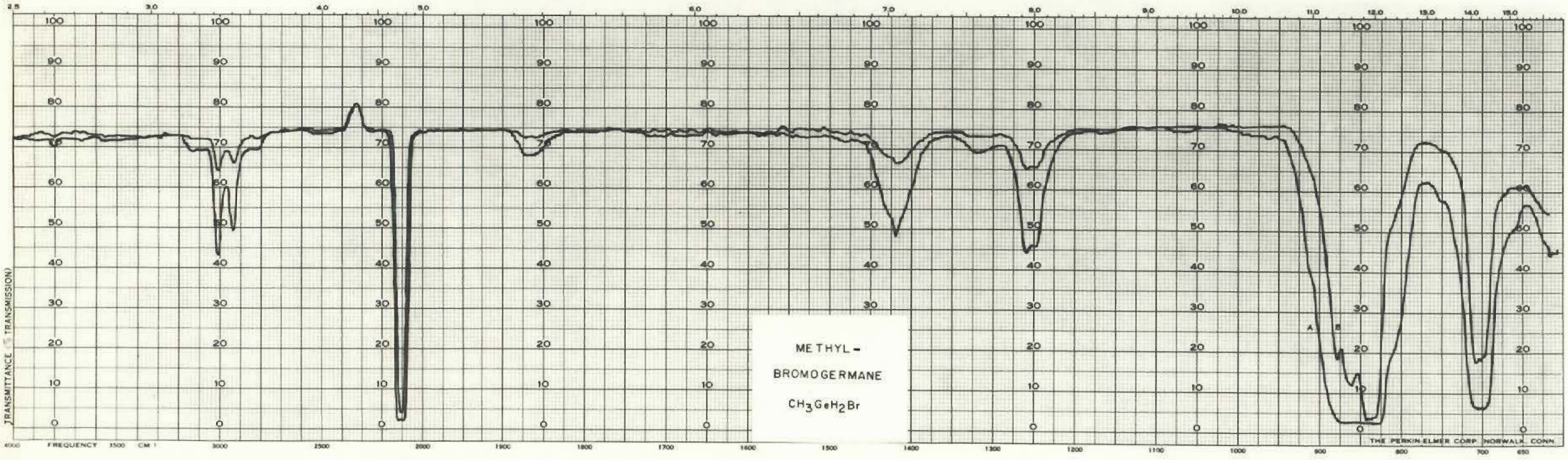
sym. = symmetric asym. = asymmetric

FIGURE 12

Infrared Spectrum of Methylbromogermane

Pressure: A, 68.3 mm.

B, 14.5 mm.



METHYL-
BROMOGERMANE
CH_3GeH_2Br

of the silver carbonate plug. Since this material could not be removed by distillation at room temperature, it was not examined further. 1,1'-Dimethyldigermoxane was probably formed according to the equation,

$$2CH_3GeH_2Br + Ag_2CO_3 \longrightarrow (CH_3GeH_2)_2O + CO_2 + 2AgBr$$

but condensed to form a complex polymer of low vapour pressure. The formation of more carbon dioxide than required by the above equation (Found: 2.15 mmoles. Required: 0.64 mmoles) suggested that silver carbonate promoted condensation of the digermoxane.

Reaction of Methylbromogermane with Sodium Methylate

Experiment 1: Considerable heat was evolved when methylbromogermane (1.17 mmoles) reacted with dry sodium methylate in vacuo at 25°. Hydrogen (0.005 mmoles), formed in the reaction, was removed. The vapour pressure at 0° of the product mixture was not constant but decreased slowly from 47.5 to 30.0 mm. (Required for CH_3GeH_2Br: v.p. at 0°, 27.1 mm.; for CH_3OH: v.p. at 0°, 30.1 mm.) and successive determinations of molecular weight gave values of 38.4 and 36.5 (Required for CH_3OH: M, 32.0; for $CH_3GeH_2OCH_3$: M, 120.6), indicating that the sample was predominantly methanol. Only a trace of material could be removed by distillation at -64° leaving a residue of almost pure methanol (Found: M, 36.5; v.p. at 0°: 30.0 mm. Required for CH_3OH: M, 32.0; v.p. at 0°: 30.1 mm.).

These results indicated that a volatile compound was formed initially and subsequently decomposed to give methanol as the only volatile product.

Experiment 2: The reaction was repeated at -80° to minimize the effect of the high heat of reaction. Methylbromogermane (1.94mmoles) and dry sodium methylate were reacted at -80° for thirty minutes (m.p. of CH_3GeH_2Br: -89.2°). Hydrogen was not produced and the molecular weight of the product mixture (1.83mmoles) was 107.4 (Required for $CH_3GeH_2OCH_3$: M, 120.6; for CH_3OH: M, 32.0).

The product mixture was involatile at temperatures less than -80°. The distillate at -70° was mainly methanol (0.60 mmoles. Found: M, 40.2. Required for CH_3OH: M, 32.0). Further distillation at -65° gave a volatile fraction (Found: 0.40 mmoles; M, 44.1) and a volatile residue (Found: 0.63 mmoles; M, 38.1. Required for CH_3OH: M, 32.0), which were predominantly methanol. A non-volatile, white, water-repellant film remained in the distillation trap.

These results indicated that methylbromogermane probably reacted with sodium methylate, according to the equation,

$$CH_3GeH_2Br + NaOCH_3 \longrightarrow CH_3GeH_2OCH_3 + NaBr$$

to form methylmethoxygermane, which subsequently decomposed rapidly to yield methanol and a white solid, which was probably a polymer of the type, $(CH_3GeH)_x$.

Trimethylgermyl Derivatives

The instability of 1,1'-dimethyldigermoxane and methylmethoxygermane prompted an investigation of the preparation and properties of hexamethyldigermoxane, $((CH_3)_3Ge)_2O$, and trimethylmethoxygermane, $(CH_3)_3GeOCH_3$, which were expected to be thermally stable. Trimethylchloro- and trimethylbromo- germane were chosen as convenient starting materials for the preparation of these derivatives.

Preparation of Trimethylchlorogermane

Trimethylchlorogermane has been prepared, in 24% yield, by the reaction of dimethyldichlorogermane with methylmagnesium chloride in ether solution (92). Since dimethyldichlorogermane was not available, the halogenation of tetramethylgermane was attempted.

Tetramethylgermane (2.27 mmoles) and hydrogen chloride (2.15 mmoles) were reacted in the presence of aluminum trichloride at room temperature for one hour. Methane, formed in the reaction was removed and the condensable mixture was separated into three fractions by distillation through a series of traps held at -80, -130 and -196°. Hydrogen chloride (0.66 mmoles) was recovered from the trap maintained at -196° while tetramethylgermane (0.14 mmoles) remained in the trap held at -130°. The fraction retained at -80°, was tensiometrically pure (v.p. at 0°: 10.0 mm.; yield: 33%) but molecular weights of small samples varied erratically between 153.1 and 165.0 (Required for $(CH_3)_3GeCl$: M, 153.1; for $(CH_3)_2GeCl_2$: M, 173.6). However, infrared spectra of samples having molecular weights of 154.3 and 163.0 were found to be identical. After a sample was removed from the molecular weight bulb by condensation in an adjacent trap, a condensable vapour was slowly given off by the stopcock grease. Consequently, high molecular weight determinations were attributed to absorption of the compound in the stopcock grease.

Characterization of Trimethylchlorogermane

Trimethylchlorogermane has been characterized by its boiling point, 115°, melting point, - 13°, and by analysis for chloride (92) but its vapour pressure - temperature relationship and infrared spectrum have not been reported.

Vapour pressures of pure trimethylchlorogermane at temperatures in the range 0 to 68.4° are given in Table XI and a plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 13. The data, calculated from this plot, are given below.

Vapour pressure equation in the range 0 to 68.4°:

$$\log_{10}p_{mm.} = \frac{-1795}{T} + 7.665$$

Boiling point at 760 mm. (extrapolated): 102°

(literature (92)): 115°

Latent Heat of Vapourization: 8075 cals./mole

Trouton's Constant: 21.5

Vapour pressure at 0° (observed): 12.8 mm.

Vapour pressure at 0° (calculated): 12.2 mm.

Rockow (92) reported the boiling point of dimethyldichlorogermane and trimethylchlorogermane as 124° and 115° respectively. Since trimethylchlorogermane was obtained by distillation from a mixture containing a large amount of dimethyldichlorogermane, it was probably contaminated with some of the dichloro derivative resulting in a high boiling point.

TABLE XI

Vapour Pressures of Trimethylchlorogermane

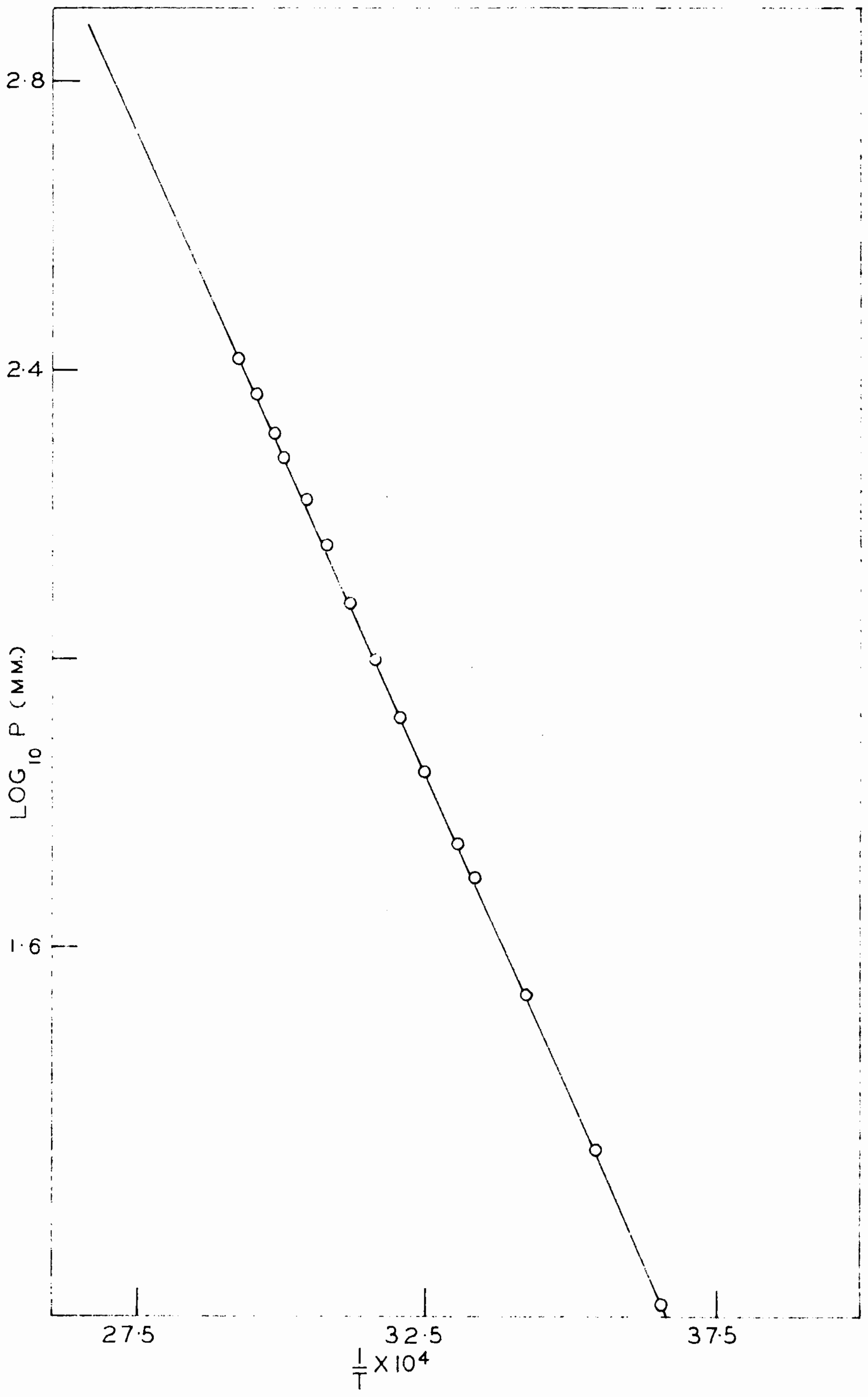
Temperature (°C)	Vapour Pressure (mm. Hg)
0.0	12.8
9.5	20.8
19.0	34.2
26.8	49.9
29.9	55.6
35.1	70.1
39.1	83.0
43.5	100.0
47.8	119.0
52.6	143.6
56.5	166.9
59.9	189.7
62.0	205.7
65.4	232.5
68.4	260.0
43.5	101.1

FIGURE 13

Vapour Pressure plot of Trimethylchlorogermane

$\log_{10}p(\mathrm{mm})$ vs. $1/T$

(0 to 68.4°)


2·8
2·4
1·6
LOG$_{10}$ P (MM.)
27·5
32·5
37·5
$\frac{1}{T}$ X 10^4

The infrared spectrum of trimethylchlorogermane, shown in Figure 14, was determined in the gas phase at a pressure of 20 mm. The principal absorption peaks and their frequency assignments are listed in Table XII.

Preparation of Trimethylbromogermane

Dennis and Patnode (32) prepared trimethylbromogermane by the reaction of tetramethylgermane with hydrogen bromide in the presence of aluminum tribromide, as represented by the following equation,

$$Ge(CH_3)_4 + HBr \xrightarrow{AlBr_3} (CH_3)_3GeBr + CH_4$$

Higher brominated derivatives were not formed.

Tetramethylgermane (6.7 mmoles) and hydrogen bromide (7.82 mmoles), in the presence of aluminum tribromide, reacted at room temperature with the evolution of heat. A clear, viscous red liquid, in which aluminum tribromide seemed to dissolve, collected at the bottom of the halogenation flask. Methane, formed in the reaction, was pumped away through a trap cooled in liquid air which retained condensable vapours. However, after pumping for three hours at a pressure of one micron, a considerable amount of viscous liquid could not be distilled out of the flask. Subsequent treatment of this liquid with 6N nitric acid resulted in the formation of nitrogen dioxide, indicating the presence of germanium tetrabromide (28). This suggested that germanium tetrabromide formed a non-volatile liquid complex with aluminum tribromide.

TABLE XII

Vibration Frequencies of Trimethylchlorogermane

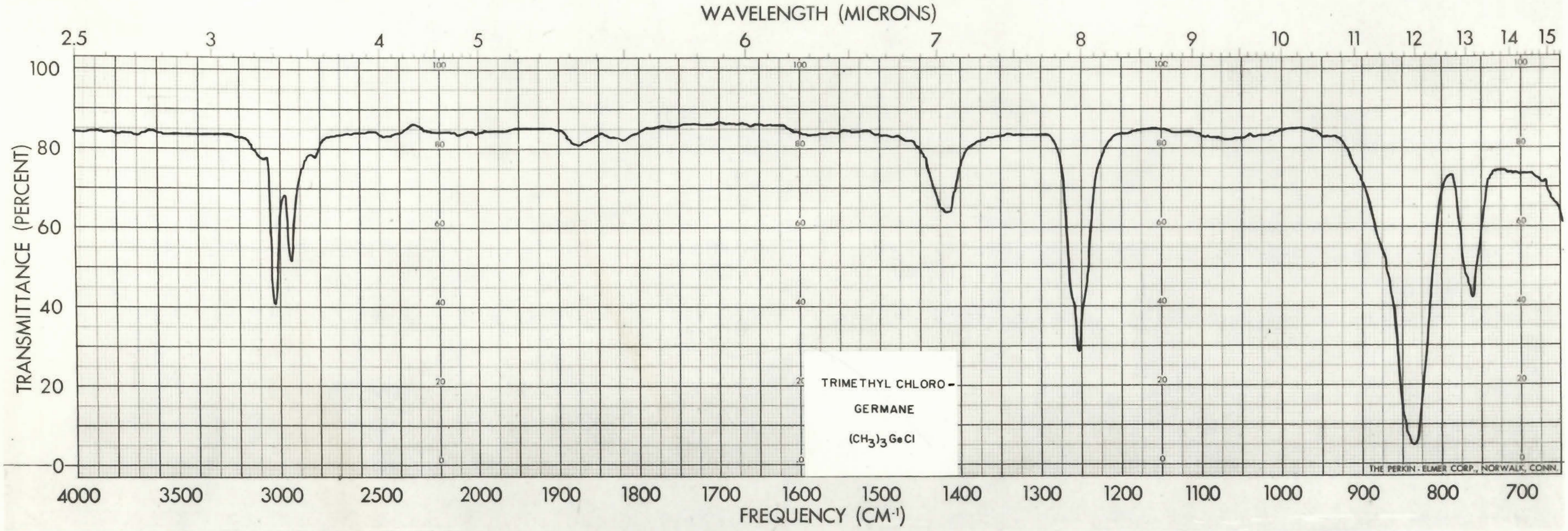
Frequency (cm.$^{-1}$)	Intensity	Assignment
3025	s.	C-H stretching
2945	m.	
2825	v.w.	
1875	v.w.	Overtone or combination
1820	v.w.	" "
1415	m.	CH_3 deformation (asymmetric)
1255	s.	CH_3 deformation (symmetric)
834	v.s.	Ge-CH_3 rock
760	s.	Ge-C stretch

s. = strong, m. = medium, w. = weak, v. = very

FIGURE 14

Infrared Spectrum of Trimethylchlorogermane

Pressure: 20. mm.



TRIMETHYL CHLORO-GERMANE

$(CH_3)_3GeCl$

The condensable fraction retained in the liquid air trap was distilled through traps maintained at -80°, -120° and at the temperature of liquid air. Hydrogen bromide (0.06 mmoles) was recovered from the trap immersed in liquid air while tetramethylgermane remained in the trap held at -120°. Impure trimethylbromogermane was retained in the trap cooled to -80°. The pale yellow colour of this sample was probably due to free bromine, for shaking the liquid with a small bead of mercury yielded tensiometrically pure trimethylbromogermane (Found: M, 198.0; v.p. at 13.0°, 13.6 mm. Required for $(CH_3)_3GeBr$: M, 197.5; v.p. at 13° (ref. 32), 12.2 mm.).

In similar preparations, small amounts of dimethyldibromogermane (Found: M, 263.5; v.p. at 27°, 5.0 mm. Required for $(CH_3)_2GeBr_2$: M, 262.4) as well as larger quantities of germanium tetrabromide were also produced.

Characterization of Trimethylbromogermane

The physical properties of this compound have been determined (32), but its infrared spectrum has not been reported. Accordingly, a sample was taken for a determination of its infrared spectrum at a pressure of 16.7 mm. A list of the principal peaks and their frequency assignments is given in Table XIII and a copy of the spectrogram is shown in Figure 15.

TABLE XIII

Vibration Frequencies of Trimethylbromogermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3002	m.	C-H stretch
2909	m.	" "
1412	w.	CH_3 deformation (asym.)
1248	s.	CH_3 deformation (sym.)
1130	v.w.	Combination or overtone
831	v.s.	CH_3 rock
756	m.	Ge-C stretch

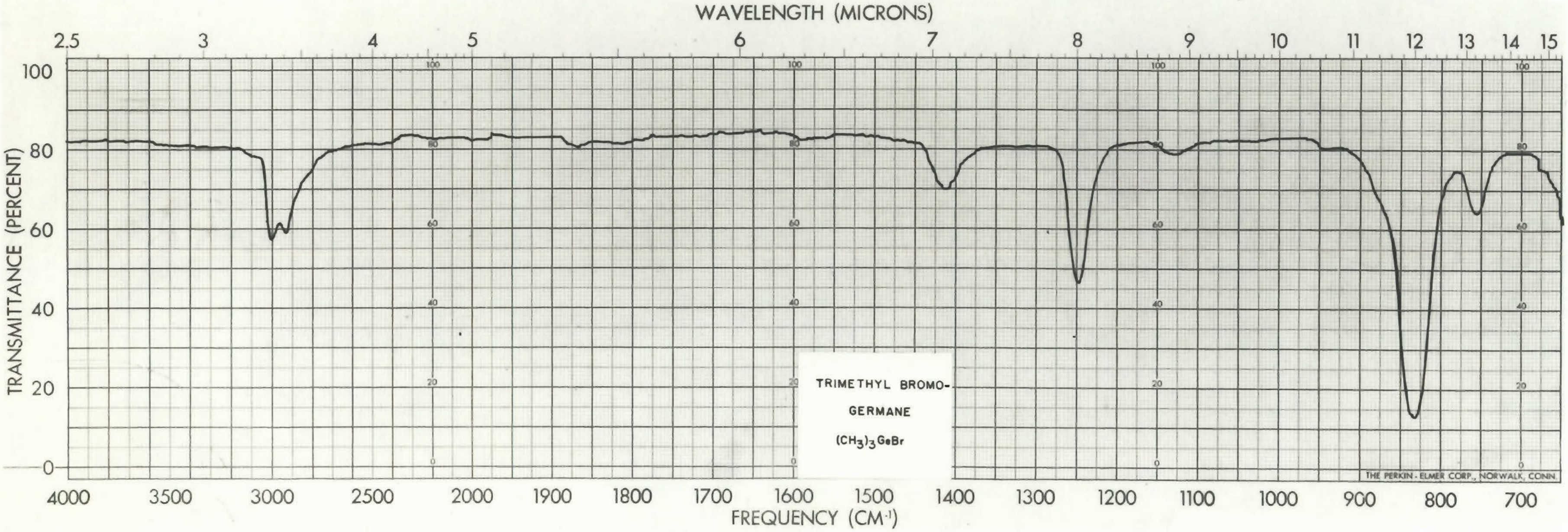
v. = very, s. = strong, m. = medium, w. = weak

sym. = symmetric asym. = asymmetric

FIGURE 15

Infrared Spectrum of Trimethylbromogermane

Pressure: 16.7 mm.



TRIMETHYL BROMO-GERMANE

$(CH_3)_3GeBr$

Preparation of Hexamethyldigermoxane, $((CH_3)_3Ge)_2O$

The hydrolyses of trimethylbromogermane (32) and trimethylchlorogermane (92) have been reported to yield an unidentified volatile product. The inferred compound was hexamethyldigermoxane, $((CH_3)_3Ge)_2O$, which would probably be difficult to separate from an aqueous hydrolysis mixture. Alternatively, the preparation of hexamethyldigermoxane, represented by

$$2(CH_3)_3GeCl + Ag_2CO_3 \longrightarrow ((CH_3)_3Ge)_2O + CO_2 + 2AgCl$$

was attempted.

Silver carbonate (1.0 gm.) and trimethylchlorogermane (1.71 mmoles) were reacted for three hours at room temperature with frequent shaking to ensure thorough mixing of the reactants. Distillation of the mixture at -80° yielded 0.86 mmoles of carbon dioxide (Found: M, 44.6. Required for CO_2: M, 44.0) and a residue of impure hexamethyldigermoxane (Found: M, 201. Required for $((CH_3)_3Ge)_2O$: M, 251.2; for $(CH_3)_3GeCl$: M, 153.1). Unreacted trimethylchlorogermane was removed by distillation at -22.9° leaving a residue of tensiometrically pure hexamethyldigermoxane (Found: M, 250; v.p. at 18.2°: 5.7 mm.; Yield, 60.5%. Required for $((CH_3)_3Ge)_2O$: M, 251.2).

Characterization of Hexamethyldigermoxane

The vapour pressure - temperature measurements, made in the range 18.2 to 72.4°, are listed in Table XIV. A plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 16 from which the following data were calculated.

Vapour Pressure equation in the range 18.2 to 72.4°:

$$\log_{10}p_{mm.} = \frac{-2290}{T} + 8.580$$

Boiling point at 760 mm. (extrapolated): 129°

Latent Heat of Vapourization: 10,540 cals./mole

Trouton's Constant: 26.2

Vapour pressure at 18.2° (calculated): 5.4 mm.

Vapour pressure at 18.2° (observed): 5.7 mm.

Hexamethyldigermoxane appears to be associated in the liquid phase (Trouton's Constant: 26.2) and, consequently, the extrapolated boiling point can only be considered as an approximation.

The melting point of a tensiometrically pure sample (v.p. at 18.0°: 5.6 mm.) was found to be -61.2°, -61.1° and -61.1° which gives an average value of -61.1 ± 0.1°.

Pure hexamethyldigermoxane was taken for an infrared spectrum determination in the vapour phase at a pressure of 7.2 mm. A higher pressure was not practical because of the possibility of condensation on the cell windows. The principal peaks and their frequency assignments are listed in Table XV, and a copy of the spectrogram is shown in Figure 17.

Preparation of Trimethylmethoxygermane

A sample of finely divided sodium methylate was placed in a reaction tube and evacuated to a pressure of less than one micron for twenty minutes. The reaction with trimethylbromogermane (2.82 mmoles) was done at -22.9° (m.p. of $(CH_3)_3GeBr$: -25°) for forty minutes. Trimethyl-

TABLE XIV

Vapour Pressures of Hexamethyldigermoxane

Temperature (°C)	v.p. (mm.)
18.2	5.2
21.5	6.0
25.2	8.2
30.2	11.2
36.6	16.2
42.0	21.5
49.1	31.6
53.3	39.7
56.0	45.4
60.2	53.7
63.5	65.0
66.8	71.6
70.0	83.0
72.4	92.5
67.5	78.8

FIGURE 16

Vapour Pressure plot of Hexamethyldigermoxane

$\log_{10}p$(mm) vs. 1/T

(18.2 to 72.4°)

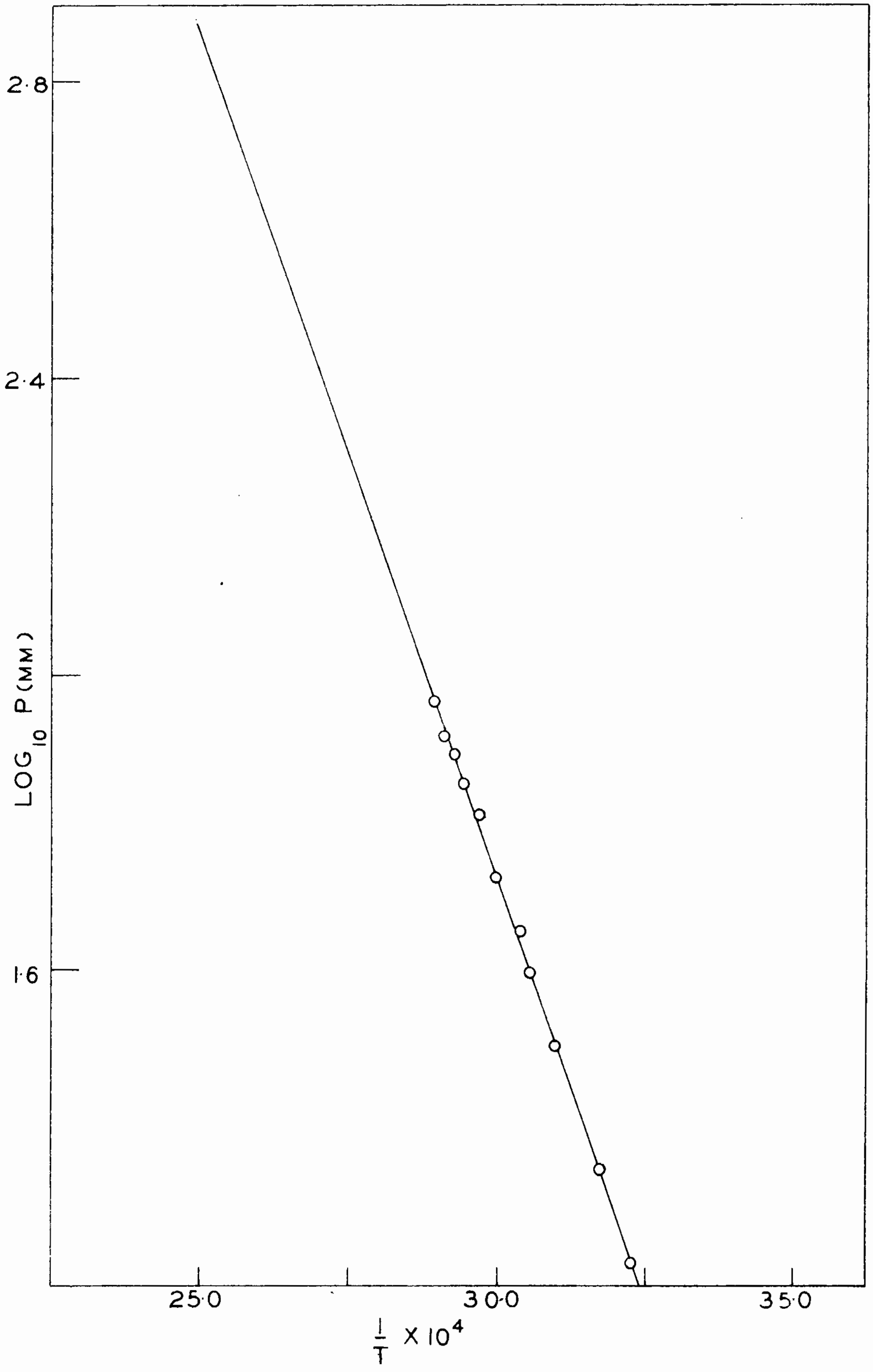

2·8
2·4
1·6
LOG$_{10}$ P (MM)
25·0
30·0
35·0
$\frac{1}{T}$ X 10^4

TABLE XV

Vibration Frequencies of Hexamethyldigermoxane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3000	s.	C-H stretching
2925	m.	
1410	w.	CH_3 deformation (asym.)
1340	w.	
1247	s.	CH_3 deformation (sym.)
950	v.w.	unassigned
880	v.s.	Ge-O-Ge stretching
817	v.s.	Ge-CH_3 rocking
800	v.s.	Ge-CH_3 rocking
754	m.	Ge-C stretching

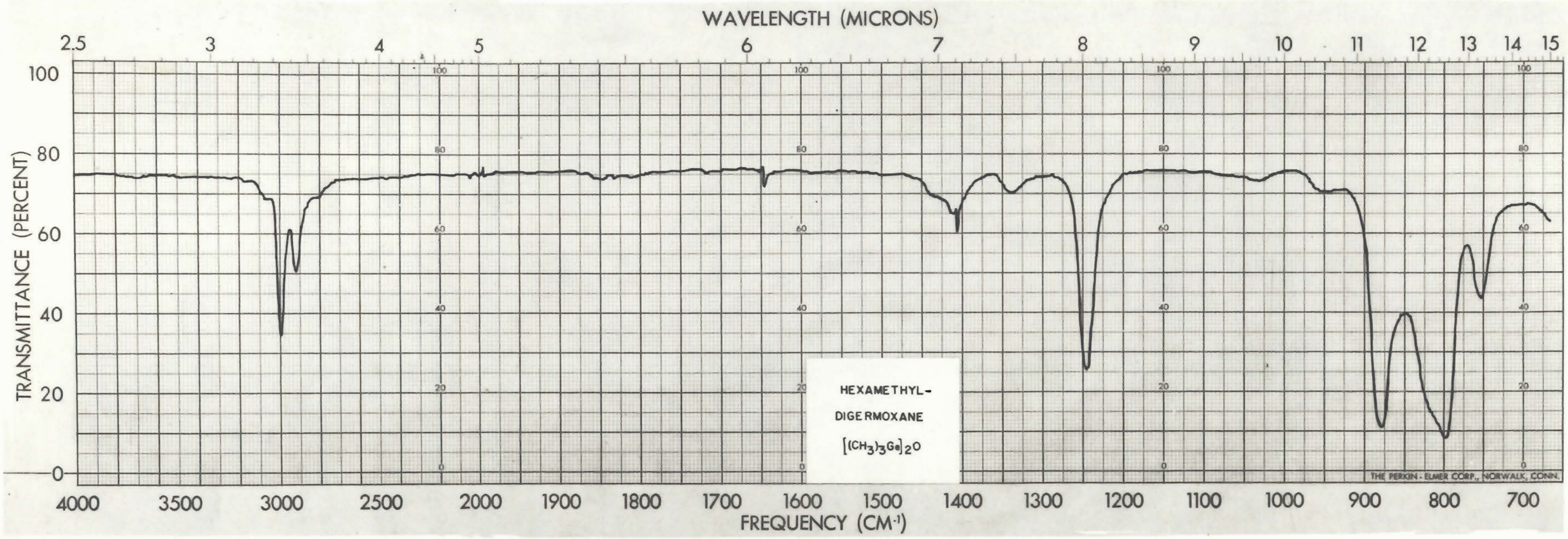
v. = very, s. = strong, m. = medium, w. = weak

sym. = symmetric asym. = asymmetric

FIGURE 17

Infrared Spectrum of Hexamethyldigermoxane

Pressure: 7.2 mm.



HEXAMETHYL-
DIGERMOXANE
$[(CH_3)_3Ge]_2O$

methoxygermane, contaminated with methanol, was obtained from the reaction mixture by distillation at room temperature (Found: M, 126.8; Yield: 78%. Required for $(CH_3)_3GeOCH_3$: M, 148.6; for CH_3OH: M, 32.0). Methanol could not be separated from trimethylmethoxygermane by fractional distillation owing to the proximity of their boiling points.

Methanol was destroyed by reaction of the crude product with metallic sodium at 35°. Tensiometrically pure trimethylmethoxygermane (Found: M, 147.6; v.p. at 14.4°: 42.6 mm. Required for $(CH_3)_3GeOCH_3$: M, 148.6) and hydrogen remained as the only volatile components. Subsequent preparations indicated that the initial amount of methanol released from the mixture during reaction could be minimized by drying the sodium methylate in vacuum at 80° for four hours before use.

Characterization of Trimethylmethoxygermane

Only the boiling point of trimethylmethoxygermane is reported in the literature (129) and, therefore, the following data were determined.

Vapour pressures, in the range 0 to 61.9°, were measured and the values are listed in Table XVI. To ensure that equilibrium conditions had been attained, several measurements were made with decreasing as well as increasing temperature. A plot of $\log_{10} p_{mm.}$ against 1/T is shown in Figure 18 from which the following data were calculated.

Vapour pressure equation in the range 0 to 61.9°:

$$\log_{10} p_{mm.} = \frac{-1695}{T} + 7.531$$

Boiling point (West, Hunt and Whipple, ref. (129)): 87°

Boiling point at 760 mm. (extrapolated): 90.9°.

TABLE XVI

Vapour Pressures of Trimethylmethoxygermane

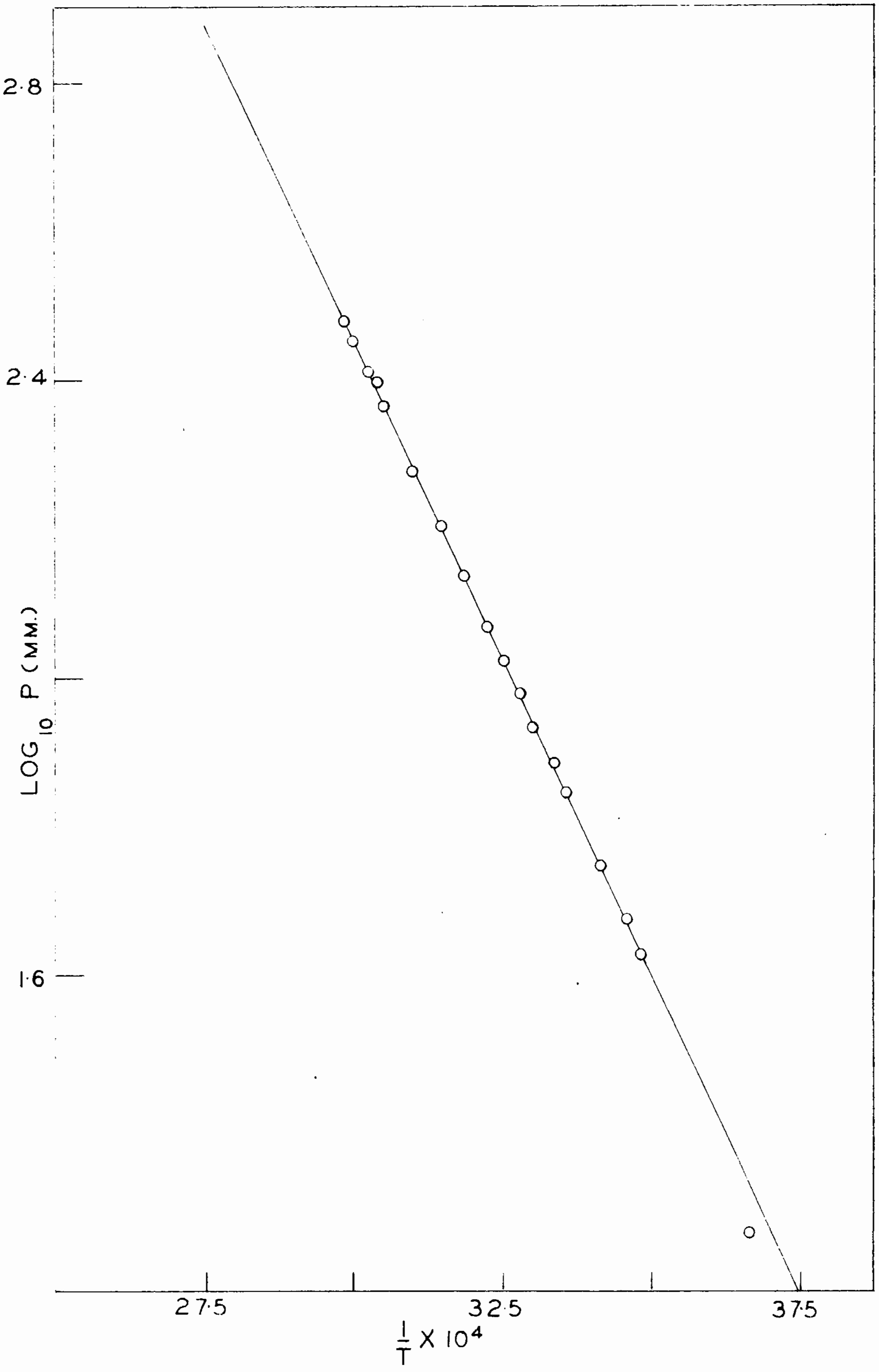
Temp. (°C)	v.p. (mm.)	Temp. (°C)	v.p. (mm.)
0.0	18.0	40.9	137.7
14.4	42.6	44.9	161.2
16.0	47.5	49.4	190.5
20.0	56.2	54.7	232.0
24.6	70.6	57.6	258.6
26.9	77.5	60.2	282.6
29.4	86.0	61.9	301.0
31.9	95.9	60.2	283.0
34.4	106.0	55.7	249.8
36.9	117.8		

FIGURE 18

Vapour Pressure plot of Trimethylmethoxygermane

$\log_{10}p(\mathrm{mm})$ vs. $1/T$

(0 to 61.9°)


2·8
2·4
1·6
LOG$_{10}$ P (MM.)
27·5
32·5
37·5
$\frac{1}{T}$ X 10^4

Latent Heat of Vapourization: 7900 cals./mole

Trouton's Constant: 21.7

The discrepancy of 3.9° between the boiling point determined here and that reported in the literature (129) can be attributed to a small amount of methanol present in the sample which gave a value of 87°, since this sample was isolated by distillation from a methanolic solution.

The infrared spectrum of trimethylmethoxygermane was determined in the vapour phase at a pressure of 50 mm. Table XVII contains a list of the principal absorption peaks and their frequency assignments while a copy of the spectrogram is shown in Figure 19. The weak absorption peak at 3600 cm.$^{-1}$, due to an O-H stretching vibration, indicated that a trace of methanol was present in the sample.

Reaction of Hexamethyldigermoxane with Boron Trifluoride

Experiment 1: Hexamethyldigermoxane (0.255 mmoles) and boron trifluoride (0.255 mmoles), in a mole ratio of 1:1, were taken for reaction. As the temperature of the mixture was raised from -185 to 0°, boron trifluoride vapourized and rapidly reacted with hexamethyldigermoxane as shown by an initial increase in pressure followed by a decrease to about 22 mm.

A white solid and a polymeric residue, from which boron trifluoride (0.012 mmoles) was gradually given off, remained in the reaction vessel after volatile products were removed by distillation. The white solid was partially soluble in water and the presence of boron trioxide was suspected. Boron trifluoride (0.03 mmoles) was recovered from the volatile products by

TABLE XVII

Vibration Frequencies of Trimethylmethoxygermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3600*	w.	O-H stretching
2935	v.s.	C-H stretching
2830	s.	
2060	w.	Overtone or combination
1450	m.	Asymmetric CH_3 deformation
1408		
1360		
1245	s.	Symmetric CH_3 deformation
1225	w.	unidentified
1060	v.s.	CH_3-O rocking
1030	s.	C-O stretching
1005	m.	
875	m.	Ge-O stretching
815	v.s.	Ge-CH_3 rocking
750	s.	Ge-C stretching

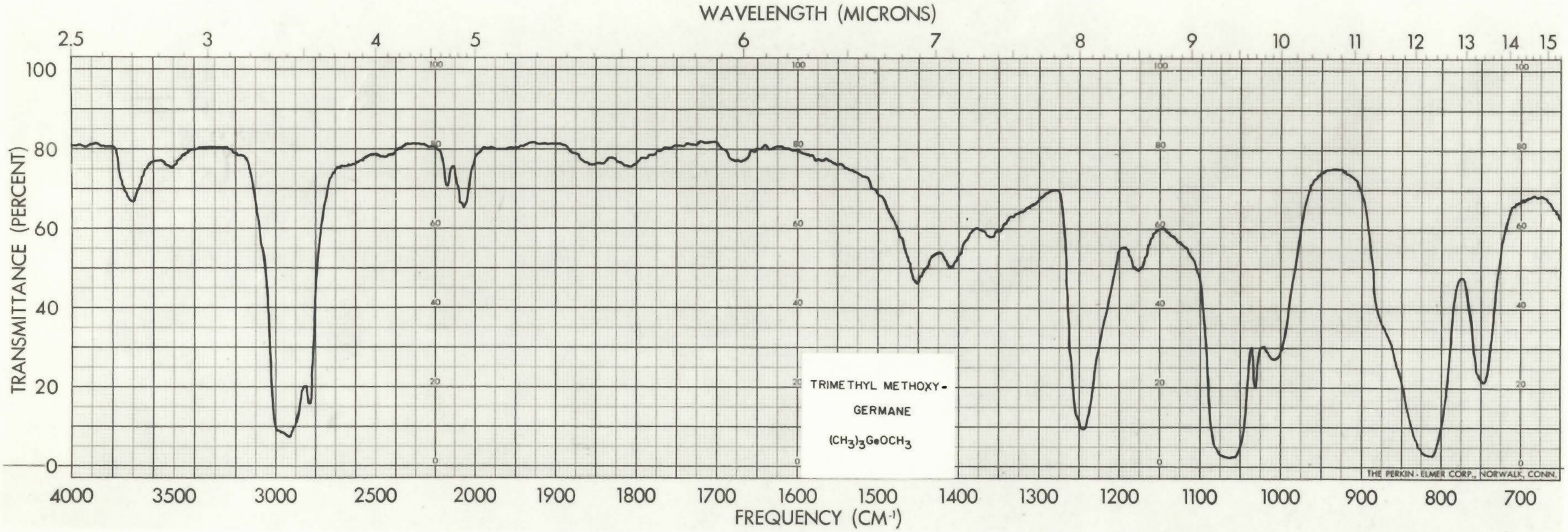
v. = very, s. = strong, m. = medium, w. = weak

*CH_3OH impurity

FIGURE 19

Infrared Spectrum of Trimethylmethoxygermane

Pressure: 50 mm.



TRIMETHYL METHOXY-GERMANE

$(CH_3)_3GeOCH_3$

distillation at -80° leaving a residue (0.367 mmoles) which appeared to be a new compound, trimethylfluorogermane (Found: M, 138.0. Required for $(CH_3)_3GeF$: M, 136.6), probably formed in the reaction represented by,

$$((CH_3)_3Ge)_2O + BF_3 \longrightarrow (CH_3)_3GeOBF_2 + (CH_3)_3GeF \qquad (1)$$

However, the yield of trimethylfluorogermane was 44% in excess of the theoretical. Trimethylgermoxyboron difluoride was not recovered but decomposed slowly into trimethylfluorogermane, boron trioxide and boron trifluoride, probably according to the equation,

$$3(CH_3)_3GeOBF_2 \longrightarrow 3(CH_3)_3GeF + B_2O_3 + BF_3 \qquad (2)$$

The yield of boron trifluoride was only 47% of that calculated for reaction (2) while the yield of trimethylfluorogermane was 72% on the basis of the overall reaction represented by,

$$3((CH_3)_3Ge)_2O + 2BF_3 \longrightarrow 6(CH_3)_3GeF + B_2O_3 \qquad (3)$$

Experiment 2: In order to obtain further information on the initial stages of the reaction and to confirm the stoichiometry of equation (3), hexamethyldigermoxane (0.672 mmoles) and boron trifluoride (0.448 mmoles), in a 3:2 mole ratio, were reacted at -80° for 12 hours. A white solid film formed on the walls of the reaction tube and 75% of the boron trifluoride was consumed. On warming the mixture to 20°, consumption of the boron trifluoride was complete and, after four hours, the white solid film on the walls of the tube disappeared. The volatile fraction was tensiometrically pure trimethylfluorogermane (1.31 mmoles. Found: M, 136.4; v.p. at 22.2°: 83.5 mm. Required for $(CH_3)_3GeF$: M, 136.6) and the residue of boron trioxide was titrated, in the presence of mannitol, with sodium hydroxide to the phenolphthalein end point. Calculations based on equation (3),

$$3((CH_3)_3Ge)_2O \; + \; 2BF_3 \qquad\qquad 6(CH_3)_3GeF \; + \; B_2O_3 \qquad (3)$$

indicated that boric oxide and trimethylfluorogermane were formed in 97.5 and 97.6% yield respectively.

Characterization of Trimethylfluorogermane

A sample of trimethylfluorogermane was taken for a determination of its vapour pressure - temperature relationship in the range -23 to +72.5°. The data are listed in Table XVIII and a plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 20. The sublimation and vapourization curves intersect at 9.8° but the angle of intersection is very close to 180°. Consequently, 9.8° must be considered only as an approximation of the melting point. The following data have been calculated from the two curves.

Vapourization Curve

Vapour pressure equation in the range 9.8° to 72.5°:

$$\log_{10}p_{mm.} = \frac{-1701}{T} + 7.693$$

Boiling point at 760 mm. (extrapolated): 80.3°

Latent Heat of Vapourization: 7830 cals./mole

Trouton's Constant: 22.1.

Sublimation Curve

Vapour pressure equation in the range -23 to 9.8°:

$$\log_{10}p_{mm.} = \frac{-2083}{T} + 9.038$$

Latent Heat of Sublimation: 9590 cals./mole

Latent Heat of Fusion: 9390-7830 = 1760 cals./mole

The melting point of trimethylfluorogermane, determined by the plunger technique, was found to be 2.0, 1.5 and 2.2° which gives an average value of 1.9 $\pm$ 0.4°.

The infrared spectrum of trimethylfluorogermane, shown in Figure 21, was determined at pressures of 56.5, 30.0 and 8.0 mm. The principal absorption peaks and their frequency assignments are listed in Table XIX.

Reaction of Trimethylmethoxygermane with Boron Trifluoride

Trimethylmethoxygermane (0.35 mmoles) and boron trifluoride (0.35 mmoles), in a 1:1 mole ratio, reacted at room temperature with the quantitative formation of a solid 1:1 addition compound,

$$(CH_3)_3GeOCH_3 + BF_3 \longrightarrow (CH_3)_3GeOCH_3 \cdot BF_3$$

which melted slowly at room temperature and could be distilled without decomposition (v.p. at -22.9°: 6.0 mm.). Boron trifluoride could not be removed from the solid adduct by distillation at -96° (b.p. of BF_3: -100.7°). However, when the adduct was heated at 69° for two hours, a trace of unidentified decomposition product, which was removed by distillation at -80°, was formed. The fraction involatile at -80° was the original adduct as confirmed

TABLE XVIII

Vapour Pressures of Trimethylfluorogermane

Temp. (°C)	v.p. (mm.)	Temp. (°C)	v.p. (mm.)
-23.0	5.0	22.2	83.5
-16.0	8.2	33.0	130.9
- 9.5	13.7	36.2	149.7
- 7.9	15.2	39.3	170.9
- 5.0	18.3	42.0	190.9
- 3.4	20.0	44.6	210.8
- 2.0	22.3	46.8	230.5
- 0.1	24.7	48.9	251.0
0.7	26.1	51.9	280.0
1.5	27.5	54.7	309.8
2.0	28.0	58.0	350.4
2.9	29.6	60.2	378.9
3.9	32.0	61.9	401.0
4.5	33.7	62.9	414.8
6.9	38.0	65.9	458.0
9.0	43.5	68.9	503.2
12.7	52.7	71.9	553.7
21.7	80.8	72.5	568.0

FIGURE 20

Vapour Pressure plot of Trimethylfluorogermane

$\log_{10}p$(mm) vs. 1/T

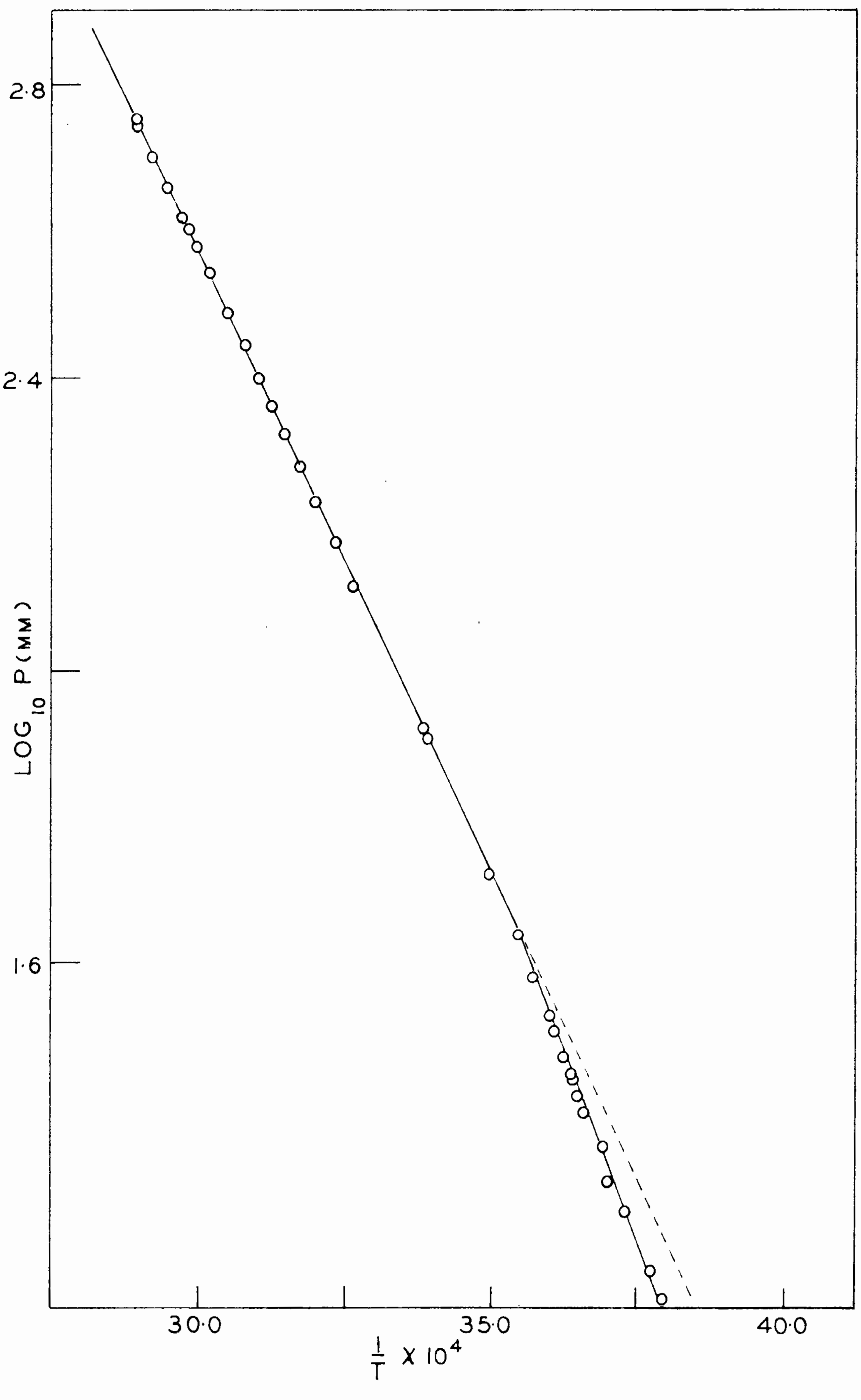

2·8
2·4
1·6
LOG$_{10}$ P (MM)
30·0
35·0
40·0
$\frac{1}{T}$ X 10^4

TABLE XIX

Vibration Frequencies of Trimethylfluorogermane

Frequency (cm.$^{-1}$)	Intensity	Assignment
3060	w.	
3005	s.	C-H stretching
2930	m.	
2820	v.w.	
1415	m.	CH_3 deformation (asym.)
1254	s.	CH_3 deformation (sym.)
1095	v.w.	unidentified
1032	m.	unidentified
828	v.s.	Ge-CH_3 rocking
753	v.s.	Ge-C stretching
745	m.	Ge-F stretching
657	v.s.	$(CH_3)_3$Ge- rocking

v. = very, s. = strong, m. = medium, w. = weak

sym. = symmetric asym. = asymmetric

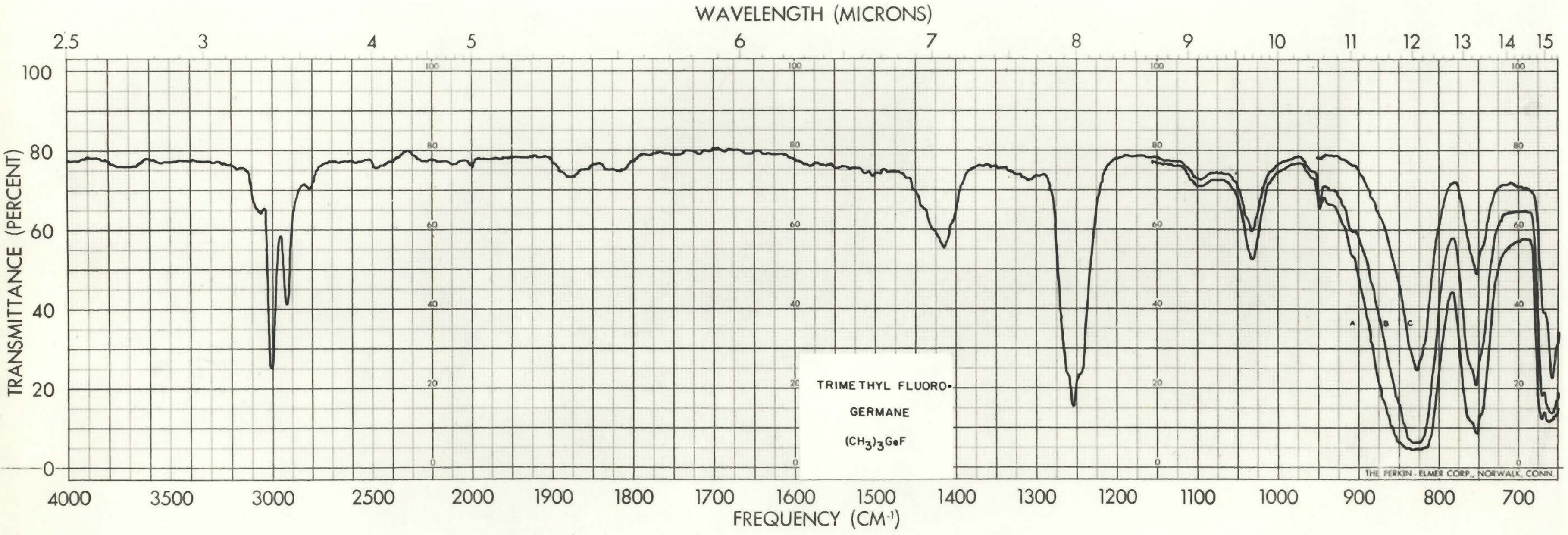
FIGURE 21

Infrared Spectrum of Trimethylfluorogermane

Pressure: A, 56.5 mm.

B, 30.0 mm.

C, 8.0 mm.


WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
A
B
C
TRIMETHYL FLUORO-GERMANE
$(CH_3)_3GeF$
THE PERKIN - ELMER CORP., NORWALK, CONN.
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
FREQUENCY (CM⁻¹)

by a measurement of its saturation vapour pressure (v.p. at -22.9°: 6.0 mm.).

The adduct was sealed in a glass vial and heated at 235° for sixteen hours. A few transparent crystals formed on the walls but most of the material polymerized to a rubber-like consistency. No permanent gases or products volatile at room temperature were found when the vial was opened but, in contact with air, slight fuming occurred. When distilled water was added to the reaction mixture, a white solid, which was partially soluble in water, separated and a qualitative test indicated the presence of boron as boron trioxide. Most of the polymeric material was not soluble in water and an odour similar to that of hexamethyldigermoxane was noted.

Other Compounds of Germanium

Germylene Chloride: GeH_2Cl_2: Germylene chloride was produced in small amounts as a by-product in the preparation of germyl chloride by the reaction of germane with hydrogen chloride, in the presence of aluminum trichloride as catalyst. Germyl chloride was separated from germylene chloride by five distillations at -96°, leaving a residue of tensiometrically pure germylene chloride (Found:M, 146.0; v.p. at 0°: 29.0 mm. Required for GeH_2Cl_2: M, 145.6; v.p. at 0° (ref. 31): 37.0 mm.).

Although the physical properties of this compound have been determined (31), its infrared spectrum is not reported in the literature. Accordingly, a sample was taken for an infrared spectrum determination in the gas phase at a pressure of 14.2 mm. The principal peaks and their frequency assignments are listed in Table XX and a copy of the spectrogram is shown in Figure 22.

TABLE XX

Vibration Frequencies of Germylene Chloride

Frequency (cm.$^{-1}$)	Intensity	Vibration	Assignment
2150	v.s.	$\nu_1(a_1)$ and $\nu_6(b_1)$	Ge-H stretch
862	s.	$\nu_2(a_1)$	GeH_2 bend
850	s.	$\nu_8(b_2)$	GeH_2 wag
783	v.s.	$\nu_7(b_1)$	$GeCl_2$ wag

v. = very, s. = strong, m. = medium, w. = weak

Preparation of Germyl Bromide

Germyl bromide, GeH_3Br, was prepared in order to obtain its infrared spectrum, which is not reported in the literature. The reaction of germane with hydrogen bromide, as represented by the equation,

$$GeH_4 + HBr \xrightarrow{AlBr_3} GeH_3Br + 1/2\ H_2$$

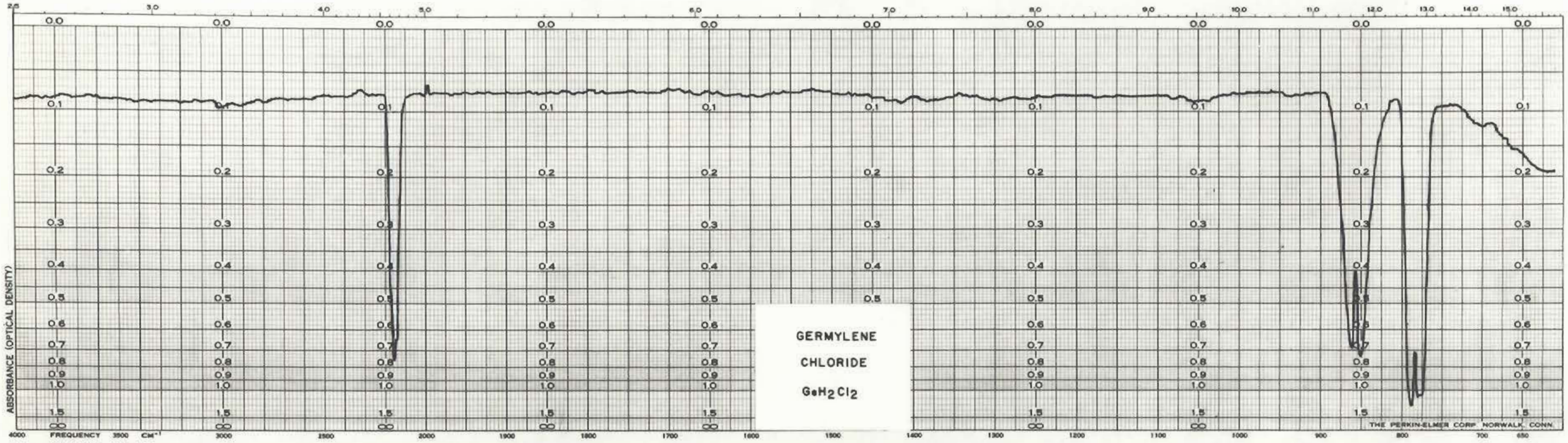
is similar to the previously described preparation of germyl chloride.

The infrared spectrum of tensiometrically pure germyl bromide (Found: M, 155.0; v.p. at -23.6°: 22.0 mm. Required for GeH_3Br: M, 155.5; v.p. at -23.6°: 21.0 mm.), shown in Figure 23, was determined in the gas phase at a pressure of 17.3 mm. The principal absorption peaks and their frequency assignments are listed in Table XXI.

FIGURE 22

Infrared Spectrum of Germylene Chloride

Pressure: 14.2 mm.



GERMYLENE
CHLORIDE
GeH_2Cl_2

TABLE XXI

Vibration Frequencies of Germyl Bromide

Frequency (cm.$^{-1}$)	Intensity	Vibration	Assignment
2120	v.s.	ν_1 and ν_4	Symmetric and asymmetric Ge-H stretch
826	v.s.	ν_2	Symmetric GeH_3 deformation
868	m.	ν_5	Asymmetric GeH_3 deformation

v. = very, s. = strong, m. = medium

Preparation of Dimethylgermane

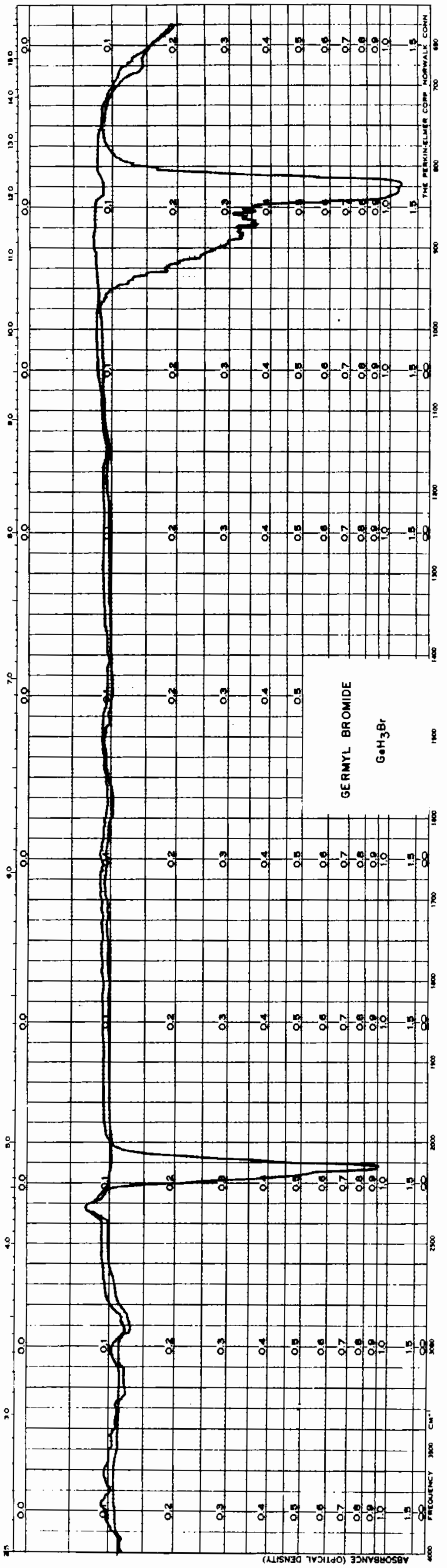
When a large excess of sodium was used in the previously described condensation method for the preparation of methylgermane, both methyl- and dimethyl- germane were produced. Dimethylgermane was not formed using the flow method.

Germane (1.91 mmoles), ammonia (6.91 mmoles) and methyl iodide (2.64 mmoles), in that order, were condensed on 0.48 gm. of freshly cut sodium. The temperature of the mixture was alternately lowered to -196° and raised to -64° several times to promote maximum interaction between the reactants. After one hour, hydrogen formed in the reaction was pumped away through a trap maintained at -196° which retained condensable vapours. Germane was removed by distillation at -164°, while in the range -140 to -125°, a mixture of ammonia, methyl- and dimethyl-germane was recovered.

FIGURE 23

Infrared Spectrum of Germyl Bromide

Pressure: 17.3 mm.

GERMYL BROMIDE
GeH_3Br
ABSORBANCE (OPTICAL DENSITY)
FREQUENCY CM⁻¹
THE PERKIN-ELMER CORP. NORWALK, CONN.
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
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
650
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
∞

Ammonia was destroyed by reaction with hydrogen chloride to form non-volatile ammonium chloride. The excess of hydrogen chloride was readily separated from the germanes by distillation at -148°. By a careful fractionation of the residue at -137°, samples were recovered with molecular weights varying progressively from 91.1 to 105.0 (Required for CH_3GeH_3: M, 90.6; for $(CH_3)_2GeH_2$: M, 104.6). The estimated yields of methylgermane and dimethylgermane were 26% and 40% respectively. Although the mixture could not be separated completely into its components, it was possible, by several distillations at -137° to recover a small sample of pure dimethylgermane.

Since only a small sample (0.63 mmoles) of dimethylgermane (Found: M, 105.0. Required for $(CH_3)_2GeH_2$: M, 104.6) was available, a complete characterization was not possible. Vapour pressures at temperatures in the range -113.6 to -54.0° were obtained and are summarized in Table XXII. A plot of $\log_{10}p_{mm.}$ against 1/T is shown in Figure 24 from which the following data were calculated.

Vapour pressure equation in the range -113.6 to -54.0°:

$$\log_{10}p_{mm.} = \frac{-887}{T} + 6.176$$

Boiling point at 760 mm. (extrapolated): -3.6°

Latent Heat of Vapourization: 4090 cals./mole

Trouton's Constant: 15.2

A sample of dimethylgermane was taken for an infrared spectrum determination in the gas phase at a pressure of 10.0 mm. The principal peaks and their frequency assignments are listed in Table XXIII and a copy of the spectrogram is shown in Figure 25.

TABLE XXII

Vapour Pressures of Dimethylgermane

Temperature (°C)	Vapour Pressure (mm.)
-113.6	3.0
-107.3	5. 0
-99.3	10.2
-93.6	16.0
-88.4	23.2
-79.6	38.7
-77.0	43.0
-72.6	56.0
-70.0	61.8
-65.6	76.8
-62.5	87.0
-59.7	96.1
-57.8	102.0
-54.3	117.0
-54.0	120.7

FIGURE 24

Vapour Pressure plot of Dimethylgermane

$\log_{10}p(\text{mm})$ vs. $1/T$

(-113.6 to -54.0°)

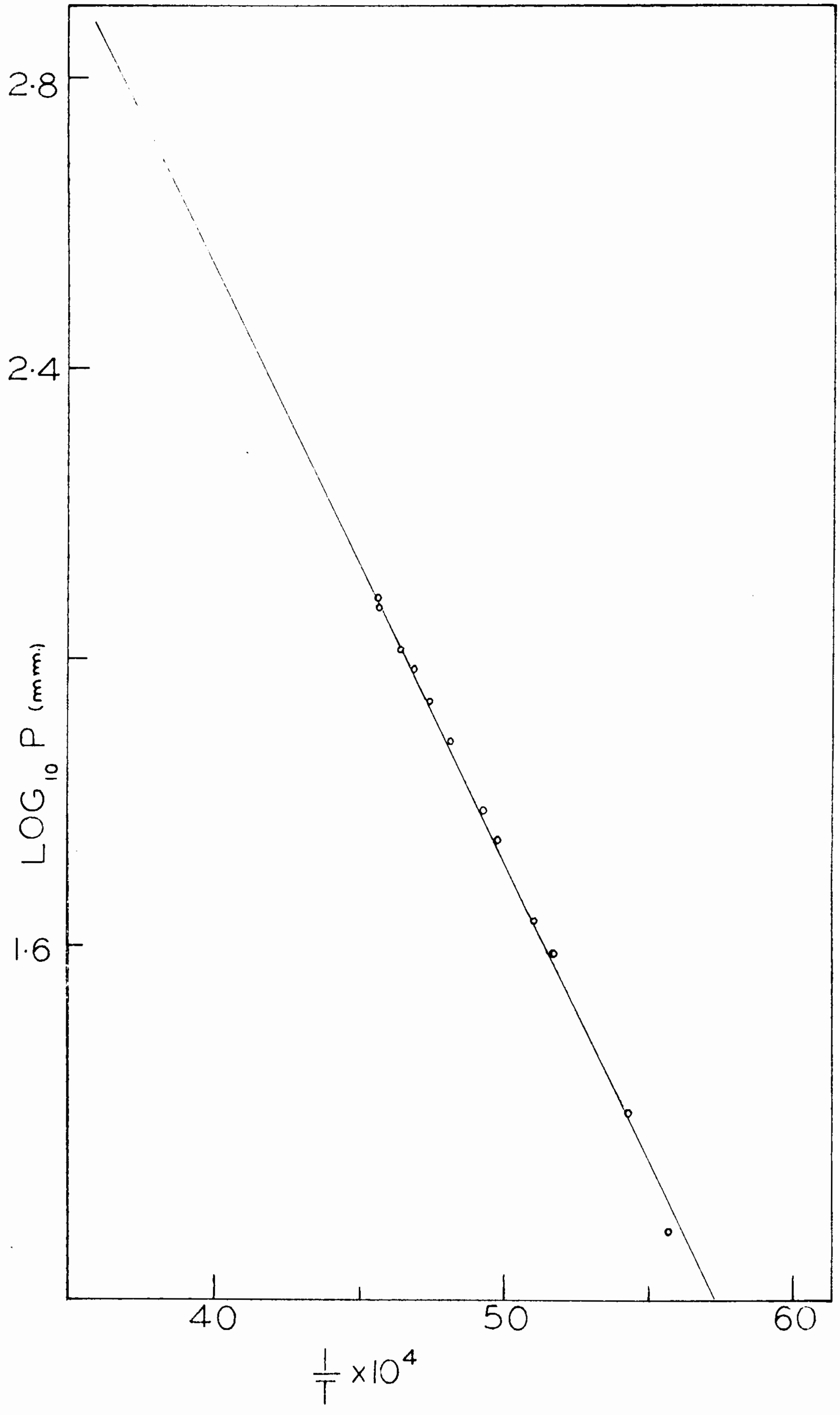

2·8
2·4
1·6
LOG$_{10}$ P (mm.)
40
50
60
$\frac{1}{T}$ x10^4

TABLE XXIII

Vibration Frequencies of Dimethylgermane

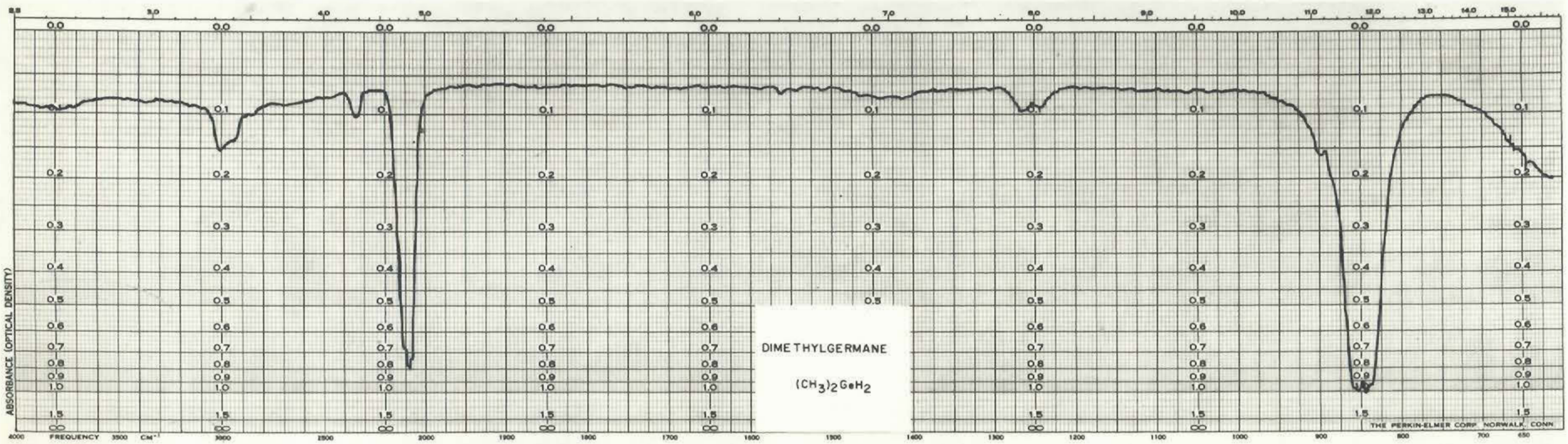
Frequency (cm.$^{-1}$)	Intensity	Vibration	Assignment
3000	w.	ν_1, ν_2, ν_{16} and ν_{22}	C-H stretching
2940	w.		
2105	v.s.	ν_3 and ν_{23}	Ge-H stretching
2090	v.s.		
1465 to 1400	v.w.	ν_4, ν_{17}, ν_{24}	CH_3 deformation
1255	w.	ν_5, ν_{18}	CH_3 deformation
898	w.	-	unidentified
849	v.s.	ν_6 and/or ν_7	GeH_2 bending and/or $Ge(CH_3)_2$ rocking

v. = very, s. = strong, m. = medium, w. = weak

FIGURE 25

Infrared Spectrum of Dimethylgermane

Pressure: 10.0 mm.


DIMETHYLGERMANE

$(CH_3)_2GeH_2$

DISCUSSION

Physical Properties of Volatile Germanium Compounds

A list of physical properties of the compounds investigated, of which four are new, is given in Table XXIV. Only hexamethyldigermoxane is appreciably associated in the liquid phase as shown by a high Trouton Constant. Since dipole interaction is usually greater for fluoro than for chloro compounds trimethylfluorogermane has an abnormally high melting point in comparison with the corresponding chloro derivative. The Trouton Constants calculated for the hydrides are abnormally low in comparison with the normal values obtained for compounds in which germanium is bonded to a more electronegative element. This implies that the entropy change accompanying vapourization of the hydrides is lower than expected and, in the liquid phase, there is a higher degree of disorder than normal.

i) Melting Points: The germanium derivatives invariably have higher melting points than the corresponding carbon and silicon derivatives as evident in Table XXV. The following silicon compounds, SiH_3Cl, SiH_2Cl_2, SiH_3Br, SiH_2Br_2, and $(CH_3)_2SiCl_2$ have lower melting points than the analogous carbon derivatives. In the series AH_3Br, CH_3AH_2Br, $(CH_3)_2AHBr$ and $(CH_3)_3ABr$ where A is C, Si or Ge, the melting points pass through a minimum at CH_3AH_2Br while, in the series AH_2Cl_2, CH_3AHCl_2 and $(CH_3)_2ACl_2$ the melting points increase as the number of methyl groups increase.

Since the melting point of a compound depends upon crystal structure, bond types, dipole moment and hydrogen bonding, the observed trends in

TABLE XXIV

Physical Properties of Germanium Compounds

Compound	Vapour Pressure^x		L_v	Trouton	B.P.	M.P.
	A	B	cals./mole	Constant	(°C)	(°C)
CH_3GeH_3	861	6.321	3965	15.9	-23.0	-153.7
$(CH_3)_2GeH_2$	887	6.176	4090	15.2	- 3.6	-
$CH_3GeHCl_2^*$	1800	7.553	8290	21.5	112.4	- 63.1
$CH_3GeH_2Br^*$	1740	7.804	7960	22.5	80.3	- 89.2
$(CH_3)_3GeF^*$	2083†	9.038	9590	-	-	1.9
	1701‡	7.693	7829	22.1	80.3	-
$(CH_3)_3GeCl$	1795	7.665	8075	21.5	102.	-13.
$(CH_3)_3GeOCH_3$	1695	7.531	7900	21.7	90.9	-
$((CH_3)_3Ge)_2O^*$	2290	8.580	10,540	26.2	129.	-61.1

† Sublimation curve

‡ Vapourization curve

* New compounds

x Vapour pressures are represented by the equation:

$$\log_{10}P_{mm.} = -\frac{A}{T} + B$$

TABLE XXV

A Comparison of Melting Points and Boiling Points of Analogous Carbon, Silicon and Germanium Compounds

Compound	M.P. (°C)	B.P. (°C)	Compound	M.P. (°C)	B.P. (°C)
CH_4	-184.	-161.5	CCl_4	-22.8	76.8
SiH_4	-185.	-111.8	$SiCl_4$	-70.0	+57.6
GeH_4	-165.	- 90.0	$GeCl_4$	-49.5	83.1
$CH_3(CH_3)$	-172.	- 88.3	CH_3Cl	-97.7	-24.2
$SiH_3(CH_3)$	-156.4	- 56.8	SiH_3Cl	-118.1	-30.4
$GeH_3(CH_3)$	-153.7	- 23.0	GeH_3Cl	- 52.0	+28.0
$CH_2(CH_3)_2$	-188.9	- 42.2	CH_3Br	- 93.7	3.6
$SiH_2(CH_3)_2$	-150.	- 20.1	SiH_3Br	- 94.	1.9
$GeH_2(CH_3)_2$	-	- 3.6	GeH_3Br	- 32.	52.0
$CH(CH_3)_3$	-145.	- 10.2	CH_3CH_2Cl	-138.7	12.2
$SiH(CH_3)_3$	-	10.	CH_3SiH_2Cl	-134.	8.0
$GeH(CH_3)_3$	-	-	CH_3GeH_2Cl	-	-
$C(CH_3)_4$	- 20.	9.5	CH_3CH_2Br	-119.	38.0
$Si(CH_3)_4$	-	26.5	CH_3SiH_2Br	-118.5	34.0
$Ge(CH_3)_4$	- 88.	43.5	CH_3GeH_2Br	- 89.2	80.3
CH_2Cl_2	- 96.7	40.1	$(CH_3)_3CF$	-	16.
SiH_2Cl_2	-122	8.3	$(CH_3)_3SiF$	- 74.3	16.5
GeH_2Cl_2	- 68.	69.5	$(CH_3)_3GeF$	+ 1.9	80.3
CH_2Br_2	- 52.8	98.2	$(CH_3)_3CCl$	-131.2	68.9
SiH_2Br_2	- 77.	66.	$(CH_3)_3SiCl$	- 57.7	57.3
GeH_2Br_2	- 15.0	89.0	$(CH_3)_3GeCl$	- 13.	102.
CH_3CHCl_2	- 96.7	57.3	$(CH_3)_3CBr$	-118.5	91.5
CH_3SiHCl_2	- 93.0	41.	$(CH_3)_3SiBr$	-	80.0
CH_3GeHCl_2	- 63.1	112.4	$(CH_3)_3GeBr$	- 25.	113.7
CH_3CCl_3	-	74.1	$(CH_3)_3COCH_3$	-	55.2
CH_3SiCl_3	- 77.8	65.7	$(CH_3)_3SiOCH_3$	-	57.2
CH_3GeCl_3	-	111.	$(CH_3)_3GeOCH_3$	-	90.9
$(CH_3)_2CCl_2$	- 34.6	69.7	$((CH_3)_3C)_2O$	- 60.	106.5
$(CH_3)_2SiCl_2$	- 76.1	70.0	$((CH_3)_3Si)_2O$	-	100.5
$(CH_3)_2GeCl_2$	- 22.0	124.	$((CH_3)_3Ge)_2O$	- 61.1	129.

the melting points of the compounds mentioned in the above series cannot be accounted for in a simple way.

ii) Boiling Points: The boiling points of silane and germane and their methyl derivatives, like those of their carbon analogues, increase with increasing molecular weight as evident in Table XXV.

Germanium compounds boil at higher temperature than the analogous carbon and silicon compounds but the boiling points of the silicon derivatives are lower than those of the corresponding carbon compounds. The anomalous behaviour of the silicon compounds can be interpreted in terms of polar interaction and $d_\pi - p_\pi$ bonding. For instance, in the AH_3Cl compounds, the polar A-Cl bond causes dipole interaction in the liquid and gas phases but the effect is greater in the liquid phase. Thus, the boiling points are higher than expected. Since the electronegativities of carbon and germanium are greater than that of silicon (94, 95), the dipole moments of methyl chloride and germyl chloride should be less than that of silyl chloride. However, the observed dipole moments are in the same order as the boiling points (GeH_3Cl (2.03 D) $>$ CH_3Cl (1.85 D) $>$ SiH_3Cl (1.31 D), ref. 72, 111, 112). Silicon, unlike carbon, forms a normal σ bond with chlorine which is enhanced by $d_\pi - p_\pi$ bonding involving vacant 3d-orbitals of silicon. As a result, the dipole moment of SiH_3Cl is less than that of CH_3Cl. Therefore, the boiling point of SiH_3Cl should be lower than expected and, in fact, is 6.2° lower than that of the carbon analogue. In germyl chloride, GeH_3Cl, the high dipole moment (2.03 D) indicates that $d_\pi - p_\pi$ bonding is not appreciable and, therefore, the high boiling point may be attributed to strong dipole interaction and a large mass effect.

In the analogous bromo series, AH_3Br, silyl bromide would be expected to have a weaker d_π-p_π bond between silicon and bromine atoms because of their lower electronegativity difference (23, 24). Consequently, the difference in boiling points between CH_3Br and SiH_3Br should be less than that between CH_3Cl and SiH_3Cl, as observed. This substantiates the suggestion that many silicon compounds have lower boiling points than their carbon analogues because of d_π-p_π bonding between silicon and a more electronegative element.

The boiling points of the two series, $(CH_3)_nGeX_{4-n}$ where X is Cl or OCH_3 and n = 0 to 4, are given below.

Formula	Boiling Points (°C)	
	X = Cl	X = OCH_3
$(CH_3)_4Ge$	43.2	43.2
$(CH_3)_3GeX$	102	87
$(CH_3)_2GeX_2$	124	118.5
$(CH_3)GeX_3$	111.	138.
GeX_4	83.1	149.

In the methoxy series, boiling points increase with increasing molecular weight unlike the chloro series in which the boiling points pass through a maximum at dimethyldichlorogermane. This behaviour is emphasized in Figure 26(a) where the boiling points of the compounds in the above series are plotted against the number of chlorine atoms or methoxy groups in the molecule. Since $(CH_3)_4Ge$, $GeCl_4$ and $Ge(OCH_3)_4$ are symmetrical molecules of zero dipole moment, the difference in boiling points between the end members of either the chloro or the methoxy series should be due to changes in mass. Therefore, the straight lines joining the end members of

FIGURE 26(a)

Boiling Points of $(CH_3)_nGeX_{4-n}$ Compounds

$X = Cl, OCH_3; n = 0$ to 4

FIGURE 26(b)

Boiling points (observed) - Boiling points indicated by the straight lines in Figure 26(a)

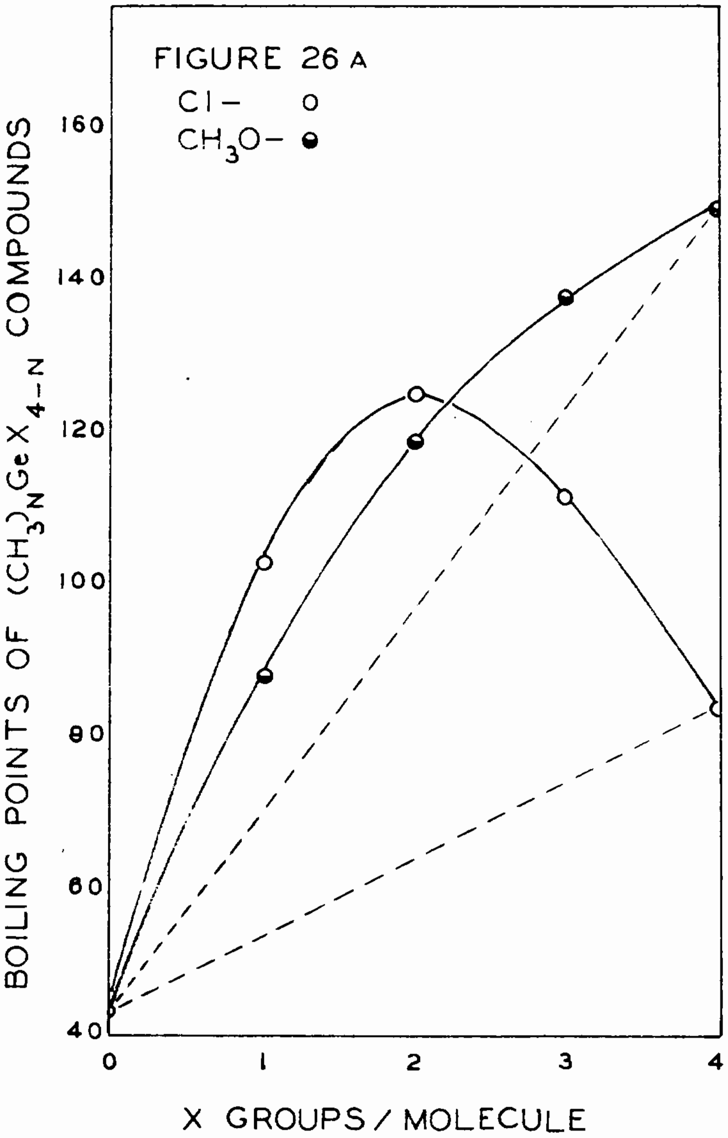


FIGURE 26 A

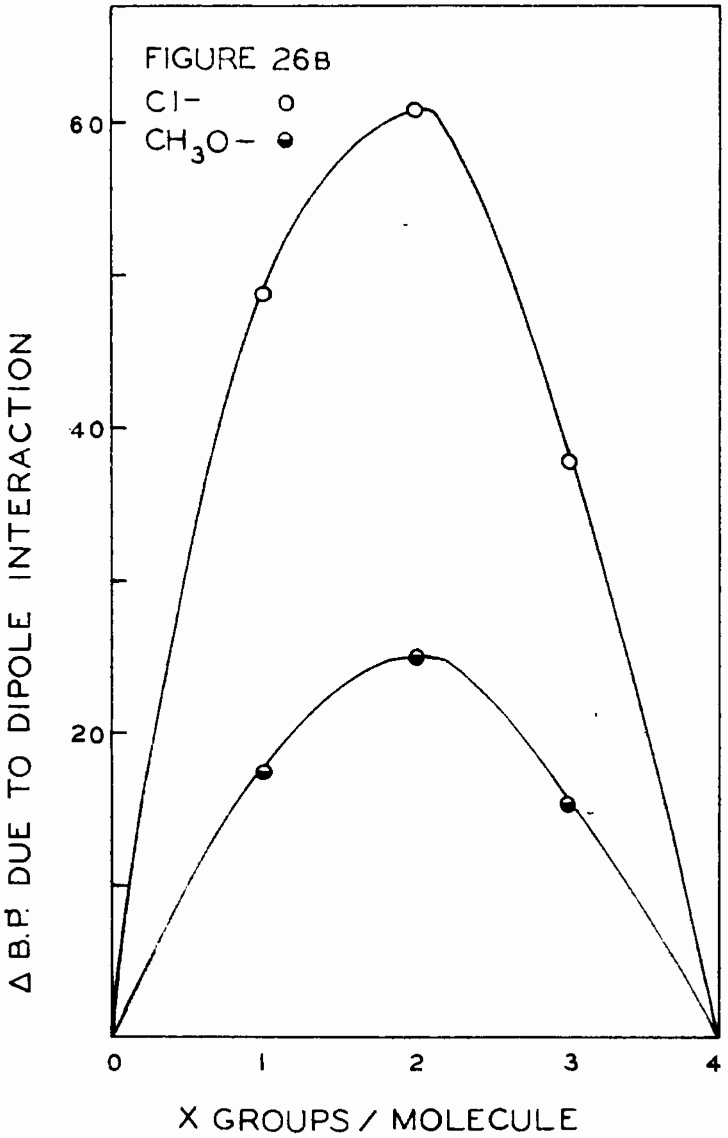


FIGURE 26B

the two series in Figure 26(a) should represent the effect on the boiling point of increasing molecular mass. Differences between these straight lines and the observed boiling point curves should be due to other effects. A plot of the difference between the observed boiling points and the boiling points indicated by the line joining the end members of the respective series against the number of chlorine atoms or methoxy groups in the molecules is shown in Figure 26(b). The similarity in the contours of these curves suggests that the factors affecting the boiling points of the compounds in the two series are similar.

When a methyl group in $(CH_3)_4Ge$ is replaced by a chlorine atom or a methoxy group, the dipole interaction between molecules due to the polar Ge-X bond manifests itself as an increase in the boiling point. The replacement of a second methyl group should further increase the dipole moment and, in turn, the boiling point of the disubstituted derivative. However, dipole moments of CH_3GeX_3 compounds should be less than those of $(CH_3)_3GeX_2$ compounds because the net dipole moment should be the vector sum of the dipole moments of individual Ge-X bonds. Consequently, the curves in Figure 26(b) should pass through a maximum at $X = 2$ as observed. The greater increase in the boiling points associated with the introduction of Ge-Cl bonds compared with that of $Ge-OCH_3$ bonds can be attributed to greater dipole interaction among molecules of the chloro series than among those of the methoxy series.

iii) Infrared Spectra: The vibrational frequencies of various groups or atoms in previously studied germanium compounds are summarized in Appendix I. In order to facilitate discussion, the frequency assignments for all the compounds studied are summarized in Table XXVI. These assignments are discussed briefly with particular emphasis on the characteristic frequencies associated with various groups. The following symbols are used: ν = valence stretching, $\delta_{as.}$ = asymmetric deformation, $\delta_{s.}$ = symmetric deformation, b = bending, w = wagging and r = rocking.

Hexamethyldigermoxane: Absorption bands characteristic of the methyl group, $\nu(CH_3)$, $\delta_{as.}(CH_3)$ and $\delta_{s.}(CH_3)$ occur in the same frequency range in germanium and silicon compounds. The methyl rocking vibrations, $r(CH_3)$, occur at 817 cm.$^{-1}$ and 800 cm.$^{-1}$, slightly lower than observed in the spectrum of tetramethylgermane (828 cm.$^{-1}$), but the strong intensity of this band makes the assignment unambiguous. The Ge-C stretching vibration, ν(Ge-C), was assigned to the band at 754 cm.$^{-1}$ by analogy with the assignments made in organosilicon molecules where the ν(Si-C) vibrations occur in the range 730 to 760 cm.$^{-1}$ (40). By analogy with the disiloxanes (25, 40), the asymmetric skeletal stretching vibration, $\nu_{as.}$(Ge-O-Ge) should result in an intense absorption band at a frequency of less than 1100 cm.$^{-1}$. Therefore, the $\nu_{as.}$(Ge-O-Ge) vibration was assigned to the band at 880 cm.$^{-1}$.

$(CH_3)_3GeX$ Compounds where X = F, Cl, Br and OCH_3: The methyl rocking vibrations, $r(CH_3)$, in the halo compounds occurred at about 830 cm.$^{-1}$ but, in the methoxy compound, this vibration was at 815 cm.$^{-1}$. Apparently, the presence of an oxygen atom reduces the frequency at which absorption takes place by about 15 cm.$^{-1}$. In the methoxy compound, the $r(CH_3\text{-}O)$ vibration occurred at 1060 cm.$^{-1}$ and the ν(C-O) vibration was assigned to the band at 1033 and 1005 cm.$^{-1}$ because the frequencies and band contours were similar

TABLE XXVI

Summary of Infrared Vibration Frequencies

LEGEND

ν - valence stretching

$\delta_{s.}$ - symmetric deformation

$\delta_{as.}$ - asymmetric deformation

r - rocking

b - bending (scissors)

w - wagging

Frequencies are given in $cm.^{-1}$

Compound	$\nu(CH_3)$	$\nu(Ge\text{-}H)$	$\nu(C\equiv N)$	$\delta_{as.}(CH_3)$	$\delta_{s.}(CH_3)$	r(Me-O)	$\nu(C\text{-}O)$	$\nu(Ge\text{-}O)$	$\delta_{as.}(GeH_3)$
Me_3GeF	3005,2930	-	-	1415	1254	-	-	-	-
Me_3GeCl	3025,2945	-	-	1415	1255	-	-	-	-
Me_3GeBr	3002,2909	-	-	1412	1248	-	-	-	-
Me_3GeOCH_3	2935	-	-	1450,1360	1245	1060	1030,1005	875	-
$(Me_3Ge)_2O$	3000,2925	-	-	1410,1320	1247	-	-	880	-
GeH_3Cl	-	2130,2114	-	-	-	-	-	-	874
GeH_3Br	-	2120	-	-	-	-	-	-	868
GeH_3CN	-	2120	2059	-	-	-	-	-	883
GeH_3CH_3	3008,2960	2100	-	1440	1256	-	-	-	-
GeH_3OCH_3	2960	2128	-	1500 ⟵	⟶ 1250	1063	1033,1005	-	-
$MeGeH_2Br$	3010,2940	2100	-	1420	1254	-	-	-	-
$MeGeHCl_2$	2995,2905	2120	-	1412	1258	-	-	-	-
$ClGeH_2Cl$	-	2150	-	-	-	-	-	-	-
$MeGeH_2Me$	3000,2940	2105,2090	-	1465,1440	-	-	-	-	-

Compound	$\delta_{s.}(GeH_3)$	$b(GeH_2)$	$w(GeH_2)$	$r(CH_3)$	ν(Ge-C)	ν(GeF)	$r(GeH_3)$	$r(Me_3Ge)$	$w(GeCl_2)$
Me_3GeF	-	-	-	828	753	745	-	657	-
Me_3GeCl	-	-	-	834	760	-	-	-	-
Me_3GeBr	-	-	-	831	756	-	-	-	-
Me_3GeOCH_3	-	-	-	815	750	-	-	-	-
$(Me_3Ge)_2O$	-	-	-	817,800	754	-	-	-	-
GeH_3Cl	847	-	-	-	-	-	-	-	-
GeH_3Br	826	-	-	-	-	-	-	-	-
GeH_3CN	844	-	-	-	-	-	-	-	-
GeH_3CH_3	845	-	-	-	743	-	-	-	-
GeH_3OCH_3	855	-	-	-	712	-	650	-	-
$MeGeH_2Br$	-	878	860	838	708,700	-	-	-	-
$MeGeHCl_2$	-	-	853	827	707,666	-	-	-	783
$ClGeH_2Cl_2$	-	862	850	-	-	-	-	-	783
$MeGeH_2CH_3$	-	849	-	849	-	-	-	-	-

to those observed for corresponding organic molecules and for trimethylmethoxysilane (84).

In the spectrum of trimethylfluorogermane, an absorption band at 745 cm.$^{-1}$, partially masked by the ν(Ge-C) band at 753 cm.$^{-1}$, was assigned to the ν(GeF) vibration because, in GeF_4, the $\nu_{as.}$ (GeF) vibrations occur at 740 cm.$^{-1}$ (132). A strong absorption band at 657 cm.$^{-1}$ was attributed to the r($(CH_3)_3$Ge-) vibration by analogy with the r(GeH_3) vibration at 604 cm.$^{-1}$ in germyl chloride (77). Although part of this band was outside the range of the instrument, the recorded band contour indicated that it might be a parallel type band. In this event, it would be necessary to change the 657 cm.$^{-1}$ assignment from r($(CH_3)_3$Ge-), which gives a perpendicular band, to the ν(GeF) parallel vibration. Assignments of other frequencies are similar to those made for hexamethyldigermoxane.

<u>GeH_3X Compounds where X is Cl, Br, CN and CH_3</u>: The molecules of this series are symmetric tops of symmetry group C_{3v}. The symmetric and asymmetric ν(GeH) vibrations are not completely resolved and occur in the range 2090 to 2150 cm.$^{-1}$. The asymmetric deformation vibration, $\delta_{as.}$(GeH_3), exhibits the expected intensity alteration of Q branches (strong, weak, weak, strong, . . .) but the symmetric deformation vibration, $\delta_{s.}$(CH_3), which is more intense, overlaps the former making the location of the band centre indefinite. However, the $\delta_{as.}$(GeH_3) vibration was assigned to the range 862 to 883 cm.$^{-1}$ and the $\delta_{s.}$(CH_3) vibration to the range 826 to 855 cm.$^{-1}$.

In the spectrum of germyl cyanide, the C≡N stretching vibration, ν_2, was assigned to the band at 2059 cm.$^{-1}$ by analogy with the spectra of other cyanides. The absorption band at 743 cm.$^{-1}$ was assigned to the Ge-C stretching vibration, ν_4, since the ν(Ge-C) vibrations in trimethylgermyl compounds occur at about 750 cm.$^{-1}$.

The methyl rocking vibration in the spectrum of methylgermane was masked by the $\delta_{s.}(GeH_3)$ band. The parallel band at 712 cm.$^{-1}$ was necessarily assigned to the parallel Ge-C stretching vibration.

Methoxygermane: Absorption bands due to vibrations of the GeH_3 group were assigned in the manner outlined above. The absorption band contours in the 1005 to 1065 cm.$^{-1}$ range were similar to those observed in the spectrum of trimethylmethoxygermane and, therefore, similar assignments were made.

Methylbromogermane, CH_3GeH_2Br: Methylbromogermane belongs to the symmetry group $C_{s.}$ and, therefore, the Ge-C stretching vibration will have an A/B hybrid band contour, while one of the two $r(CH_3)$ rocking vibrations should have an A/B band contour and the other a type C band contour (P, Q and R branches with a prominent Q branch). On this basis, the ν(GeC) and the $r(CH_3)$ vibrations were assigned to the 700 and 835 cm.$^{-1}$ regions respectively. By analogy with the CH_3SiH_2X compounds (40), the $b(GeH_2)$ and $w(GeH_2)$ vibrations were assigned to the bands at 878 and 860 cm.$^{-1}$ respectively. The ν(GeH), $\nu(CH_3)$, $\delta_{as.}(CH_3)$ and $\delta_{s.}(CH_3)$ vibrations were assigned to the usual regions.

Methyldichlorogermane, CH_3GeHCl_2: This molecule has one plane of symmetry and belongs to the symmetry group $C_{s.}$ so that vibrations which cause a dipole change in the plane of the chlorine atoms will have A/B hybrid band contours and those causing a dipole change perpendicular to this plane will have type C contours. The assignments in the range 3000 to 900 cm.$^{-1}$ follow the lines already established. The bending vibration of the one Ge-H bond was assigned to the 853 cm.$^{-1}$ band. The ν(GeC) and r(CH_3) vibrations were assigned to the 700 and 827 cm.$^{-1}$ regions respectively to correspond with the assignments made for the CH_3GeH_2Br molecule. The band at 783 cm.$^{-1}$ was attributed to the w($GeCl_2$) vibration on the basis of a similar assignment made for the GeH_2Cl_2 molecule.

Germylene Chloride, GeH_2Cl_2: If the bonds are considered to be tetrahedrally directed, the molecule belongs to the symmetry group C_{2v}. There are nine fundamental vibrations including the torsion mode which is forbidden in the infrared spectrum. The asymmetric and symmetric $GeCl_2$ stretching vibrations as well as the $GeCl_2$ bending vibration (scissors) are expected to occur at low frequencies.

The GeH_2 stretching vibrations, $\nu_1(a_1)$ and $\nu_6(b_1)$ are not resolved but occur together at 2150 cm.$^{-1}$leaving three unassigned fundamentals. The b(GeH_2) vibration should have a B type band contour (P-R doublet without a central Q branch) while the w(GeH_2) and w($GeCl_2$) vibrations should have A type contours (P, Q and R branches, often of comparable intensity). On this basis, the b(GeH_2) and w(GeH_2) vibrations were assigned to the bands at 862 and 850 cm.$^{-1}$ respectively. The remaining band at 783 cm.$^{-1}$ was assigned to the w($GeCl_2$) fundamental, which is higher than expected.

Dimethylgermane, $(CH_3)_2GeH_2$: This molecule should belong to the symmetry group C_{2v} with 27 modes of vibration of which only 22 are active in the infrared. Due to the low resolution of the instrument used, it was practically impossible to distinguish different bands when they occurred in the same region. The $\nu(CH_3)$, $\nu(GeH)$ and $\delta_{as.}(CH_3)$ bands are present in the expected regions but in the range 900 to 625 cm.$^{-1}$ only one intense type B contour is present. This is surprising since the $r(CH_3)$, $\nu(GeC)$, $b(GeMe_2)$, $w(GeMe_2)$, $b(GeH_2)$ and $w(GeH_2)$ vibrations were expected to appear in this region of the spectrum. The $r(CH_3)$, $\nu(GeC)$ and $b(GeH_2)$ vibrations would have type B contours (P-R doublet without a central Q branch) and, therefore, the band at 849 cm.$^{-1}$ is tentatively assigned to the $b(GeH_2)$ and/or the $r(CH_3)$ vibrations.

The following is a summary of the principal vibrations in the spectra of the volatile germanium compounds studied.

Vibration	cm.$^{-1}$
$\nu(CH_3)$; C-H stretching	2905-3025
$\nu(GeH)$; Ge-H stretching	2090-2150
$\nu(C{\equiv}N)$; C≡N stretching	2059
$\delta_{as.}(CH_3)$; Asymmetric CH_3 deformation	1410-1465
$\delta_{s.}(CH_3)$; Symmetric CH_3 deformation	1245-1260
$r(CH_3-O)$; Methyl -O rocking	1060
$\nu(C-O)$; C-O stretching in CH_3-O	1005, 1030
$\nu(Ge-O)$; Ge-O stretching	875-880
$\delta_{as.}(GeH_3)$; Asymmetric GeH_3 deformation	860-885
$\delta_{s.}(GeH_3)$; Symmetric GeH_3 deformation	825-855
$b((GeH_2)$; GeH_2 bending (scissors)	850-880
$w(GeH_2)$; GeH_2 wagging	850-860

. . . .

r(CH_3); Methyl rocking	800-840
w($GeCl_2$); $GeCl_2$ wagging	783
ν(GeC); Ge-C stretching	700-760
ν(GeF); Ge-F stretching	740-745
r(GeH_3); GeH_3- rocking	600-655
r($(CH_3)_3Ge$); Me_3Ge- rocking	655

Halogenation of Germane

Silane and germane react with hydrogen chloride in the presence of aluminum trichloride as catalyst yielding silyl chloride (75% yield) and germyl chloride (20% yield) respectively. Smaller amounts of the dichloro derivative are also produced.

The first step in the chlorination of germane and silane may be formulated as,

$$AlCl_3 + HCl \longrightarrow AlCl_4^- + H^+ \qquad (1)$$

by analogy with the formation of AlI_4^- ions which were postulated for reactions involving silicon-carbon bond cleavage (130). Subsequent attack by the $AlCl_4^-$ ions on the central atom, M, of the hydride may be represented as follows,

$$\equiv M - H + AlCl_4^- \longrightarrow \left[\begin{matrix} \equiv M - H \\ | \\ AlCl_4 \end{matrix}\right]^- \qquad (2)$$

The formation of a siliconium ion by dissociation is improbable (47) and, therefore, the displacement of a negative hydrogen ion probably occurs,

$$\left[\begin{matrix} \equiv M - H \\ | \\ AlCl_4 \end{matrix}\right]^- \longrightarrow \left[\equiv M - AlCl_4\right] + :H^- \qquad (3)$$

followed by dissociation of the complex to form aluminum trichloride and an

M-Cl bond.

$$\left[\equiv M - AlCl_4\right] \longrightarrow \equiv M - Cl + AlCl_3 \qquad (4)$$

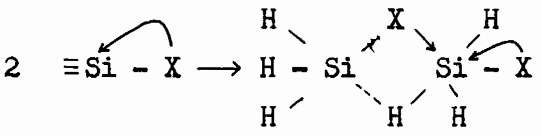
Hydrogen would result from the recombination of protons and negative hydrogen ions.

$$H^+ + :H^- \longrightarrow H_2 \qquad (5)$$

Reactions 3, 4 and 5 are expected to be fast compared with reactions 1 and 2. Since the rate of reaction 1 is the same in the preparation of silyl and germyl chloride, reaction 2 must determine the relative yields.

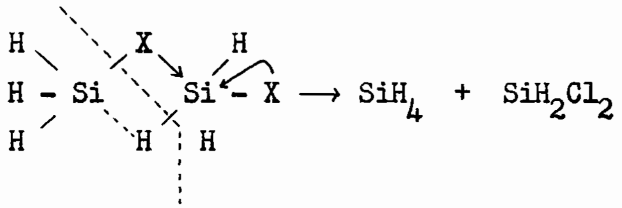
The stability of germane in 33% alkaline solution suggests that Ge-H bonds in germane are not polarized (41). Silicon-hydrogen bonds are readily broken in very dilute alkaline solution indicating that the Si-H bonds are polarized. Therefore, silane should be more susceptible to nucleophilic attack than germane by virtue of the $\overset{\delta+}{Si} - \overset{\delta-}{H}$ bond polarization. Consequently, $AlCl_4^-$ ions probably attack silicon more readily than germanium atoms, resulting in a higher yield of silyl chloride.

MacDiarmid (78) has proposed a mechanism for the disproportionation of silyl halides which involves the formation of an activated complex,



(6)

followed by its decomposition into silane and silylene halide.



(7)

The yield of dihalide decreases with increasing size of the halogen, which is in accord with the theoretical prediction that the strength of π bonds decreases with decreasing electronegativity differences of the atoms (23, 24). The introduction of methyl groups in the silyl compounds also decreases the yield of dihalide. This has been attributed to a decrease in the number of active hydrogen centres in the molecules which reduces the probability of formation of the activated complex (83).

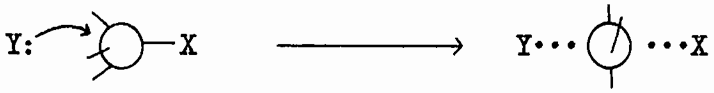
The high dipole moment of germyl chloride (2.03 D) indicates that the polarity of the Ge-Cl bond is not appreciably reduced by d_π-p_π bonding. The presence of a strong $\overset{\delta+}{Ge} - \overset{\delta-}{Cl}$ dipole in germyl chloride would make the central germanium atom more electropositive and, therefore, more susceptible to nucleophilic attack by the $AlCl_4^-$ ions (equation 2). Therefore, it is suggested that germylene chloride results from further halogenation of germyl chloride rather than from disproportionation. Additional evidence to support this suggestion was obtained in the bromination of tetramethylgermane. If the introduction of more than one atom of bromine in the molecule results from disproportionation, the yield of methyltribromo- and tetrabromo-germane would be small compared with the yield of dimethyldibromo- and trimethylbromo-germane. However, the yield of tetrabromogermane was always high.

Reactions of Germyl Chloride

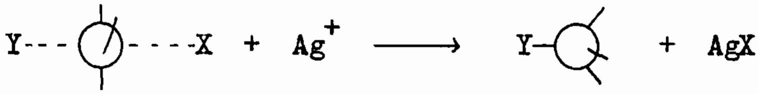
Silyl halides readily react with silver salts, halo acids or mercuric salts in accordance with the following conversion series (78),

$$(H_3Si)_2Te \rightarrow H_3SiI \rightarrow (H_3Si)_2Se \rightarrow (H_3Si)_2S \rightarrow H_3SiBr \rightarrow H_3SiCl \rightarrow H_3SiNC$$
$$\rightarrow H_3SiNCS \rightarrow (H_3Si)_2O \rightarrow H_3SiF$$

in which any compound can be converted into any other on its right but not into one on its left. The electronegativities of the atoms or groups attached to the silicon atom in the above compounds increase from left to right while their polarizabilities decrease in the same order. Moreover, the fact that silver or mercuric salts are effective in promoting these conversions in the absence of a solvent implies that metal atoms assist in removing anions from the silicon atom. These factors suggest that the reactions proceed by an S_n2 mechanism in which the initial attack occurs at the "backside" of the silicon atom forming a transition state complex,



which loses the less electronegative X atom to a neighbouring metal ion, as represented by,



Since silicon and germanium are predominantly tetracovalent and have similar covalent radii (Si = 1.17 A., Ge = 1.22 A., ref. 88), germyl and silyl derivatives would be expected to undergo similar reactions with silver salts. From the following summary of germyl chloride reactions, it is evident that only germyl cyanide and methoxygermane were formed.

Reactions of Germyl Chloride

Reactant	Results	Product
H_2S	-	none
CH_3SH	-	"
HgS	-	"
AgCNO	-	"
Ag_2O	-	"

Reactant	Results	Product
Ag_2CO_3	-	CO_2
AgCN	+	GeH_3CN
$NaOCH_3$	+	GeH_3OCH_3

Germyl chloride did not react with H_2S, CH_3SH or HgS to form GeH_3SH, GeH_3SCH_3 or $(GeH_3)_2S$ respectively, as predicted by the expected conversion series. Reactions of germyl chloride with silver cyanate, silver oxide or silver carbonate, which were expected to occur as follows,

$$GeH_3Cl + AgCNO \longrightarrow GeH_3CNO + AgCl$$

$$2GeH_3Cl + Ag_2O \longrightarrow (GeH_3)_2O + 2AgCl$$

$$2GeH_3Cl + Ag_2CO_3 \longrightarrow (GeH_3)_2O + CO_2 + 2AgCl$$

did not yield the desired products. There was no reaction with either silver cyanate or silver oxide while silver carbonate appeared to promote the decomposition of germyl chloride.

Since silicon is more electropositive than germanium, the dipole moment of silyl chloride should be greater than that of germyl chloride, but the opposite is observed. The low dipole moment of silyl chloride (1.31 D), as compared with that of germyl chloride (2.03 D), suggests that the Si-Cl bond has greater double bond character than the Ge-Cl bond. Consequently, the chlorine atom would be expected to withdraw electrons to a greater extent from the germyl group than from the corresponding silyl group. Therefore, the hydrogen atoms of the germyl group should be more protonic than those of the silyl group. An attacking species, having a free electron pair available for bond formation, would be preferentially attracted towards the hydrogen atoms of the germyl group rather than towards the central germanium atom. In contrast, the less positive hydrogen atoms of the silyl group permit the attack of an electronegative group or atom at the central silicon atom.

The thermal instability of germyl derivatives, containing an electronegative group or atom, can also be interpreted in terms of induced polarization of the Ge-H bonds. If the protonic character of the hydrogen atoms is appreciable, the molecule should tend to be thermally unstable by virtue of the interaction arising between the electronegative group or atom of one molecule and the electropositive hydrogen atoms of a second neighbouring molecule. Consequently, germyl chloride should be less stable thermally than methylgermane, since the methyl group in the latter molecule tends to decrease the protonic character of the hydrogen atoms by releasing electrons to the germyl group. It was found experimentally that methylgermane can be stored without decomposition for long periods at room temperature while germyl chloride decomposes under the same conditions.

Since methyl groups have the property of releasing electrons, the successive substitution of methyl groups for hydrogen atoms in the germyl group should increase the electron density on the germanium atom. This should tend to decrease the polarity of the Ge-X bond, where X is a Group VI or VIIB element, in the resulting molecules which, in turn, should decrease the protonic character of the remaining hydrogen atoms. When all the hydrogen atoms are replaced as in trimethylgermyl compounds, the reactions of $(CH_3)_3GeX$ derivatives should be similar to those of analogous silyl and trimethylsilyl compounds. This is substantiated by the following silver salt conversion series which has been established for trimethylgermyl compounds (5).

$$\mathrm{R_3GeI} \rightarrow \mathrm{(R\ Ge)_2S} \rightarrow \mathrm{R_3GeBr} \rightarrow \mathrm{R_3GeCN} \rightarrow \mathrm{R_3GeNCS\ and\ Cl} \rightarrow \mathrm{R_3GeNCO}$$
$$\rightarrow \mathrm{(R\ Ge)_2O} \rightarrow \mathrm{R_3GeOCOR} \rightarrow \mathrm{R_3GeF}$$

Furthermore, trialkylgermyl derivatives are as thermally stable as their corresponding silicon compounds.

The preparation of germyl bromide by the reaction of germane with bromine at low temperature

$$\mathrm{GeH_4} + \mathrm{Br_2} \longrightarrow \mathrm{GeH_3Br} + \mathrm{HBr}$$

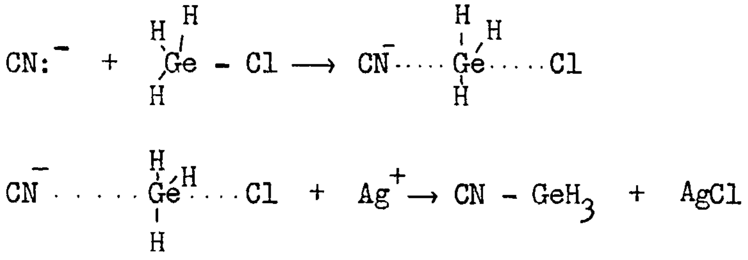
has been described very recently (119). Germyl bromide was converted to the cyanide,

$$\mathrm{GeH_3Br} + \mathrm{AgCN} \longrightarrow \mathrm{GeH_3CN} + \mathrm{AgBr}$$

which decomposed to yield germylene and hydrogen cyanide,

$$\mathrm{GeH_3CN} \longrightarrow \mathrm{GeH_2} + \mathrm{HCN}$$

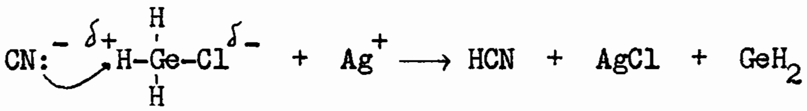
In the present investigation, it was found that germyl chloride reacted with silver cyanide yielding substantial amounts of hydrogen cyanide and germyl cyanide. This suggests that besides the following S_n2 reaction,



$$\mathrm{CN}:^{-} + \mathrm{H_3Ge-Cl} \longrightarrow \mathrm{CN^{-}}\cdots\mathrm{GeH_3}\cdots\mathrm{Cl}$$

$$\mathrm{CN^{-}}\cdots\mathrm{GeH_3}\cdots\mathrm{Cl} + \mathrm{Ag^{+}} \longrightarrow \mathrm{CN-GeH_3} + \mathrm{AgCl}$$

yielding germyl cyanide, the reaction of cyanide ion with protonic hydrogen atoms of the germyl group, forming hydrogen cyanide, also occurred,



$$\mathrm{CN:}^{-}\ \overset{\delta+}{\mathrm{H}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{Ge}}}-\mathrm{Cl}^{\delta-} + \mathrm{Ag}^{+} \longrightarrow \mathrm{HCN} + \mathrm{AgCl} + \mathrm{GeH_2}$$

It is likely that the protonic character of the hydrogen atoms of the germyl group promotes the decomposition of germyl cyanide forming additional hydrogen cyanide and germylene. However, since the molecular weight of the impure product did not decrease to a value less than 46.5 (Required for GeH_3CN: M, 101.6; for HCN: M, 27.0), it appears that the decomposition of germyl cyanide is an equilibrium process,

$$\mathrm{GeH_3CN} \rightleftharpoons \mathrm{HCN} + \mathrm{GeH_2}$$

The slow formation of germane probably occurred by the following reaction (50),

$$3(\mathrm{GeH_2})_x \rightleftharpoons x\ \mathrm{GeH_4} + 2(\mathrm{GeH})_x$$

The formation of large amounts of methanol in the reaction of germyl chloride with sodium methylate can be accounted for in two ways, namely (a) attack of a methoxy group on a protonic hydrogen atom bonded to germanium, and (b) inter- or intra-molecular decomposition of methoxygermane.

Reactions of Methylbromogermane

The substitution of a methyl group for a hydrogen atom in the germyl group should facilitate the reaction of methylgermyl derivatives with silver salts by an S_n2 mechanism by decreasing the effect of protonic hydrogen atoms. Accordingly, methylgermyl halides should be more reactive than germyl halides. Although methylbromogermane reacted rapidly with silver carbonate, the resulting 1,1'-dimethyldigermoxane decomposed to yield hydrogen and a clear viscous polymer. Similarly, methylmethoxygermane, $CH_3GeH_2OCH_3$, was formed according to the reaction,

$$CH_3GeH_2Br + NaOCH_3 \longrightarrow CH_3GeH_2OCH_3 + NaBr$$

but decomposed at room temperature to give methanol and a polymeric residue.

The room temperature decomposition of volatile germanium compounds, containing both Ge-H and Ge-O bonds suggest that the Ge-O bond, like the Ge-Cl bond, is strongly polar, thereby increasing the protonic character of the hydrogen atoms bonded to germanium. Polarized Ge-H bonds probably promote inter- or intra-molecular decomposition of the germanium compounds. This behaviour is in sharp contrast with the thermal stability of analogous silicon compounds in which Si-O bonds have considerable π type character (43, 83). Therefore, it appears that d_π-p_π bonding between germanium and more electronegative elements is not appreciable.

Reactions of Trimethylgermyl Halides

Differences between the chemical properties of silyl and germyl chloride have been attributed to the difference in polarity between the Si-Cl and Ge-Cl bonds. The greater polarity of the Ge-Cl bond appears to endow the hydrogen atoms of the germyl group with considerable protonic character which, in turn, inhibits attack on the germanium atom by an electronegative group or atom. If this is true, complete replacement of hydrogen in germyl chloride by electron releasing methyl groups should increase the electron density at the central germanium atom and thereby decrease the polarity of the Ge-Cl bond. Since carbon is more electronegative than either hydrogen or germanium, the central germanium atom in trimethylgermylchloride should be the most electropositive atom in the molecule and, therefore, more susceptible to nucleophilic attack. Moreover, in the absence of hydrogen atoms bonded to germanium, which appear to promote decomposition of germyl and methylgermyl derivatives, the thermal stability of trialkylgermyl compounds should approach that of their silicon analogues.

These theoretical considerations are in complete agreement with the following experimental observations. Trimethylgermyl chloride, unlike germyl chloride, reacted at room temperature with silver carbonate to form hexamethyldigermoxane,

$$2(CH_3)_3GeCl + Ag_2CO_3 \longrightarrow ((CH_3)_3Ge)_2O + CO_2 + 2AgCl$$

while trimethylbromogermane was easily converted to trimethylmethoxygermane according to the following reaction,

$$(CH_3)_3GeBr + NaOCH_3 \longrightarrow (CH_3)_3GeOCH_3 + NaBr$$

Both products appeared to be as thermally stable as their silicon analogues.

Reaction of Hexamethyldigermoxane with Boron Trifluoride

The reaction of hexamethyldigermoxane with boron trifluoride at room temperature is represented quantitatively by the following reaction,

$$3((CH_3)_3Ge)_2O + 2BF_3 \longrightarrow 6(CH_3)_3GeF + B_2O_3 \qquad (1)$$

and affords a new method for the preparation of trialkylfluorogermanes. Quantitative formation of trimethylfluorogermane, as the only volatile product, is the outstanding feature of the reaction.

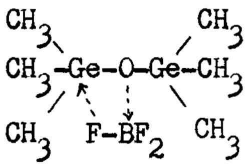
A mechanism for the reaction of boron trifluoride with hexamethyldigermoxane must account for the following experimental observations:

(a) A rapid reaction of boron trifluoride with hexamethyldigermoxane at room temperature yields trimethylfluorogermane and a white solid which decomposes gradually into trimethylfluorogermane and boron trioxide.

(b) The overall stoichiometry of the reaction is represented by the equation,

$$3((CH_3)_3Ge)_2O \ + \ 2BF_3 \longrightarrow 6(CH_3)_3GeF \ + \ B_2O_3$$

Since the reaction of hexamethyldisiloxane with boron trifluoride gave similar results, it is likely that both reactions proceeded by similar mechanisms. Initially, an activated complex is probably formed by electrophilic attack of boron trifluoride on two centres of the hexamethyldigermoxane molecule, represented diagrammatically by,



(1)

Strong polar interaction between (a) oxygen and boron atoms, and (b) fluorine and germanium atoms probably promotes rapid decomposition of the complex into trimethylfluorogermane and trimethylgermoxyboron difluoride,

$$\begin{bmatrix}\text{Activated}\\ \text{Complex}\end{bmatrix} \longrightarrow (CH_3)_3GeF \ + \ (CH_3)_3GeOBF_2$$

Although trimethylgermoxylboron difluoride was not isolated, it can be identified as the white solid film, initially formed in the reaction, which subsequently decomposed on standing at room temperature. Two mechanisms can account for its ultimate conversion into boron trioxide and trimethylfluorogermane.

Mechanism A:

A rapid stepwise defluorination of trimethylgermoxyboron difluoride might occur by reaction with hexamethyldigermoxane,

$$(CH_3)_3GeOBF_2 + ((CH_3)_3Ge)_2O \longrightarrow [\text{Activated Complex}]$$

$$\longrightarrow (CH_3)_3GeF + ((CH_3)_3GeO)_2BF \qquad (2)$$

$$((CH_3)_3GeO)_2BF + ((CH_3)_3Ge)_2O \longrightarrow [\text{Activated Complex}]$$

$$\longrightarrow (CH_3)_3GeF + ((CH_3)_3GeO)_3B \qquad (3)$$

followed by rapid reaction of boron trifluoride with tris-trimethylgermyl borate to form boron trioxide and trimethylfluorogermane.

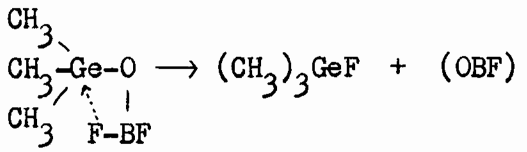
$$((CH_3)_3GeO)_3B + BF_3 \longrightarrow 3(CH_3)_3GeF + B_2O_3 \qquad (4)$$

The overall reaction would be given by,

$$3((CH_3)_3Ge)_2O + 2BF_3 \longrightarrow 6(CH_3)_3GeF + B_2O_3 \qquad (5)$$

Mechanism B:

Trimethylgermoxyboron difluoride might undergo intramolecular decomposition by strong dipole interaction between the electropositive germanium atom and the electronegative fluorine atom forming unstable boron oxyfluoride,



$$(CH_3)_3Ge\text{-}O\text{-}BF\text{-}F \longrightarrow (CH_3)_3GeF + (OBF) \qquad (6)$$

which would rapidly decompose into boron trioxide and boron trifluoride,

$$3(OBF) \longrightarrow B_2O_3 + BF_3 \qquad (7)$$

This mechanism is also in agreement with the observed stoichiometry of the overall reaction represented by equation 5.

If the reaction proceeds by Mechanism A, the defluorination steps must be quantitative in order to account for the stoichiometry of the overall reaction. Since the Ge-O bond in hexamethyldigermoxane appears to be readily cleaved in the initial attack of boron trifluoride, it is not improbable that Ge...F interaction in subsequent steps (equations 2, 3 and 4) is sufficiently strong to cause further cleavage of Ge-O bonds.

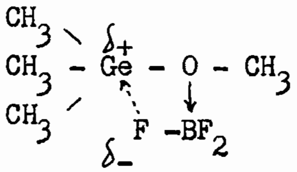
Alternatively, Mechanism B involves the formation and decomposition of boron oxyfluoride, OBF, which must be rapid in order to preserve the stoichiometry of the overall reaction. Baumgarten and Bruns (11, 12) found that boric oxide and boron trifluoride reacted at 450° to form a volatile boron oxyfluoride, $(OBF)_3$, which was not a simple addition compound but most likely a cyclic trimer. However, since this occurred at high temperature, it is unlikely that boron oxyfluoride would result from the room temperature reaction of boron trifluoride with hexamethyldigermoxane. Furthermore, after removal of trimethylfluorogermane from the reaction vessel, analysis of the residue indicated only boron trioxide. Therefore, the decomposition of trimethylgermoxyboron difluoride probably proceeds by Mechanism A rather than by Mechanism B.

Reaction of Trimethylmethoxygermane with Boron Trifluoride

The ability of dialkyl ethers to form co-ordination compounds of varying stability with Group III Lewis acids has been the subject of many investigations (116). Similar studies with disiloxanes have shown that the electron donor activity of the oxygen atom is appreciably reduced when bonded to silicon (42, 43). This has been attributed to a reduction in the electron density at the oxygen atom due to the formation of π type bonds involving vacant 3d-orbitals of silicon and 2p-orbitals of oxygen (8, 23, 24, 43, 117). Since theoretical calculations indicate that p_π electrons of an oxygen atom should also form π type bonds with germanium (23, 24), a similar decrease in electron donor activity was expected in trimethylmethoxygermane. The absence of appreciable d_π-p_π bonding in trimethylmethoxygermane is evident from its rapid reaction with boron trifluoride to form a stable 1:1 addition compound.

Since the formation of a co-ordination complex of this kind undoubtedly involves an acid-base neutralization of the Lewis type, the stability of the adduct will depend largely on the acid and base strengths of acceptor and donor molecules respectively. Boron trifluoride is the strongest Lewis acid of the electron deficient boron compounds and forms stable addition compounds with a variety of donor molecules (116). It is found that the stability of such adducts depends to a large extent on the factors affecting the electron density at the donor atom. In general, the stability of addition compounds decrease as the electronegativity of the group attached to the donor atom increase.

The cleavage of a Ge-O bond in the reaction of boron trifluoride with hexamethyldigermoxane suggests that the Ge-O bond is highly polar and, therefore, the region of maximum electron density would be closer to the oxygen atom than to the germanium atom. The presence of an electron releasing methyl group in the ether linkage of trimethylmethoxygermane should facilitate the formation of a strong donor-acceptor bond with boron trifluoride by increasing the electron density at the oxygen atom. The withdrawal of electrons at the oxygen atom of trimethylmethoxygermane, which would accompany the formation of an $>O \rightarrow B$ bond, should also increase the electrostatic attraction between the germanium and fluorine atoms by increasing the electropositivity of germanium and the electronegativity of fluorine. Consequently, the stability of the resulting co-ordination complex is probably enhanced by a Ge- - -F interaction, represented diagrammatically by,



Polar interaction of this type must be strong, for the reaction of hexamethyldigermoxane with boron trifluoride occurred with cleavage of a Ge-O bond. Since the 1:1 addition compound, resulting from the reaction of trimethylmethoxygermane with boron trifluoride under similar conditions, was stable at room temperature, it would be advantageous to undertake a comprehensive study of the factors affecting the stability of the trimethylmethoxygermane-boron trifluoride adduct. This might be conveniently accomplished by determining the vapour phase heats of dissociation (14) of the following addition compounds.

Series A	Series B
(1) $(CH_3)_3GeOCH_3 \cdot BF_3$	(5) $(CH_3)_3GeOC(CH_3)_3 \cdot BF_3$
(2) $(CH_3)_3GeOCH_3 \cdot BCl_3$	(6) $(CH_3)_3GeOC(CH_3)_3 \cdot BCl_3$
(3) $(CH_3)_3GeOCH_3 \cdot BH_3$	(7) $(CH_3)_3GeOC(CH_3)_3 \cdot BH_3$
(4) $(CH_3)_3GeOCH_3 \cdot B(CH_3)_3$	(8) $(CH_3)_3GeOC(CH_3)_3 \cdot B(CH_3)_3$

Series C	Series D
(9) $(CH_3)_3GeSCH_3 \cdot BF_3$	(13) $(CH_3)_3GeSC(CH_3)_3 \cdot BF_3$
(10) $(CH_3)_3GeSCH_3 \cdot BCl_3$	(14) $(CH_3)_3GeSC(CH_3)_3 \cdot BCl_3$
(11) $(CH_3)_3GeSCH_3 \cdot BH_3$	(15) $(CH_3)_3GeSC(CH_3)_3 \cdot BH_3$
(12) $(CH_3)_3GeSCH_3 \cdot B(CH_3)_3$	(16) $(CH_3)_3GeSC(CH_3)_3 \cdot B(CH_3)_3$

In each of the four series, heats of dissociation should decrease with decreasing strength of the Lewis acids ($BF_3 > BCl_3 > BH_3 > B(CH_3)_3$). However, differences between the heats of dissociation of the BX_3 and $B(CH_3)_3$ adducts should also be a measure of the electrostatic interaction between the germanium atom and the boron substituent. Since the tert.-butyl group has a greater electron releasing power than the methyl group, differences between the heats of dissociation of the series B compounds and those of their corresponding series A compounds should indicate the effect on the stability of these adducts of increasing the electron density at the oxygen atom.

The substitution of a sulfur atom for the oxygen in trimethylmethoxygermane should allow an evaluation of the effect on the stability of the series C addition compounds of decreasing the polarity of the bond joining the germanium atom to the Group VIB donor atom. The heats of dissociation of series C compounds should be lower than those of corresponding series A compounds, since the expected lower polarity of the Ge-S bond should result in a lower electron density at the sulfur atom than at the oxygen atom of trimethylmethoxygermane.

Differences between the heats of dissociation of series D compounds and those of series C should indicate the effect on the stability of these adducts of increasing the electron density at the sulfur atom.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. Germyl cyanide and methoxygermane, prepared by the reactions of germyl chloride with silver cyanide and sodium methylate respectively, were found to be unstable at room temperature and, therefore, were not isolated in the pure state.

2. Germyl chloride did not react with mercuric sulfide, hydrogen sulfide, methanethiol, silver cyanate or silver oxide under the experimental conditions used. Silver carbonate, however, appeared to catalyse the decomposition of germyl chloride.

3. Vapour pressures of methylgermane in the range -114.4 to -37.8° are given by the equation: $\log_{10} p(\text{mm.}) = -\frac{861}{T} + 6.321$ which was used to calculate the following constants: boiling point = -23.0°; latent heat of vapourization = 3695 cals./mole; Trouton constant = 15.9. The melting point was -153.7 ± 0.3°.

4. Dimethylgermane was prepared by the reaction of germane with methyl iodide and excess sodium in liquid ammonia. Its vapour pressure-temperature relationship in the range -113.6 to -54.0° can be expressed by the equation, $\log_{10} p\ (\text{mm}) = \frac{-887}{T} + 6.176$. The constants calculated from this equation are: boiling point = -3.6°; latent heat of vapourization = 4090 cals./mole and Trouton constant = 15.2.

5. Methyldichlorogermane was prepared by the chlorination of methylgermane with hydrogen chloride in the presence of aluminum trichloride as catalyst at 100°. Its physical properties were found to be: vapour

pressure equation in the range 7.9 to 73.0°, $\log_{10}p(\text{mm}) = -\frac{1800}{T} + 7.553$; boiling point, 112.4°; latent heat of vapourization, 8290 cals./mole; Trouton constant, 21.5; melting point, - 63.1 ± 0.1°.

6. Methylbromogermane was prepared by the reaction of methylgermane with hydrogen bromide in the presence of aluminum tribromide as catalyst at 100° and had the following physical properties: vapour pressure equation in the range 0 to 60°, $\log_{10}p(\text{mm}) = -\frac{1740}{T} + 7.804$; boiling point, 80.3°; latent heat of vapourization, 7960 cals./mole; Trouton constant, 22.6; melting point, -89.2 ± 0.2°.

7. 1,1'-Dimethyldigermoxane, formed in the reaction of methylbromogermane with silver carbonate, decomposed rapidly at room temperature yielding hydrogen and a viscous polymer.

8. Methylbromogermane reacted with dry sodium methylate at -80° giving methylmethoxygermane which decomposed rapidly at room temperature into methanol and a polymeric residue.

9. Trimethylchlorogermane was prepared by the chlorination of tetramethylgermane with hydrogen chloride in the presence of aluminum trichloride as catalyst at room temperature. Its physical properties are: vapour pressure equation in the range 0 to 68.4°, $\log_{10}p(\text{mm}) = -\frac{1795}{T} + 7.665$; boiling point, 102°; latent heat of vapourization, 8075 cals./mole; Trouton constant, 21.5.

10. Hexamethyldigermoxane was prepared by the reaction of trimethylchlorogermane with silver carbonate at room temperature,and its physical properties were: vapour pressure equation in the range 18.2 to 72.4°,

$\log_{10}p(\text{mm}) = -\frac{2290}{T} + 8.580$; boiling point, 129°; latent heat of vapourization, 10,540 cals./mole; Trouton constant, 26.2; melting point, -61.1 ± 0.1°.

11. Hexamethyldigermoxane reacted quantitatively with boron trifluoride at room temperature according to the equation,

$$3((CH_3)_3Ge)_2O + 2BF_3 \longrightarrow 6(CH_3)_3GeF + B_2O_3$$

yielding only trimethylfluorogermane and boron trioxide.

12. The following physical properties of trimethylfluorogermane were determined: vapour pressure equation in the range 9.8 to 72.5°, $\log_{10} p(\text{mm}) = -\frac{1701}{T} + 7.693$; boiling point, 80.3°; latent heat of vapourization, 7830 cals./mole; Trouton constant, 22.1; sublimation pressure equation in the range -23 to 9.8°, $\log_{10}p(\text{mm}) = -\frac{2083}{T} + 9.038$; latent heat of sublimation, 9590 cals./mole; latent heat of fusion, 1760 cals./mole; melting point 1.9 ± 0.4°.

13. Trimethylmethoxygermane was prepared by the reaction of trimethylbromogermane with dry sodium methylate at room temperature, and its physical properties were: vapour pressure equation in the range 0 to 61.9°, $\log_{10}p(\text{mm}) = -\frac{1695}{T} + 7.531$; boiling point, 90.9°; latent heat of vapourization, 7900 cals./mole; Trouton constant, 21.7.

14. Trimethylmethoxygermane reacted rapidly with boron trifluoride to form a stable 1:1 addition compound.

15. The infrared spectra of thirteen volatile germanium compounds were determined in the gas phase and frequency assignments were made for

absorption bands in the range, 4000 to 625 $cm.^{-1}$

16. Mechanisms were proposed for: (a) the chlorination of germane with hydrogen chloride in the presence of aluminum trichloride as catalyst. It was also suggested that germylene chloride resulted from the chlorination of germyl chloride rather than from disproportionation. (b) the interaction of hexamethyldigermoxane with boron trifluoride, and (c) the reactions of germyl-, methylgermyl- and trimethylgermyl-halides with silver salts.

17. It was concluded that germanium does not utilize its vacant 4d- orbitals to form π type bonds with p_π orbitals of Group VI and VIIB elements. The consequences of this are: (a) the Ge-X bond, where X is a more electronegative atom than germanium, is strongly polar and renders the hydrogen atoms of the germyl- and methylgermyl- groups more protonic than expected, (b) germyl chloride does not react with silver salts as readily as silyl chloride because the protonic hydrogen atoms of the germyl group reduce the probability of nucleophilic attack, and (c) compounds containing both Ge-H and Ge-X bonds are unstable thermally because of inter- or intramolecular decomposition arising from the presence of protonic hydrogen atoms in the molecules.

APPENDIX I

Infrared Spectra of Germanium Compounds

Infrared spectra of only a few volatile compounds of germanium are available in the literature so that the data can be conveniently summarized in tabular form. The frequencies at which particular vibrations occur in the compounds previously studied are listed below. The following symbols are used: ν = valence stretching, r = rocking, δ = deformation, τ = torsion.

Infrared Vibration Frequencies of Germanium Compounds

Vibration	Frequency (cm.$^{-1}$)	Compounds	References
$\nu(CH_3)$	2920-2985	Me_4Ge, Me_2GeH_2	76, 133, 128
		Et_2GeCl_2, $EtGeCl_3$	125
		$(RO)_4Ge$	58
ν(Ge-H)	2060-2130	GeH_4	52, 69, 81, 10, 113, 118
		GeH_3D, GeD_3H	74
		GeH_3Cl	77
		$(CH_3)_2GeH_2$	128
		Ge_2H_6	36
ν(Ge-D)	1520-1530	GeH_3D, GeD_3H	74
		GeD_3Cl	77

Vibration	Frequency (cm.$^{-1}$)	Compounds	References
$\delta(CH_3)$	1440-1460	$(CH_3)_4Ge$	76, 133
	1240-1265	$(RO)_4Ge$	58
$r(CH_3-O)$	1181	$(RO)_4Ge$	58
$\nu(C-O)$	1040	$(RO)_4Ge$	58
$\nu(Ge-O)$	897	$(RO)_4Ge$	58
$\delta(Ge-H)$	755-932	GeH_3Cl, Ge_2H_6	77, 36
		GeH_4	10, 52, 69, 81, 113, 118
$r(CH_3)$	828	$(CH_3)_4Ge$	76, 133
$\nu(GeF)$	740, 800	GeF_4	19, 132
$r(GeH_3)$	600	GeH_3Cl	77
$\nu(Ge-C)$	560-605	$(CH_3)_4Ge$	76, 133
		Et_2GeCl_2, $EtGeCl_3$	125
$\delta(Ge-Ge)$	407	Ge_2H_6	36
$\nu(Ge-Cl)$	376-450	$GeCl_4$	125, 132, 52, 53
		Et_2GeCl_2, $EtGeCl_3$	125
$\delta(C-C-Ge)$	320, 333	Et_2GeCl_2, $EtGeCl_3$	125
$\nu(Ge-Br)$	283, 329	$GeBr_4$	52, 53,
$\delta(GeF)$	200, 260	GeF_4	19
$\delta(Ge-Cl)$	132-174	$GeCl_4$, Et_2GeCl_2	52, 53, 125, 132
$\delta(Ge-C)$	175	$(CH_3)_4Ge$	76, 133
$\delta(C-Ge-Cl)$	150, 165	Et_2GeCl_2, $EtGeCl_3$	125

Vibration	Frequency (cm.$^{-1}$)	Compounds	References
τ(C-C-Ge-Cl)	112	Et_2GeCl_2, $EtGeCl_3$	125
δ(GeBr)	78, 111	$GeBr_4$	52, 53, 132
ν(Ge-Ge)	229	Ge_2H_6	36

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