AN INVESTIGATION OF DISILYL ALKANES

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AN INVESTIGATION OF DISILYL ALKANES

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PREFACE

The work described in this thesis consists of three different approaches to the organic chemistry of Group IV elements. Included are the syntheses of some new organo-silicon compounds, an attempted synthesis of a volatile titanium hydride and a mathematical correlation of boiling point data of various Group IV hydrides.

These are all included in the classification of organic chemistry following the suggestion of Kraus (1) who stated that the volatile hydrides of elements other than carbon should be considered to be organometallic compounds.

Note re 1,2-Disilylethane, page 71.

The analytical figures for this compound had not been received from the National Research Council at the time of presentation of this thesis.

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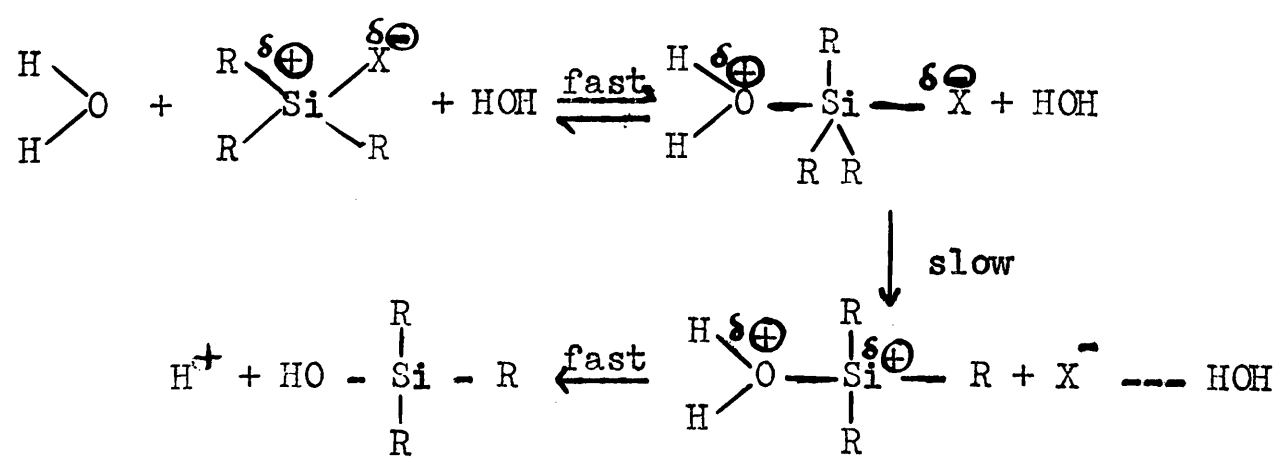
GENERAL INTRODUCTION

The chemistry of organo-metallic compounds has been an important field of investigation, providing a link between organic and inorganic chemistry. Valuable organo-metallic compounds of many uses have been discovered or synthesized: drugs, such as the arsenic compounds; reaction intermediates, such as Grignard reagents and lithium alkyls; and polymeric substances, such as the silicones.

The organic chemistry of Group IV elements is interesting because these elements, being tetracovalent, can act much more like carbon than any other hetero elements can. One major difference between carbon and the rest of Group IV is that all the other elements can expand their valence shells, as can all elements above Period I in the periodic table, and so have a means of reaction that is impossible to carbon. For instance, it has been suggested that the reaction of a silicon halide with water proceeds as follows:



Another difference in behaviour is due to the fact that all the other members of Group IV are more electropositive than carbon and so have a greater "affinity" for oxygen than for hydrogen, the halogens or carbon.

Of the work done in this field, most has dealt with compounds containing quaternary hetero atoms or else with compounds which had halogens attached to the metallic atom. A quaternary atom has all its valencies attached to carbon atoms, as the lead in tetraethyllead ($(CH_3)_4Pb$).

The organohalo silanes have been investigated mainly in regard to their hydrolysis products, as, for example, dimethyldichlorosilane ($(CH_3)_2SiCl_2$) is used to form methyl silicones (methyl siloxane polymers).

Little attention has been paid to compounds with more than one silicon atom in the molecule except to polymers with the -Si-O- grouping. The other compounds could be expected to be more like inorganic covalent compounds and to have less organic character. This difference is of degree and not of kind. For instance, the covalent metallic carbonyls are much more similar to organic compounds than to inorganic salts. The presence of more than one silicon atom should lead to greater instability, greater reactivity and increased density among other differences.

It was felt that it would be of interest to synthesize compounds of this type and investigate their properties. Compounds synthesized are listed in Table I.

TABLE I

Compounds Synthesized

Name	Empirical Formula	Structure
Trichlorosilyldichlorosilylmethane*	$CSi_2H_3Cl_5$	$SiCl_3-CH_2-SiHCl_2$
Bis-trichlorosilylmethane*	$CSi_2H_2Cl_6$	$SiCl_3-CH_2-SiCl_3$
1,2-Bis-trichlorosilylethane*	$C_2Si_2H_4Cl_6$	$SiCl_3-(CH_2)_2-SiCl_3$
1,4-Bis-trichlorosilylbutane	$C_4Si_2H_8Cl_6$	$SiCl_3-(CH_2)_4-SiCl_3$
1,1-Bis-trichlorosilylethane	$C_2Si_2H_4Cl_6$	$(SiCl_3)_2-CH-CH_3$
1,2-Bis-trichlorosilylpropane	$C_3Si_2H_6Cl_6$	$SiCl_3-CH(CH_3)-CH_2-SiCl_3$
Disilylmethane	CSi_2H_8	$SiH_3-CH_2-SiH_3$
1,2-Disilylethane	$C_2Si_2H_{10}$	$SiH_3-(CH_2)_2-SiH_3$
1,1-Disilylethane	$C_2Si_2H_{10}$	$(SiH_3)_2-CH-CH_3$
1,2-Disilylpropane	$C_3Si_2H_{12}$	$SiH_3-CH(CH_3)-CH_2-SiH_3$

* Previously reported.

Titanium, the first member of the IVb group in the periodic table, is similar in many ways to the members of the IVa group. One of the greatest similarities is that it forms covalent tetrahalides with much the same properties as the tetrahalides of silicon and germanium. The tetrachlorides of the three elements are compared in Table II. All are soluble in organic solvents and are decomposed by water.

TABLE II

Physical Properties of Some

Group IV Tetrachlorides (2)

Compound	Molecular Weight	Boiling Point °C	Freezing Point °C	Density
Silicon tetrachloride	169.89	57.6	-70	1.483
Titanium tetrachloride	189.73	136.4	-30	1.726
Germanium tetrachloride	214.43	83.1	-49.5	1.879

An attempt was made to synthesize a volatile titanium hydride which would correspond to those of the Group IVa elements, but the attempt was a failure.

The correlation of the physical properties of chemical compounds has been an important factor in showing the relationship of one molecule to another in terms of structural and electrical factors. Empirical constants calculated in these correlations have often led to discovery of important physical quantities or forces, and also to finding discrepancies in existing information. An example of such was the discovery of the constant b in van der Waals' equation of state. Van der Waals tried to find an equation which better represented the pressure-volume relations of a gas than Boyle's law. This constant is a measure of intermolecular attraction.

Relationships which link the properties of many compounds or which compare one group with another are particularly valuable. For example, the correlation of refractive index and density with structure led to the

concept called "Molecular Refraction". Valuable theoretically are relationships of properties which are measured under conditions which are more strictly comparable, the so-called corresponding states. Liquids at the boiling point (which is approximately two-thirds of the critical temperature) are approximately in corresponding states. Because boiling points are the only corresponding state data which are commonly available, especially for unstable compounds or substances prepared infrequently, correlation of this property was attempted in the present thesis. Rules obtained from such a correlation, if successful, would help in the prediction of boiling points of compounds prepared for the first time. An article based on this correlation has been accepted for publication by the Journal of the American Chemical Society.

The terms "curve-fitting" and "goodness of fit" have been used in this thesis. These are standard statistical terms (3) and mean, respectively, the calculation of empirical equations to correlate observed data, and the accuracy with which data calculated from the empirical equation compares with observed data.

HISTORICAL INTRODUCTION

ORGANO-SILICON COMPOUNDS

Wöhler, the founder of synthetic organic chemistry, was also interested in pseudo-organo silicon chemistry. In 1857 (4) he prepared silane (SiH_4) from aluminum silicide and hydrochloric acid, expecting to uncover a science analagous to that of carbon's organic compounds. He was disappointed, as silicon is so electropositive that silicon-hydrogen bonds are not stable in the presence of water.

The first true organo-silicon compound was silicon tetraethyl (tetraethylsilane) ($(C_2H_5)_4Si$) which was synthesized by Friedel and Crafts (5) in 1863 by heating zinc diethyl with silicon tetrachloride to 160°C in a sealed tube. In 1865 (6) they prepared tetramethylsilane ($(CH_3)_4Si$) from zinc dimethyl by a similar method. The next step was in 1872 when Ladenburg (7) prepared an alkyl silane in which one of the silicon valences was attached to hydrogen instead of to carbon. The compound was triethylsilane ($(C_2H_5)_3SiH$) and was derived from zinc diethyl, sodium metal and ethyl silicate ($(C_2H_5O)_4Si$). He further found, in 1874 (8), that to form aryl silanes, mercury aryls instead of zinc compounds must be used.

Then, in 1880, the first alkyl silane with more than one silicon atom in the molecule was synthesized. This was hexaethyldisilane, ($(C_2H_5)_3SiSi(C_2H_5)_3$) prepared by Friedel and Ladenburg (9) from hexaiododisilane and zinc diethyl. In 1884 Pape (10) produced the first alkylhalo silane by bromination of tripropylsilane ($(C_3H_7)_3SiH$) to tripropylbromosilane ($(C_3H_7)_3SiBr$). In the same paper he recorded the first use of the Wurtz synthesis in organo-silicon chemistry, preparing tetraisobutylsilane from silicon tetrachloride, iso-butyl chloride and sodium.

A major advance was the introduction of the Grignard reaction. In 1904 both Kipping (11) and Dilthey (12) reported successful syntheses of tetraalkyl silanes by condensing silicon tetrachloride with an alkyl magnesium halide in ether solution.

Kipping's work, which was begun in 1899 at the University of Nottingham and extended over forty-five years, is the basis for most of the present knowledge of the organic chemistry of silicon. He prepared completely substituted silicon compounds, with a wide variety of alkyl, alkoxy and other substituents. He discovered the polymer siloxanes which result from the hydrolysis of molecules containing silicon-hydrogen or silicon-halogen bonds. These polymers he termed "silicones" as at first they were thought to be analagous to ketones. That hypothesis has been found wrong, but the name is still applied to the polymers. A complete bibliography of Kipping's work may be found in Rochow's book on the silicones (13).

In 1917, Grüttner and Krause (14) produced the first compounds containing more than two elements from Group IV in the periodic table. Their compounds, synthesized by the Grignard reaction, contained carbon, silicon, and lead or tin. In 1918 Grüttner and Cauer (15) reported the first preparation of an organo-silicon compound containing more than one silicon atom in which the silicon atoms were not joined to each other but joined through carbon atoms. The compound was para-bis-(triethylsilyl)-benzene ($(C_2H_5)_3Si\langle\bigcirc\rangle Si(C_2H_5)_3$). Stock and Somieski (16) were the first to prepare a silicon alkyl which contained a primary silicon atom, methylsilane (CH_3-SiH_3). Stock and his collaborators worked mainly on the hydrides of silicon. The preparation, purification and investigation of their chemical reactions were covered in a series of papers from 1916 to 1926 (17) and were then noted in a monograph (18).

MODERN SYNTHETIC METHODS

The Grignard reaction applied to silicon halides by Kipping (11) is perhaps the most widely used method to synthesize organo silanes. In the last fifteen years there have been several important new methods published, many of them vapour-phase, continuous reactions which are more useful industrially than the batchwise Grignard.

An addition reaction to produce alkylchloro silanes was discovered by Shtetter (19). Unsaturated hydrocarbons absorbed silicon tetrachloride in the presence of aluminum oxychloride (Al_2OCl) under high pressure. No catalyst was necessary at 400°C, 1000 pounds per square inch, according to Barry, et al, (20) if trihalo silanes ($SiHX_3$), alkyldihalo silanes ($SiHRX_2$) or dialkylhalo silanes ($SiHR_2X$) were used. R is any alkyl or aryl group and X is chlorine or bromine. There had to be at least one hydrogen and one halogen present if addition was to take place without a catalyst.

A somewhat similar process was involved in the heating together of silicon tetrachloride and an aliphatic hydrocarbon above 450°C to produce alkylchloro silanes, as patented by Miller and Schreiber (21). No catalyst was mentioned. According to Levy (22) brick, pumice, platinum or palladium catalyzed the reaction. Vapour phase alkylation was also studied by Hurd (23) who passed a mixture of silicon halide and alkyl halide vapours over aluminum or zinc powders at elevated temperatures to produce alkylhalo silanes. If, instead of an alkyl halide, hydrogen chloride or hydrogen was mixed with the silicon halide and passed through the reactor, chlorine on the silicon was replaced by hydrogen.

The use of lithium alkyls was patented by Fleming (24). The lithium alkyl dissolved in ether was caused to react with a compound containing a silicon-chlorine bond, and the chlorine was replaced by the alkyl group

formerly attached to the lithium.

A departure from the classical methods was the direct synthesis of alkylhalo silanes from elementary silicon, developed recently by Rochow (25, 26). In this procedure, alkyl halides were passed over elementary silicon at an elevated temperature in the presence of a metallic catalyst, generally copper, to yield a mixture of alkylhalo silanes. Both methyl and ethyl halides were used, each yielding a mixture of alkylhalo silanes of the general formula R_aSiX_b $(a + b = 4)$. This work was actually an extension of the method of Stock and Zeidler (27) who passed hydrogen chloride gas over a copper-silicon mixture at 300°C to prepare trichlorosilane ($SiHCl_3$). The mechanism of the reaction was postulated by Hurd and Rochow (28) to be as follows:

$$2\ Cu + CH_3Cl \xrightarrow{250^\circ} CuCl + CuCH_3 \quad \ldots\ldots \quad 1$$

$$Si + CuCl \longrightarrow Cu + (SiCl)^* \text{ active} \quad \ldots\ldots \quad 2$$

$$\left.\begin{array}{ll} & (SiCl)^* + CH_3 \longrightarrow (CH_3SiCl)^* \\ \text{or} & (SiCl)^* + CuCH_3 \longrightarrow (CH_3SiCl)^* + Cu \\ \text{or} & (SiCl)^* + CuCl \longrightarrow (SiCl_2)^* + Cu \end{array}\right\} \ldots\ldots \quad 3$$

Reaction 3 proceeded by all possible paths until the silicon was tetrasubstituted, $(CH_3)_nSiCl_{(4-n)}$, $n < 5$. One evidence cited for a course such as the above was obtained when a glass microscope slide was plated with silicon and copper strips lying side by side. If a stream of heated methyl chloride was passed over the slide so that it passed over the silicon before the copper, copper was removed, but the silicon was unchanged. If the gas stream passed over the copper first, then copper was displaced from its side of the slide and deposited amongst the silicon particles, and silicon was removed from the slide. Because of the presence of methyl radicals at high temperature, there was generally some pyrolysis which in turn gave rise to free hydrogen atoms. These atoms reacted with the active

"molecules", giving a fourth equation in reaction 3.

$$(SiCl)^* + H \longrightarrow (SiHCl)^*$$

A number of silicon-hydrogen bonds were found in the products of the reaction.

It was later discovered by Sprung and Gilliam (29,30) that diluting the alkyl chloride with hydrogen or nitrogen to the extent of about fifty per cent gave better yields, and some of the residual halogens on the silicon were replaced with hydrogen if hydrogen was the diluent. If, in addition to the copper catalyst, aluminum was added, Hurd (31) announced that the proportion of trialkylmonohalo silanes was increased. The use of polyhalo alkanes was disclosed in patents issued to Patnode and Schiessler (32, 33), where dichloromethane and 1,2-dichloroethane yielded alkylhalo silanes with more than one silicon atom in the molecule, and both chain and cyclic types of molecules. If a saturated hydrocarbon plus a halogen were passed over the silicon at 500°, all the possible alkylhalo silanes were formed (22). A similar reaction between an olefin, a hydrogen halide and silicon-copper was patented by Dow (34). Rochow (35) found later that an ether plus a hydrogen halide would yield alkylhalo silanes.

The Rochow synthesis was extended to other members of Group IV in 1947 when Rochow (36) made alkylhalo germanes from alkyl halides and a germanium-copper alloy. Further work on the Rochow synthesis has indicated that when aromatic groups are to be added to the silicon, silver is the best catalyst, and a great excess of the aryl halide should be used (25,37).

The processes of both Hurd and Rochow have the advantage of being continuous, instead of being done in batches, and the Rochow process is further distinguished by the use of elementary silicon and not hydro-

lizable silicon halides. Both the Grignard synthesis and the Rochow synthesis are used in the industrial preparation of alkylhalo silanes (38,39). The Grignard is favored because it gives better control of the products, while the Rochow is both simpler and cheaper. Rochow gives flow sheets and a discussion of the industrial applications of both syntheses in his book on the silicones (40).

An interesting extension of the lithium alkyl reaction was reported by Hurd (41). Silicon tetrachloride was alkylated with lithium aluminum tetramethyl to yield tetramethylsilane.

SYNTHESIS OF POLYSILICON ORGANIC COMPOUNDS

In the preparation of molecules with more than one silicon atom, almost all of the various procedures have been used. The preparation by Grüttner and Cauer, previously mentioned (14), of para-bis-(triethylsilyl)-benzene was done by repeated Grignard steps. In 1933, Kraus and Eatough (42) prepared tin compounds of this type by a reaction that has yet to be extended to the silanes. Alkyl sodium stannanes were condensed with alkyl halides,

$$2\ NaSn(C_6H_5)_3 + CH_2Cl_2 \longrightarrow ((C_6H_5)_3Sn)_2CH_2 + 2\ NaCl$$

In 1945, the direct reaction or Rochow synthesis of polysilicon organic compounds was patented by Patnode and Schiessler (31,32). They caused methylene chloride and ethylene chloride to react with copper-silicon at elevated temperatures and produced bis(trichlorosilyl)-methane ($SiCl_3$-CH_2-$SiCl_3$) and similar substances. The mechanism was assumed to be the same as that outlined previously. Because of its simplicity, this was the reaction used in the research reported in this thesis.

Sommer et al (43,44) used both the Grignard synthesis and lithium alkyls to prepare a group of compounds of the general formula

$$(CH_3)_3\text{-}Si\text{-}CH_2\text{-}((CH_3)_2Si\text{-}CH_2\text{-})_n\text{-}X$$

where X was chlorine or hydrogen and n varied from one to four. These compounds were synthesized in order to compare them with the low molecular weight members of the linear polysiloxane series,

$$(CH_3)_3\text{-}Si\text{-}O\text{-}((CH_3)_2Si\text{-}O\text{-})_n\text{-}Si(CH_3)_3$$

Addition of trichlorosilane to unsaturated compounds was reported by Burkhard and Krieble (45), Barry et al (19) and Agre (46). Two moles of trichlorosilane could be added to an acetylene (45) or one mole to a mono-unsaturated compound already containing one silicon atom such as allyl trichlorosilane. Burkhard and Krieble and also Agre said that a catalyst was necessary, either benzoyl peroxide or ultra-violet light, while Barry et al found no catalyst necessary. Surprisingly, Burkhard and Krieble found that when added to acetylene or vinyltrichlorosilane trichlorosilane did not obey Markownikoff's rule. Instead,

$$CH{\equiv}CH + 2\ SiHCl_3 \xrightarrow[\text{or}\ BzO_2]{\lambda} SiCl_3\text{-}CH_2\text{-}CH_2\text{-}SiCl_3$$

$$CH_2{=}CH\text{-}SiCl_3 + SiHCl_3 \xrightarrow[\text{or}\ BzO_2]{\lambda} SiCl_3\text{-}CH_2\text{-}CH_2\text{-}SiCl_3$$

Sauer and Hadsell (47) reported that this type of compound could be obtained in small yield from the thermal disproportionation and rearrangement of alkylhalo silanes with or without silicon tetrachloride in the presence of aluminum chloride above 375°C.

$$2\ CH_3SiCl_3 \xrightarrow[AlCl_3]{\Delta} CH_4 + SiCl_3\text{-}CH_2\text{-}SiCl_3$$

From trimethylchlorosilane they obtained 3.5 per cent of crude bis-(dimethylchlorosilyl)-methane.

$$2\ (CH_3)_3SiCl \xrightarrow[AlCl_3]{\Delta} ((CH_3)_2\text{-}\underset{\underset{Cl}{|}}{Si}\text{-})_2CH_2 + CH_4$$

Bluestein (48) produced several compounds with alternate silicon and

carbon atoms, similar to those of Sommer et al already mentioned, through the hydrolysis and fluorination of complex chlorine-containing siloxanes.

$$(CH_3)_3\text{-}Si\text{-}O\text{-}Si(CH_3)_2\text{-}CH_2\text{-}SiCl(CH_3)_2$$

$$\Big\downarrow \begin{array}{l} H_2O,\ \text{ice} \\ \text{dil. acid} \end{array}$$

oil

$$\Big\downarrow \text{fractionated}$$

oil boiling above $130^{\circ}C_{54mm.}$

$$\Big\downarrow \begin{array}{l} H_2SO_4\ (\text{conc.}) \\ HF\ \text{gas} \end{array}$$

$$F\text{-}Si(CH_3)_2\text{-}CH_2\text{-}Si(CH_3)_2\text{-}F$$

A Wurtz-type synthesis which led to similar products was reported by Goodwin et al (49). Compounds such as chloromethyldimethylchlorosilane ($ClCH_2Si(CH_3)_2Cl$) in ether solution were caused to react with sodium.

REPLACEMENT OF HALOGENS WITH HYDROGEN

There are only a few methods recorded in the literature to replace silicon-halogen bonds with silicon-hydrogen bonds. The ordinary methods of organic chemistry will not work. Removal of halogen with alcoholic potassium hydroxide leads to formation of esters. These esters cannot be reduced with sodium amalgam or zinc-hydrochloric acid, but yield polymers instead. Silicon-halogen bonds do not form any compounds analagous to the Grignard reagents so this route cannot be used. Neither do the ordinary metallic hydrides, such as sodium hydride (NaH) dehalogenate silicon halides (50).

In 1945, Hurd (23) announced that passage of a halosilane or an alkylhalo silane mixed with hydrogen chloride or hydrogen over aluminum or zinc powders at elevated temperature replaced the halogen with hydrogen. All possible hydrogenation products were formed, and there was a good deal

of disproportionation as the minimum temperature for the reaction was 400°C.

A more convenient method was the process which was developed by Schlessinger (50,51) and his coworkers to dehalogenate and hydrogenate silicon-halogen bonds by the use of lithium aluminum hydride ($LiAlH_4$) in ether solution. This reaction was fast and easy to control. Mole for mole replacement of halogen atoms took place at a speed generally associated with ionic reactions in inorganic chemistry. Johnson et al (52) discovered that reduction of metal-halogen to metal-hydrogen bonds could be done easily with lithium hydride when small amounts of lithium aluminum hydride were present. Evidently, the aluminum chloride formed was reconverted to lithium aluminum hydride by the excess lithium hydride.

Because of the ease of handling and the rapid, complete reaction, replacement of chlorine atoms by hydrogen was done by means of lithium aluminum hydride in the work reported in this thesis.

ANALYTICAL METHODS

The first organo-silicon compound prepared was not analyzed for elements, only a vapour density molecular weight was determined. (5).

Macrocombustion techniques were afterward used to determine carbon and hydrogen (5). Silicon was determined separately as silica by wet-oxidations such as a Kjeldahl-type of digestion (5) or by oxidation with nitric acid in a sealed tube (53). Oxidation in the Parr bomb with sodium peroxide was reported recently (54). In all these methods the silica formed was dehydrated and weighed as in the usual inorganic procedure. A microcombustion technique was recently reported in which carbon, hydrogen and silicon were all determined (55).

Silicon-silicon bonds have been determined by treating the compound in a closed system with aqueous alkali to liberate hydrogen. One molecule of hydrogen is released for each bond between two silicon atoms (56). A similar method was used to determine hydrogen attached to silicon (57). Again, one mole of hydrogen was collected for each silicon-hydrogen bond.

Halogen atoms attached to silicon have been determined very easily in several ways, all of which depend on the hydrolysis of silicon-halogen bonds with water or aqueous alkali. Stock and Somieski (57) titrated the halide ion released with silver nitrate, using potassium chromate as an indicator. Patnode (58) hydrolyzed the compound in water and titrated the hydrohalic acid released. Hyde and DeLong (59) hydrolyzed the silicon halide in standard aqueous alkali and titrated the remaining alkali.

The method of Hyde and DeLong was used in the work reported in this thesis to determine chlorine and the resulting polymer was then dehydrated and decomposed and silicon determined as silica. Hydrogen attached to silicon was determined by Stock's method (57) and the resulting mixture was analyzed for silica.

ORGANO-TITANIUM COMPOUNDS

In spite of the similarity between the tetrahalides of silicon, germanium and titanium (Table II), no organic-titanium compound with a carbon-titanium bond has been definitely prepared and analyzed (60). There is some evidence for intermediate complexes in reactions of titanium tetrachloride with organic compounds (61). Gilman thinks that if organic titanium compounds are ever prepared they will be aryl compounds (61) since, as in other unstable organo-metallic groupings, the aromatic compounds are more stable than other types.

There have been claims for the preparation of a volatile titanium

hydride, the only important one being that of Klauber (62). Using the Paneth apparatus with 0.2 N sulphuric acid and titanium electrodes, a gas which he said was titanium tetrahydride (TiH_4) was prepared which yielded a yellow solution in hydrogen peroxide and which burned in air to give a deposit of titanium dioxide. No reports have been published which claim a successful repetition of this work.

Reduction of titanium tetrachloride with hydrogen (63) yielded only titanium, its di- and trichlorides and hydrogen chloride. Sodium amalgam and titanium tetrachloride produced the lower chlorides only (64).

Because of the simplicity and the directness of the reaction, and also because previously unknown hydrides such as zinc dihydride (ZnH_2) (51) have been prepared in similar reactions, the synthesis from lithium aluminum hydride and titanium tetrachloride was attempted as reported herein.

BOILING POINT RELATIONSHIPS

The first attempt to relate the boiling point of organic compounds to some structural property was published by Kopp (65) in 1842. He stated that in any homologous series the boiling point increased 18°C for the addition of each methylene group, but it is now known that the increment becomes less as the size of the molecule is increased. Since the time of Kopp there have been many equations published relating the boiling point to other values.

One of the first was that of Walker (66)

$$T = aM^b$$

where T was the boiling point in °K, M the molecular weight, and a and b

were empirical constants*.

Then in 1899 Boggio-Lera (67) put forward an equation in two forms

$$T = K\sqrt{M + C}$$

or

$$T = \sqrt{ND + B}$$

K, C and B vary from series to series, while D had an empirical value of 20,500 for all series. B was 7000 for n-alkanes.

Since 1900, boiling points have been related to physical and chemical properties ranging from critical temperature (68) to octane rating (69). The present survey however, is confined mainly to equations which relate the boiling point to the number of atoms or the molecular weight or structure.

The next relation published was that of Ramage (70).

$$T = a\sqrt{M\,(1 - 2^{-N})}.$$

Then in 1905 Young (71) showed how to calculate the boiling point of the next member of an homologous series when the boiling point of one member was known.

$$T_{N+1} - T_N = \frac{144.86}{T_N^{0.0148\sqrt{T_N}}}$$

This equation gave good results for the n-alkanes only, but in most series better than any previous equation. However, the fit was often in error as much as 10° (71).

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* In all the equations in this section the following symbolism is adhered to unless specially noted: T is b.p. in $^{\circ}K$, t is b.p. in $^{\circ}C$, M is molecular weight, N is number of atoms. Other symbols indicate empirical constants unless otherwise identified.

Next Sugden developed the equation (72,73)

$$T = A\sqrt{M} - BM$$

and later replaced BM with two new terms

$$T = a\sqrt{M} + \frac{b}{\sqrt{M}} + \frac{a}{b}M$$

where A, B, and a and b were empirical functions of M, A and a being related to the a in van der Waals' equation. The values of a and b were within the limits

$$22.89 < a < 45.71$$

$$-2038.0 < b < +890.0$$

These equations were only for homologous series of hydrocarbons and the second one fitted to + 5°C, or excellently compared to previous attempts.

One of the barriers to producing an accurate relation was the inaccuracy with which boiling points were known at the time. For instance, the fourth edition of Beilstein which contained data up to 1910 gave only one determination of the boiling point of ethane at one atmosphere pressure, that of -93°C from the work of Olszewski (74). The modern value of -88.5°C (75) differs by no less than 4.5°C.

Thompson's equation (76)

$$\frac{T}{\rho^{0.235}} M^{0.5} = \text{const.}$$

where ρ is density, did not fit as well as Sugden's second equation. In 1915 an equation that fitted the normal alkanes from butane to heptadecane very well was published by Ferguson (77)

$$\log T = 1.929 \left(\log M \right)^{0.4134}$$

Agreement was poor outside of the defined range.

In the same year Casale (78) calculated an expression for difference in boiling point that held for many homologous series,

$$\Delta = \frac{109.2}{N^a}$$

where Δ is the difference in boiling point for two adjacent members of the series. a had the value 0.675 for normal alkanes. Another empirical equation was published in 1915 by Plummer (79). This equation considered hydrogen the first member of the n-alkane series (N = 0) and fitted as far as octadecane.

$$T = 800 \log (0.2323N + 1.290) - \frac{70}{2^N}$$

This was the best equation that had been published to that time.

Between 1916 and 1929 there were four more relations published, three empirical and one derived theoretically from refractive index and structural considerations. The empirical equations were those of Soebel (80)

$$T = \frac{Mp_x V_x}{1.49}$$

where p_x is vapour pressure at T, V_x is vapour volume at T; of Herz (81)

$$\frac{M}{T^2} = 0.00017$$

and of Adams (82)

$$T = \sqrt{20,000\ m}$$

where m equals the sum of the number of atoms of each element multiplied by the row number of the periodic table where the element is found minus one. This relation held for all covalent compounds, organic and inorganic, but did not differentiate isomers.

The derived equation of Nekrassow (83) included the specific refraction, R,

$$\text{const.} = \frac{T\sqrt{R}}{\sqrt{M}\ (1-R)}$$

In 1929, Nekrassow (84) published the first equation which included

structural factors in the calculation of the parameters.

$$T = \frac{A\ (M - \Sigma)}{\sqrt{\Sigma}}$$

Σ was the sum of certain atomic and structural factors. The equation was applied to all organic compounds. For hydrocarbons $A \sim 29$. As an example of the application of this formula, he calculated that C = 2.0, H = 1.0: for ethane, then, $\Sigma = 2 \times 2 + 6 \times 1 = 10$. Then by calculation the boiling point of ethane was 183°K. The observed value is 184.6°K (75).

The next year he published a third equation which was simpler, fitted slightly better and again marked the difference between boiling points of isomers (85)

$$T = \frac{KM^{0.75}}{\Sigma}$$

where K was peculiar to each class of compounds. This equation was only for non-polar compounds.

A relation that held for all the paraffins, the silanes, and the alkyl silanes was published by Mokrushin and Kouilov (86).

$$T = a\left(\frac{M}{d}\right)^{2/3} + b$$

in which d is density. They also (87) brought forth the relation

$$T^2 = aN + B$$

where N is the number of atoms or homologous groups.

In 1932 van Arkel published the first of a series of papers (88) which discussed the following formula for non-polar compounds of carbon and the halogens.

$$T = \frac{(V - V_c)^2 K}{V_a}$$

where V is molecular volume, V_c is the atomic volume of carbon, while

K_a is a constant involving the square root of a in the van der Waals' equation of state. It generally gave values within one or two degrees of the observed boiling point, although with symmetrical compounds or in cases where the central atom was completely shielded the calculated values were much further off (89). E.g., b.p. CF_4 calc. = 150°K, obs. = 143°K. The differences could be used to calculate dipole moments (88d).

In 1935 a paper by Cox (90) proposed a logarithmic equation of three parameters which fitted the normal alkanes from propane on.

$$\log_{10}T = 1.07575 + 0.949128 \log_{10}M - 0.101 \log_{10}^{2}M$$

No work has been reported on the calculation of constants for any of the isomeric series and Francis (69) stated that it held to decane only.

In 1937 another logarithmic equation was reported, this one by Merkel (91)

$$\log T = a \log \left[(N - 1)^2 - (N - 1) + 1 \right] + b$$

where a and b were empirical constants that changed for isomeric series or for boiling points at different pressures. This equation gave a fit of ± 1°C for the n-alkanes where a was 0.212 and b was 0.1986.

An exponential equation was published in 1937 by Chu-Yao Chen et al (92) correlating boiling point with atomic radius.

$$T = a + bV_m + cV_m^2$$

where V_m is the molecular volume:- $V_m = Nr^3$ with r the atomic radius. This is another equation which does not fit the first two members of the methane series. Three equations were published in 1938. Burnop (93) calculated empirically that

$$b = M \log_{10}T + 8.0\sqrt{M}$$

where b is additive from various calculated values relating the structure and constitution. A consideration of the parachor by Lewis (94) led to

the theoretical equation

$$T = k \log P - a$$

with P the molecular parachor, k a universal constant for all paraffins and a a constant that varied for isomeric series. The equation also held for the silanes with the same values of k and a as for the n-alkanes. However, it related to the parachor, not the structure of the molecule directly.

The third equation published in 1938 was that of Kinney (95).

$$T = 230.14 \sqrt[3]{R - 543}$$

R was a value calculated from the structure. Boiling points calculated with this equation were far from the observed values for complex structures, as shown by Neyman-Pilat (96). Later Kinney (97) himself showed that it did not differentiate cis-trans isomers when it was applied to olefins and also that in many other cases it was out as much as 10°C or more. Lewis and Newkirk (98) applied it fairly accurately to silicon compounds, but made the comment that the calculation of R was a very complex operation.

In 1949, Kinney (99) published another paper containing corrections to the previous papers. Closer agreement for both alkanes and olefins was reached through correction of observed boiling points and new boiling point numbers (R) for structural features not considered previously. Kinney did not consider a correction necessary unless observed and calculated boiling points differed by more than 10°C. He says in regard to some resynthesized hydrocarbons,

"The boiling points of all these (now) come well within the ten degree limit and may, also, be removed from the original list (of compounds whose calculated boiling points seem too far from the observed)."

None of the formulae developed up to this time could predict the boiling points of cis-trans isomers with any accuracy, and the authors of most did not attempt to do so.

In 1940 Stevels (100) argued that the boiling point should be the sum of several intermolecular forces. He said that if the London intermolecular attraction, the Debye induced polarization, and the Keesom attraction of permanent dipoles were all calculated in degrees absolute, the sum would be equal to the boiling point at atmospheric pressure. This calculation fitted the hydrogen, mixed hydrogen-chlorine, and chlorine derivatives of carbon, silicon, germanium, tin and titanium to $\pm$ 1 per cent.

EGLOFF'S EQUATION

In the same year Egloff (101) published the equation which is the basis of the work in this thesis.

$$T = a \log (N + b) + k \quad . \quad . \quad . \quad . \quad . \quad 1$$

This equation was applied to alkanes, alkenes and alkynes of many different structures, a total of thirty-seven different types of molecules including cis-trans isomers. It was found that k varied from series to series while a and b were constant. The mean deviation for one hundred and forty-three hydrocarbons was only 0.7°C and this close agreement for so many compounds was unusual. In this regard Francis (69) stated that the equations of Burnop (93), Kinney (95) and Merkel (91) all failed to an average of $\pm$ 1.3°C over the range ethane-dodecane. For this set of compounds the mean deviation of equation 1 is $\pm$ 0.10°C. In a later paper (102) Egloff applied the equation to aromatic compounds. For the aromatics both a and k varied while b was usually constant. Accuracy was not as high as with aliphatic compounds.

RECENT WORK

Francis (69) introduced an equation with six empirical constants which held from ethane to octadecane,

$$t = -76.4 + 36.4N - 1.047N^2 + 0.016N^3 - \frac{270}{N} + \frac{216}{N^3} \quad . \quad . \; 2$$

and fitted as well as equation 1. Instead of calculating additional equations or constants for isomeric alkanes, he introduced "Increment Equations". These gave a δt to add to straight chain values. The increment equation for a 2-methyl group was

$$\delta t = 20.7 - 0.75N + \frac{288}{N^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; 3$$

where N is the number of atoms in the straight chain to which the methyl group is joined in the 2 position. For example, the boiling point of 2-methylhexane is obtained by substituting N = 6 in equations 2 and 3 and adding the answers. These equations of Francis gave no better fit than that of Egloff, even with so many more parameters, and were not applied to nearly as many compounds. They were not tried on unsaturated hydrocarbons at all.

A more recent paper by the same author (103) developed a method to predict the change in boiling point of a saturated hydrocarbon when a new carbon atom was joined in any position. Very good agreement was obtained for most of the isomeric octanes, nonanes, decanes and undecanes.

In 1943 Klages (104) brought out a new version of Mokrushin's second equation (86),

$$\sigma_{n\text{-}C_NH_{2N+2}} = T^2 \times 10^{-4} = N\sigma_c + 2\delta_{Me}$$

for the case of n-alkanes. This equation was the sum of a value σ_c, which was characteristic for the main structural units in the molecule, (CH_2 groups in the n-alkanes) plus a correction factor, δ_{Me}, for the

atoms which were not of this type ($-CH_3$ in this case). The equation was applied to polar as well as non-polar compounds, and also to silanes, germanes and the boron hydrides. Since the values are recorded only to the nearest degree in the original paper, it can be assumed that the equation is good only to $\pm$ 1°C, and about one-fifth of those calculated are in error by at least that amount.

A paper by Rossini and his collaborators (105) outlined a very complex method for calculating the boiling point of isomers or olefins from straight chain saturated compounds of five or more carbon atoms. The equations, which varied from compound to compound, might have as many as eight parameters, most of which considered the interaction of different atomic groupings. The average deviation of calculated from observed boiling points for the saturated compounds was $\pm$ 0.55°C and $\pm$ 1.33°C for the olefins.

A somewhat similar set of equations was worked out by Platt (106) who claimed the parameters he used had a greater significance relating to the various physical and electrical forces at work in any one molecule and between molecules. Though the equation only applied from pentane on, the error in boiling point that resulted if a lower member was calculated could be obtained from the equation.

In 1947 Weiner (107) developed an equation similar to Francis' (69) for predicting the boiling point of any compound having one carbon atom more in any position than a compound with a known boiling point.

$$\delta t = \frac{98}{N^2} A + 5.5 B$$

A and B vary with the position taken up by the new atom and may be calculated. The results from this equation were not quite as accurate as those from equation 1, but they permitted the calculation of boiling points of isomers for which no Egloff k values existed.

TABLE III

Classification of Organo-Silicon Derivatives

Class	Normal Series	Structural Formula	Iso Series	Structural Formula
Monoalkyl silanes	Mono-n-alkyl silanes	$CH_3(CH_2)_nSiH_3$	----	----
Polyalkyl silanes	Poly-n-alkyl silanes	$CH_3(CH_2)_nSiH_2(CH_2)_nCH_3$	Dimethyl-n-alkyl silanes	$CH_3(CH_2)_nSiH(CH_3)_2$
Disilyl alkanes	α,ω-Disilyl-n-alkanes	$SiH_3(CH_2)_nSiH_3$	α,ω-Disilyl-α-methyl-n-alkanes	$SiH_3(CH_2)_nCH(CH_3)SiH_3$

COMPOUNDS CORRELATED

The classes of compounds to which Egloff's equation was applied were monoalkyl silanes (terminal silicon atoms), polyalkyl silanes (internal silicon atom) and disilyl alkanes (two terminal silicon atoms). There was only one structural type of the monoalkyl silanes, the mono-n-alkyl silanes. The other two classes existed in normal and in iso structures, Table III.

EXPERIMENTAL

REACTIONS BETWEEN ALKYL DIHALIDES AND COPPER-SILICON

APPARATUS

The Reaction Furnace

The reactor which was constructed for this research (Fig. 1) consisted of an 18-8 stainless steel tubular furnace, one meter long and four centimeters internal diameter. The tube was threaded at the top end, and a flange of two centimeters' width, with eight holes of one-quarter inch diameter spaced equally around it, was welded to the other end. A threaded iron cap fitted to the top end of the furnace carried two four centimeter lengths of stainless tubing welded on opposite sides near the edge. These tubes were 3/8 in. o.d., 1/4 in. i.d. Through the center of the cap was drilled a hole of three-eights inch diameter. A circular plate, eight centimeters in diameter, with holes corresponding to those in the flange was bolted to the flange with a one-eight inch thick gasket of asbestos between the flange and the plate. At one and three-quarters centimeters from the center of the plate, a four centimeter stainless steel tube (3/8 in. o.d., 1/4 in. i.d.) was welded. There was a threaded hole in the center of the plate which fitted the threads of a stainless steel tube of three-eights inch outside diameter. This last-mentioned tube was 130 centimeters long and one-quarter inch inside diameter and was threaded at both ends for a distance of twenty centimeters. It was placed so that it ran inside the furnace and projected about fourteen centimeters from each end, at the top through the hole in the cap, at the bottom end threaded through the hole in the plate. A nut was screwed down securely against the cap on this central tube at the top end. When the furnace was in use, all openings around

THE FURNACE REACTOR

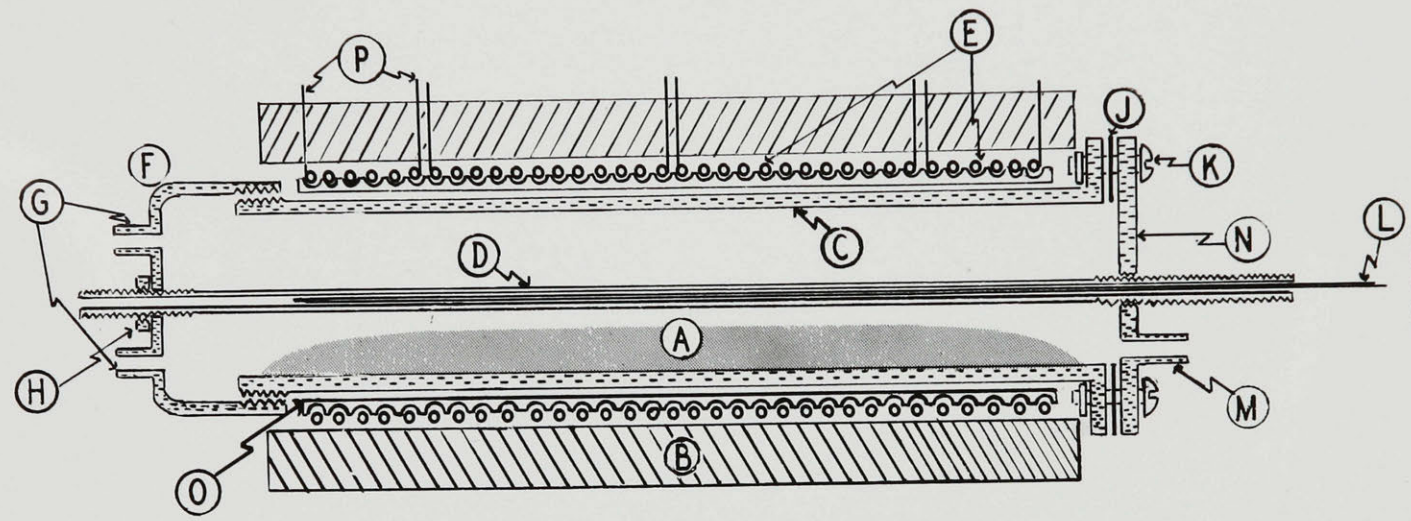


FIGURE I

A -COPPER-SILICON MIXTURE
B - ASBESTOS INSULATION
C - STAINLESS STEEL TUBE
D - THERMOWELL
E - HEATERS

F- METAL CAP
G- INLET TUBES
H- NUT
J- ASBESTOS GASKET
K- NUT AND BOLT

L-THERMOCOUPLE
M-OUTLET TUBE
N-END PLATE
O-ALUNDUM REFRACTORY
P- WIRES TO HEATERS

threads or bolt holes were sealed with Insalute cement.

The furnace was placed inside Alundum core refractories which were wound with three Fisher 10-468-10-B Chromel A heating units. Two complete heating units were placed around the central part of the furnace and two half-length units were placed one at each end of the furnace. The complete heating units were each controlled by means of a separate Variac V-5 auto-transformer. The half units were controlled together with a third Variac, but either could be removed from the heating circuit leaving the other in. The Variac was protected with a switching system arranged so that when either end heater was switched off, a resistance could be placed in the circuit. A wiring diagram of the circuit is presented in Figure 2.

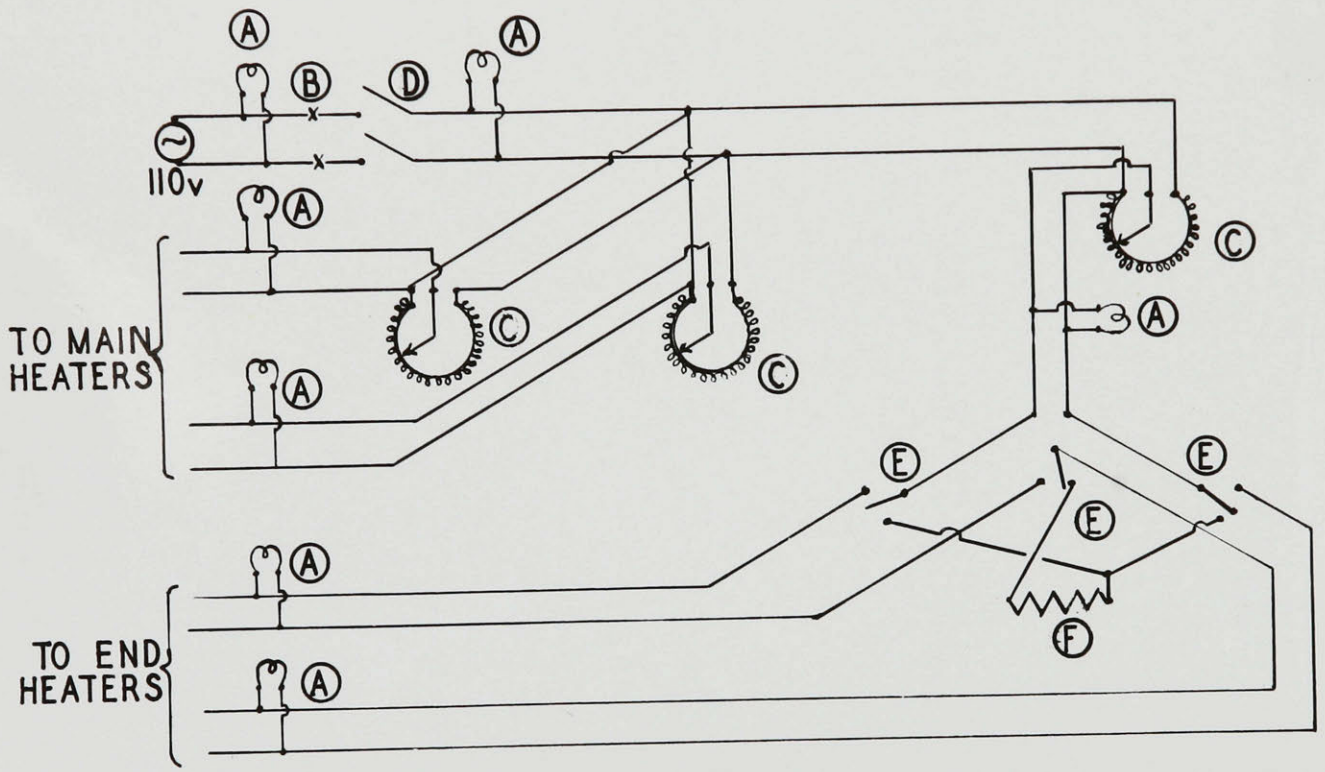
The furnace and heating system were covered with a two inch layer of asbestos pipe and wrapped with asbestos paper.

Temperatures were measured by a special thermocouple, a multi-wire, six-junction Chromel-Alumel unit of special design to reduce the number of wires (Fig. 3). Voltages developed by the thermocouple were measured on a Leeds and Northrup double-range potentiometer type 8657-C. The potentiometer had a temperature compensation circuit so no cold junction was needed. The thermocouple was insulated with Insalute and placed inside the central tube of the furnace.

The furnace reactor was used in a position 10° of arc from the horizontal for most experiments. Since trouble quickly developed in the vertical position, it was found that an almost horizontal position gave better results.

The copper-silicon reaction mixture was placed in an even layer over the whole length of the bottom of the furnace.

CONTROL CIRCUIT

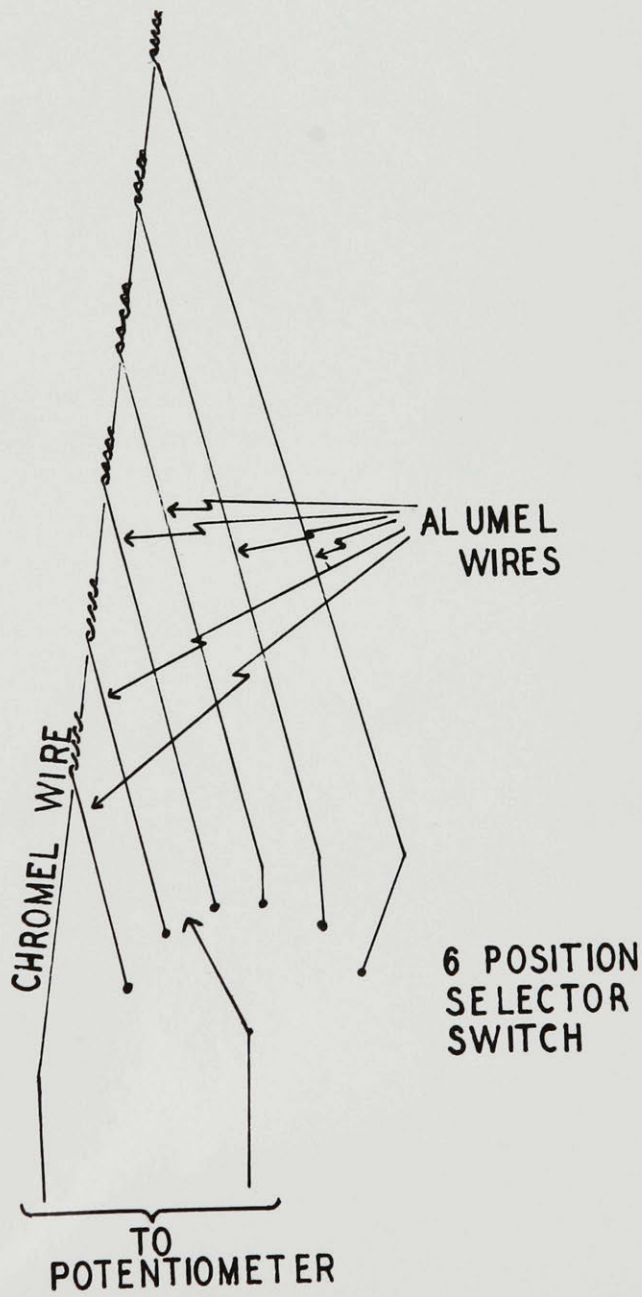


A.- 7 w. PILOT LAMPS
B.- 15 AMP. FUSES
C.- VARIAC V-5 AUTOTRANSFORMER
D.- DOUBLE-POLE, SINGLE-THROW SWITCH
E.- SINGLE-POLE, DOUBLE-THROW SWITCH
F.- 500 w. RESISTANCE

FIGURE 2

FIGURE 3

SPECIAL THERMOCOUPLE



The Deoxygenator

As it was believed that oxygen might interfere with the Rochow synthesis, a device was built to remove traces of oxygen from the nitrogen used as a diluent. This apparatus (Fig. 4) was described by Uhrig, Roberts and Levin (108), and depended on passage of the gas over a fresh copper surface. The copper reacted with oxygen present, removing it from the gas stream as copper oxide, and the copper surface was kept fresh by dissolution of the oxide with an aqueous solution of ammonium hydroxide-ammonium chloride. The purified nitrogen was bubbled through water, dilute sulphuric acid, concentrated sulphuric acid and then passed through a tube packed with anhydrous calcium chloride. The bubblers were to remove ammonia and water and the calcium chloride tube was to smooth out surges due to the bubbling. The purified nitrogen was delivered into the furnace through the upper inlet (Fig. 1).

The Feed System

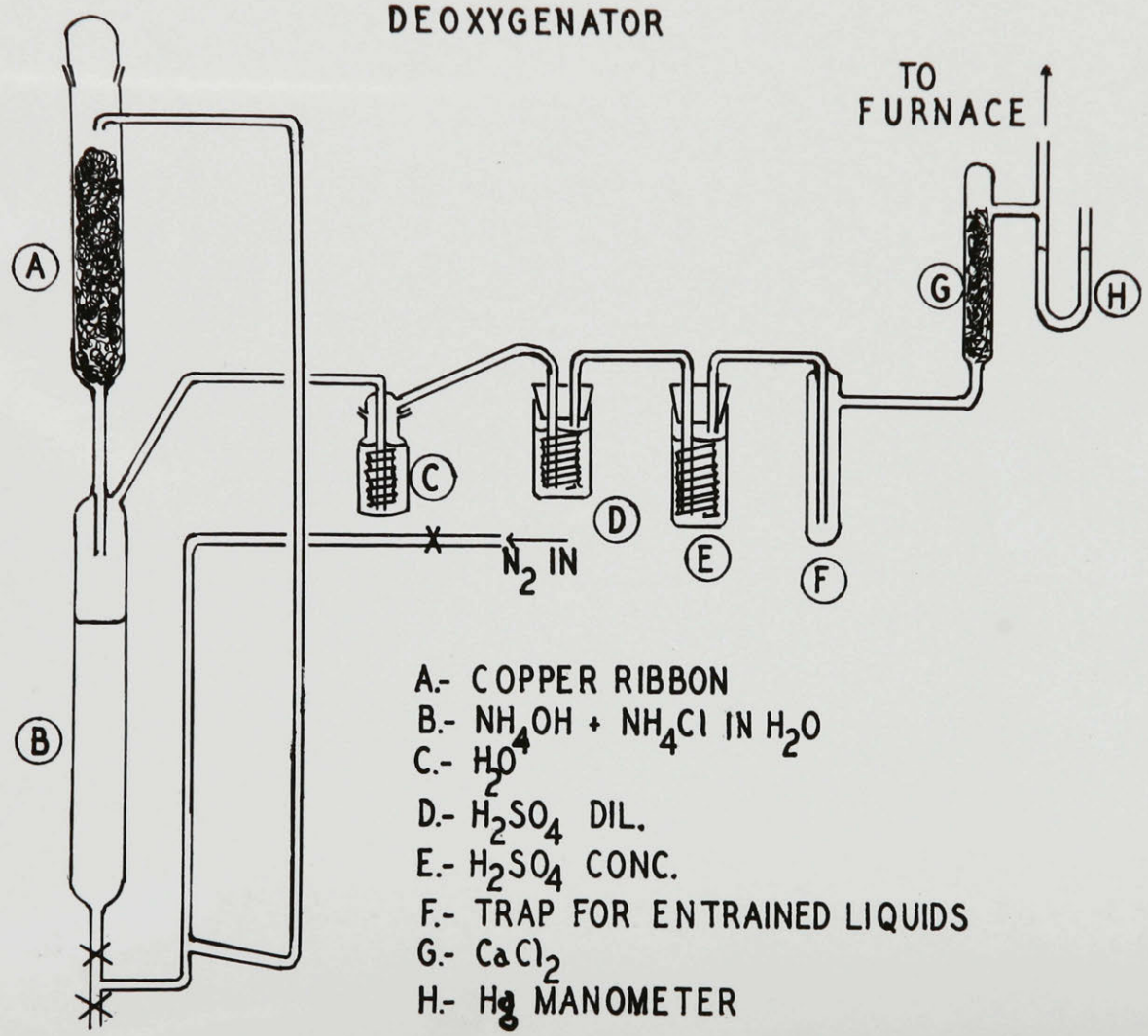
The feed system was a standard type displacement-by-mercury arrangement (Fig. 5) using a large graduated cylinder to contain the reactant.

The Condensing System

The condensing system was changed several times as the work progressed. At first the furnace was connected through a Y-tube to a Friedrich's condenser (Fig. 6). Gases that passed through the condenser were cooled in a dry-ice-acetone trap. Any gas not condensed by the trap was allowed to escape to the air through a drying tube. Later, heated traps (Fig. 7) were added between the furnace and the condenser. At first these traps were heated in steam jackets (Fig. 7a) and later by oil baths (Fig. 7b).

Distillation of Products

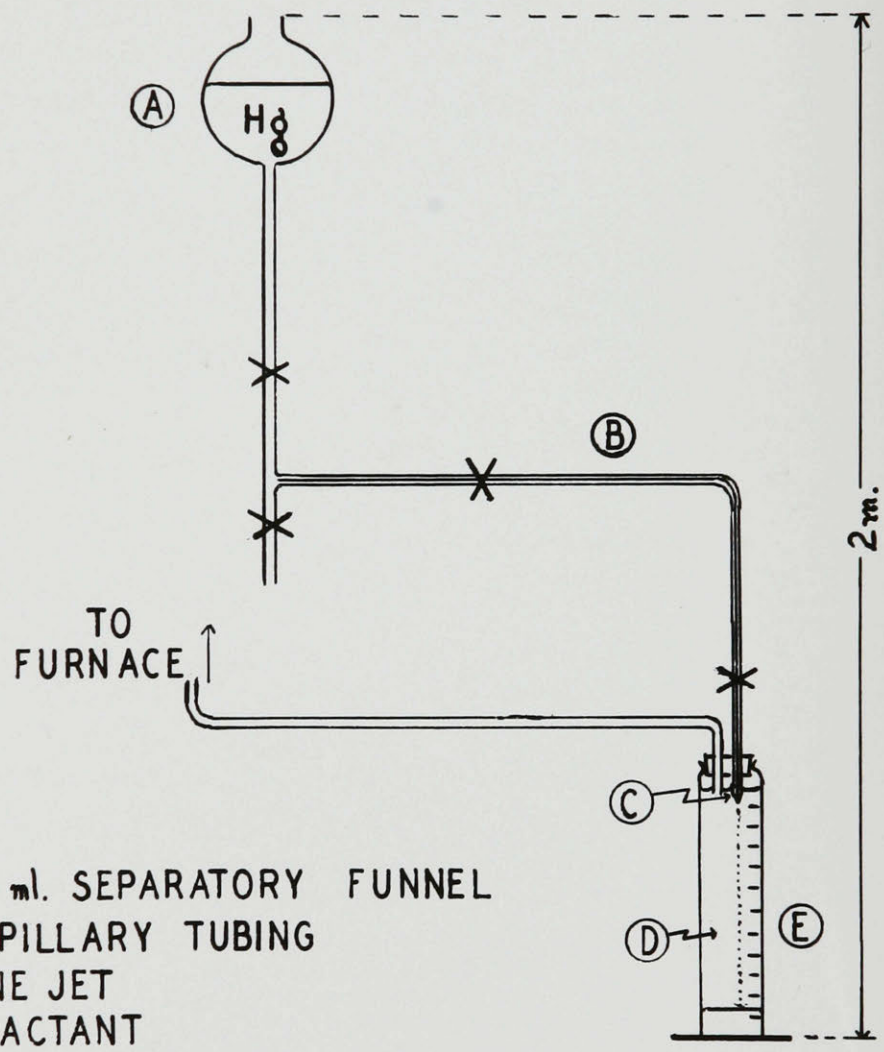
Fractional distillations were carried out in a jacketed, glass-helix



A.- COPPER RIBBON
B.- NH_4OH + NH_4Cl IN H_2O
C.- H_2O
D.- H_2SO_4 DIL.
E.- H_2SO_4 CONC.
F.- TRAP FOR ENTRAINED LIQUIDS
G.- $CaCl_2$
H.- Hg MANOMETER

FIGURE 4

FEED SYSTEM



A.- 500 ml. SEPARATORY FUNNEL
B.- CAPILLARY TUBING
C.- FINE JET
D.- REACTANT
E.- 300 ml GRADUATED CYLINDER

FIGURE 5

ORIGINAL CONDENSING SYSTEM

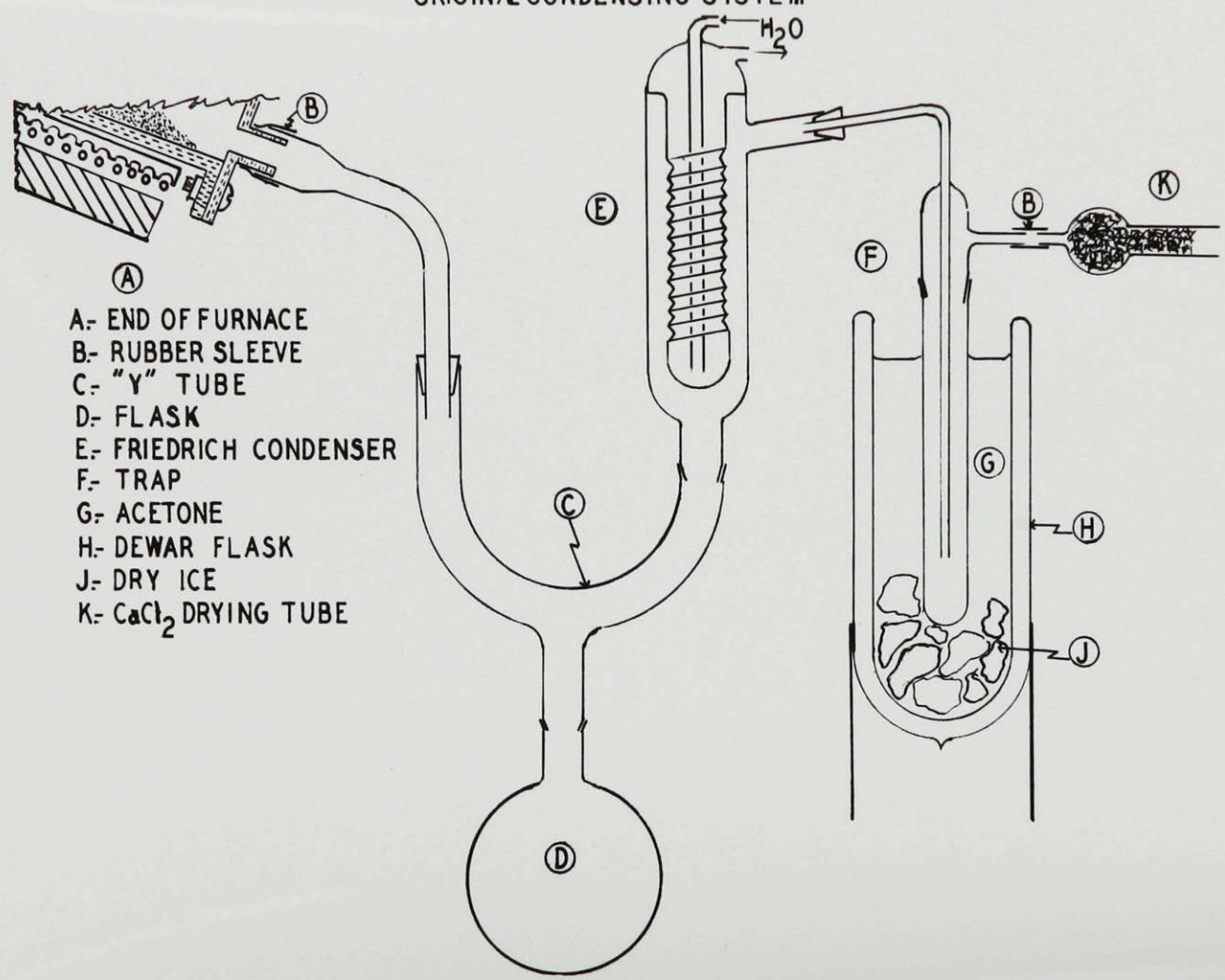


FIGURE 6

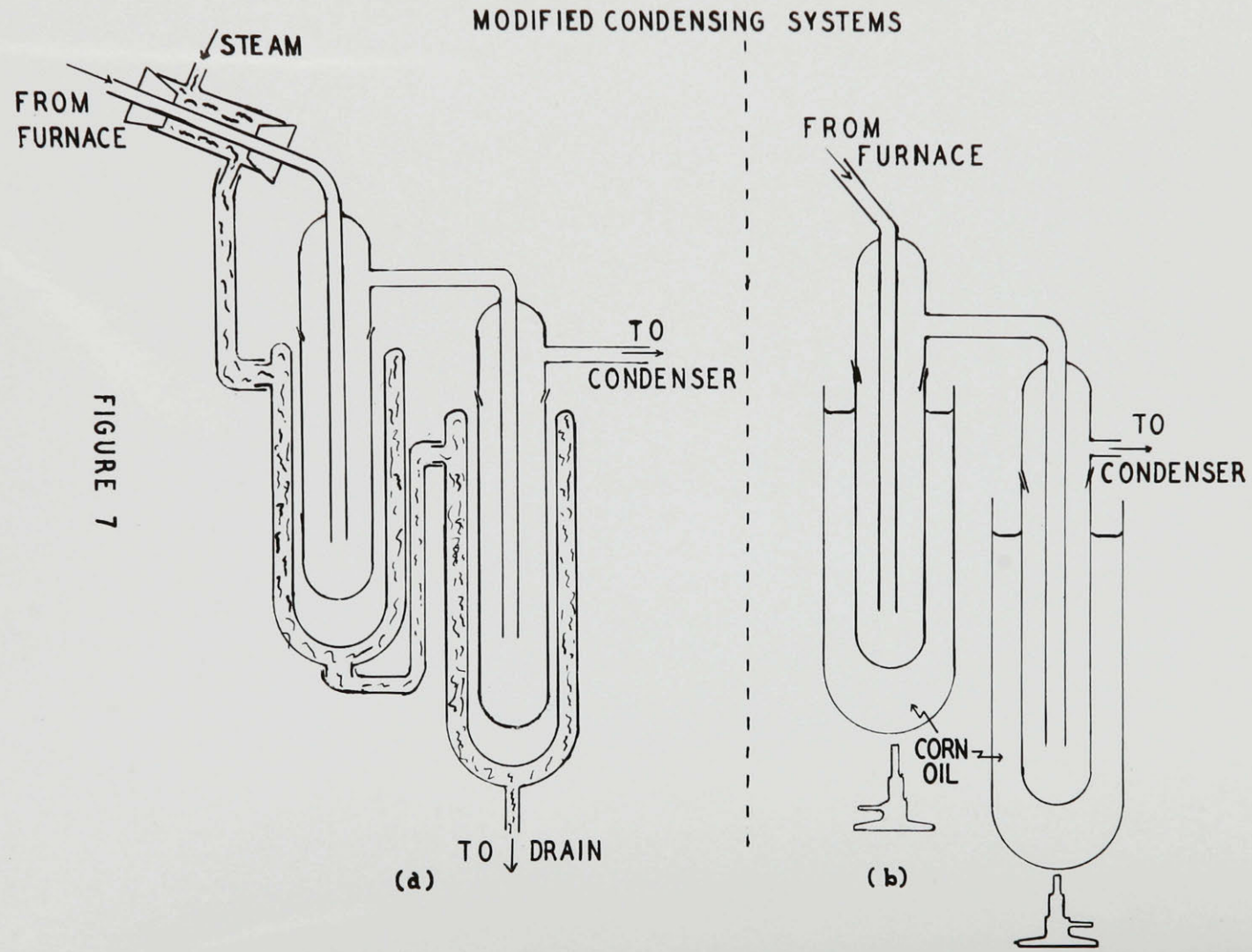

MODIFIED CONDENSING SYSTEMS
STEAM
FROM FURNACE
TO CONDENSER
TO DRAIN
(a)
FROM FURNACE
TO CONDENSER
CORN OIL
(b)

FIGURE 7

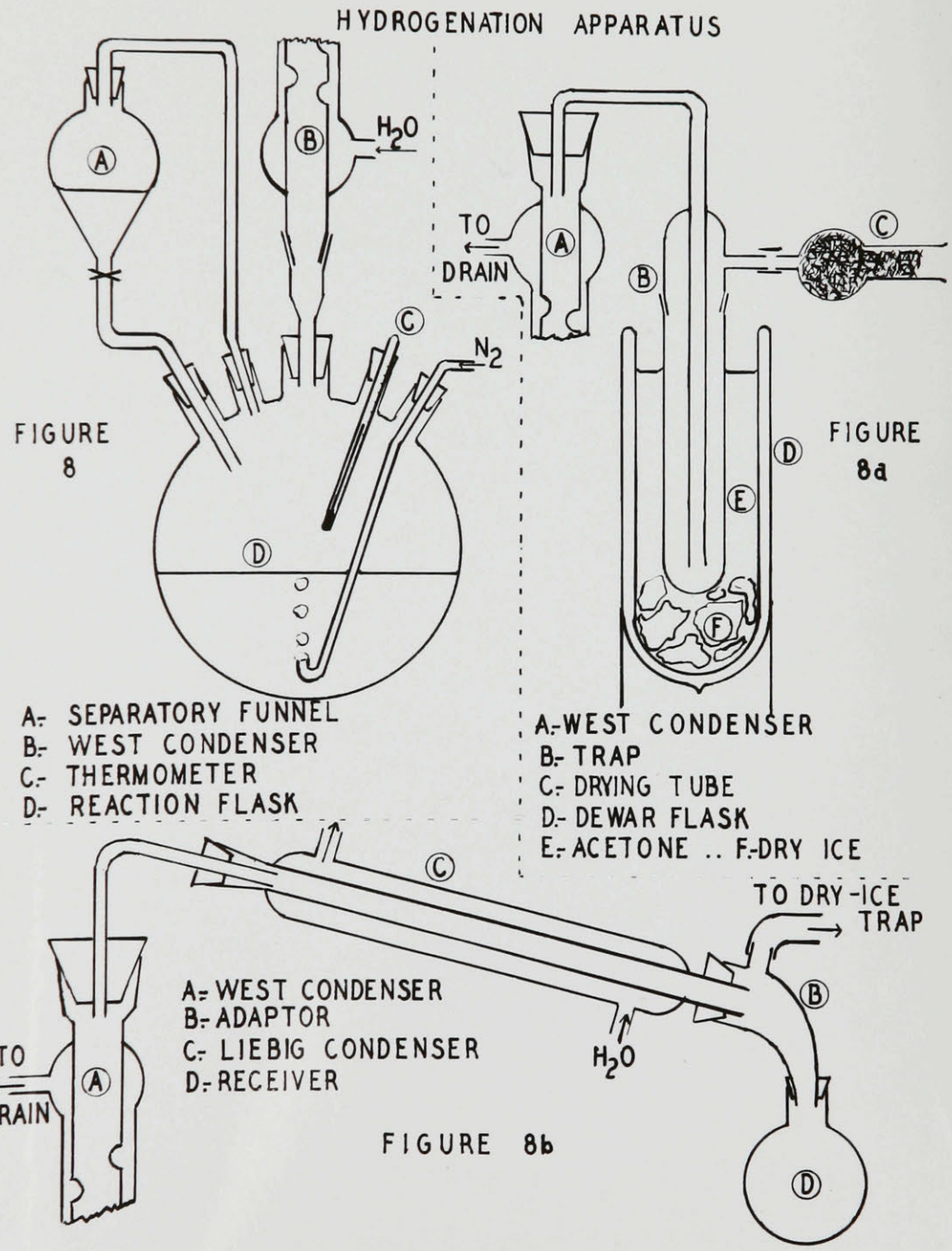
packed column, the packed section being 95 centimeters in height and 1.2 centimeters in diameter. The column had been used in previous research in this department, see Tonks (109), and had an estimated efficiency of thirty theoretical plates.

Hydrogenation Apparatus

The apparatus for hydrogenation of chlorosilanes with lithium aluminum hydride (Fig. 8) consisted of a round-bottomed, five-necked flask, the size of which was varied depending on the quantities of reactants. A separatory funnel, an indented West condenser for reflux, a nitrogen inlet and a thermometer were connected to the flask. There was also a connection between the reaction flask to the top of the separatory funnel to equalize any pressure developed in the flask so that the solution flowed smoothly out of the funnel. Different systems were attached to the top of the reflux condenser (Figs. 8a and 8b) depending on the properties of the substance being prepared. If the compound being prepared boiled at a temperature greater than that of ether, the system shown in Figure 8a was used. If the compound boiled below the boiling point of ether there was a chance that it might not condense even though the ether refluxed, and a system with a distillation condenser before the trap was used (Fig. 8b).

GENERAL PROCEDURE

The furnace was heated to some temperature greater than 300°C, the nitrogen was passed through the deoxygenator and into the furnace. The various condensers and traps were set at the desired temperatures, and the mercury-displacement feed system was then turned on. Temperature and volume of reactant added were noted periodically. When all the alkyl dihalide had been added, the feed was turned off, but the furnace was kept at the desired temperature and nitrogen was passed in for a short time.


HYDROGENATION APPARATUS
A
B
H_2O
C
N_2
D
FIGURE 8
A.- SEPARATORY FUNNEL
B.- WEST CONDENSER
C.- THERMOMETER
D.- REACTION FLASK
TO DRAIN
A
B
C
D
E
F
FIGURE 8a
A.-WEST CONDENSER
B.- TRAP
C.- DRYING TUBE
D.- DEWAR FLASK
E.- ACETONE .. F.-DRY ICE
C
TO DRY-ICE TRAP
B
A.- WEST CONDENSER
B.- ADAPTOR
C.- LIEBIG CONDENSER
D.- RECEIVER
H_2O
TO DRAIN
A
D
FIGURE 8b

Then the furnace was heated to at least 100°C more than the reaction temperature and was then turned off. Nitrogen was passed through until the furnace was fairly cool. This procedure was adopted to remove any products which might have remained in the furnace.

The products of the run were fractionated through a 10.5 inch Vigreaux column (overall height 16 inches). If a product was very high boiling (over 200°C), the distillation system was changed to a vacuum distillation apparatus with a three inch high Vigreaux column.

Products were analyzed for hydrolyzable chlorine* by dissolving them in standard aqueous sodium hydroxide and titrating the remainder of the alkali. Silicon was determined by acidifying the products from titration, dehydrating, recovering the insoluble silica on a filter paper, dehydrating and fuming down the silica with sulphuric acid.

Vapour pressure curves were investigated with the aid of a distilling flask one milliliter capacity with the side-arm bent upwards to carry a condenser (Fig. 9). A thermometer was inserted so that its bulb came at a constriction just below the side-arm. When liquid was boiled in the flask, it condensed in the side-arm and ran back down. Because of the constriction the liquid was forced into contact with the thermometer bulb as it flowed into the flask. At the same time fresh vapour was forcing its way past the bulb as it boiled out of the flask. The system produced an intimate mixture of vapour and liquid in the neighborhood of the bulb which established equilibrium conditions, eliminating superheating effects. The end of the side-arm was attached through the dry-ice-acetone trap to a manometer and a Cenco Hyvac pump. There was also a stopcock-controlled

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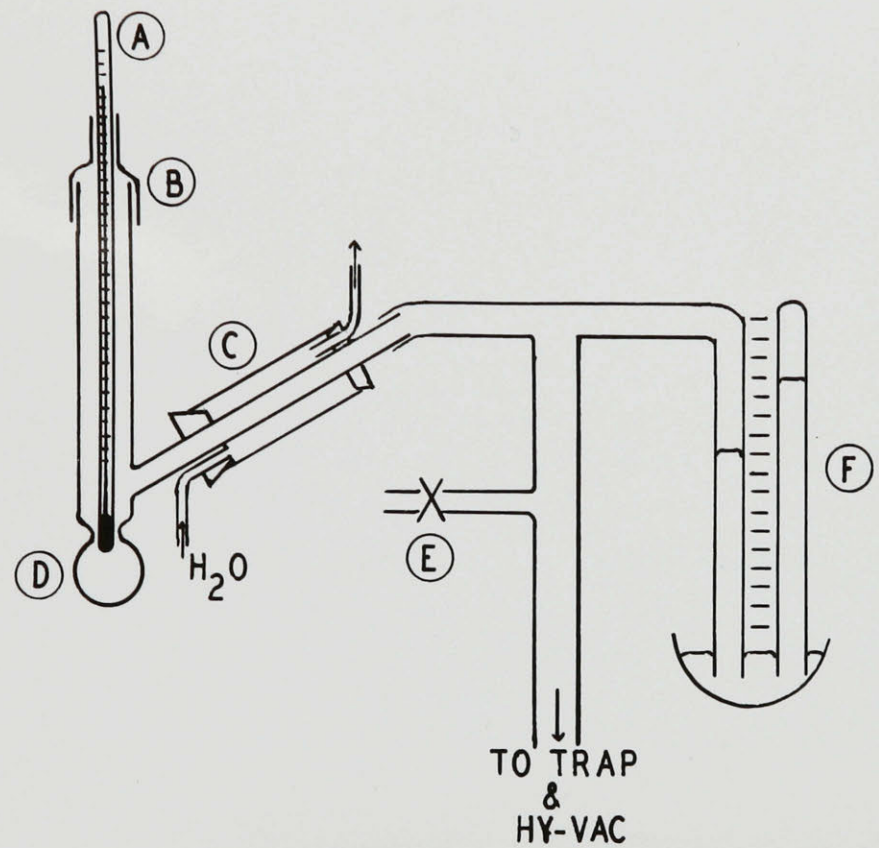
* Chlorine analyses were done by Mrs. M.M. English, to whom grateful acknowledgment is expressed.

FIGURE 9

VAPOUR PRESSURE APPARATUS



A.- THERMOMETER
B.- RUBBER SLEEVE
C.- CONDENSER
D.- 1 ml. FLASK
E.- "LEAK" STOPCOCK
F.- Hg MANOMETER

"leak" into the system, allowing air to enter at a controlled rate so that any desired pressure could be maintained. A five liter "balloon" prevented sudden pressure fluctuations. When a reading was to be taken the "leak" stopcock was adjusted so that the system was at the pressure desired, then the liquid in the flask was boiled until a steady temperature was reached. Temperature and pressure readings were recorded.

Densities were measured by a Fisher-Davidson gravitometer. Molecular weights were determined by the depression in the freezing point of benzene caused by a weighed amount of substance. A Beckmann thermometer was used to measure the freezing point depression.

Hydrogenation of the chlorosilanes produced was done in the apparatus described (Fig. 8). Lithium aluminum hydride dissolved in ether placed in the separatory funnel and added at a rate such as to cause gentle reflux. Nitrogen gas was bubbled through the flask to stir the mixture. After complete addition of the chlorosilane solution, reflux was maintained for a short time by heating on a steam-cone or a Glass-col. After refluxing, all the liquids were distilled from the reaction flask and collected together. If the desired disilyl alkane boiled very much above the boiling point of ether, a higher boiling liquid was added as a "chaser" before distillation. The distilled solution was then fractionated through the column described previously.

PREPARATION OF THE COPPER-SILICON MIXTURE

Copper, which had been supplied in powder form*, was screened to various

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* The copper was donated free of charge by Canadian Copper Refineries Ltd., Montreal East, P.Q.

sizes. Similarly, 97.6 per cent silicon powder* was screened to the same sizes as the copper. Mixtures of the powders were made consisting of nine parts of silicon powder to one part of copper powder by weight. Particle sizes of the various mixtures are given in Table IV.

TABLE IV

Particle Sizes of Copper-Silicon Mixtures

Mixture	Size (A.S.T.M. Mesh) Copper	Silicon
A	-50,+100	-50,+100
B	-100,+150	-50,+100
C	-100,+150	-100,+120
D	-150,+200	-100,+120
E	-100,+150	-120,+150
F	-150,+200	-120,+150
G	-100,+150	-100,+150
H	-150,+200	-100,+150
J	-150,+200	-150,+200

Pellets were made of several of the mixtures**. These pellets were one-half inch in diameter and about one-quarter inch thick but most were of poor quality. They are described in Table V.

TABLE V

Properties of Pellets from Different Mixtures at Various Pressures

Mixture	Pressure tons/in.^{2}	Properties
A	5	Fair pellet, edges crumbled, brittle
B	5	Similar to A, not as good
G	5	More brittle than A
J	5	Very brittle, caps
A	15	Good pellet, least brittle, edges strong, some pellets cap
B	15	No pellets formed in press
A+J(1:1)	15	No pellets formed in press

Because of the hardness of the silicon, the pelleting machines were

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* The silicon was donated free of charge by St. Lawrence Alloys and Metals Ltd., Beauharnois, P.Q. It contained as impurities: Fe, 0.89% -- Al, 0.78% -- Ca, 0.24% -- Mn, 0.03% -- 0.01% when a representative sample was analyzed by the donor. ** Pelleting was done at Defence Industries Limited, Cherrier, P.Q. Labor and the use of pelleting machines were donated free of charge by the company.

scored badly in a short time. Graphite was added to the mixture to act as a lubricant. However, pellets formed of these mixtures had little cohesive strength and crumbled at the slightest shock. As the pellets made from mixture A at fifteen tons pressure seemed the best a batch of this type was made.

REACTANTS

The reagents used were tested for purity by distillation of a ten milliliter sample of each and by noting the temperature when ten and when ninety per cent had distilled. The results (Table VI) were satisfactory and the reagents were used without further purification.

TABLE VI

Boiling Points of Reagents

Substance	Supplier	Corrected Boiling Point °C 10%	90%	Literature (2) Boiling Point °C
Dichloromethane	B	40.7	40.7	40.1
Chloroform	E	61.0	61.5	61.3
1,1-Dichloroethane	K	55.8	57.8	57.3
1,2-Dichloroethane	C	83.0	84.0	83.6
1,2-Dichloropropane	B	95.1	96.1	96.8
1,4-Dichlorobutane**	D	152	153	155*
1,4-Dichlorobutane**	D	f.p.=-38.8		f.p.= -38.7
Titanium tetrachloride	S	131.5	132.0	136

B = Brickman & Co., Montreal; K = Eastman Kodak Co., Rochester; C = Chemicals Ltd., Montreal; D = E.I. DuPont DeNemours & Co. Inc., Wilmington; E = Eimer & Amend, New York; S = Chemical Specialties Ltd., Montreal.

* Ref. 110.
** The 1,4-dichlorobutane was donated by E.I. DuPont DeNemours & Co. Inc., free of charge, to whom grateful acknowledgment is expressed.

The pellets, 150 grams, were placed in the furnace. The system was flushed with oxygen-free nitrogen, the furnace turned on, and hydrogen passed through until furnace temperature reached 1100°C (1.6 hours). Then the heaters were turned off and the system flushed with nitrogen.

REACTION OF DICHLOROMETHANE WITH COPPER-SILICON

Synthesis of Bis-trichlorosilylmethane and Dichlorosilyltrichlorosilylmethane

Dichloromethane was passed over heated copper-silicon several times under different conditions. It was found that a furnace temperature greater than 340°C was necessary to obtain any product. The rate of addition of the dichloromethane had no effect on the yield. When conditions were correct for synthesis of the desired product, there were always obtained fairly large quantities of decomposition products, including silicon tetrachloride, trichlorosilane ($SiHCl_3$) and a substance that condensed in the dry-ice trap, was volatile at room temperature and did not discolor bromine dissolved in carbon tetrachloride. If the temperature of the reactor was below 340°C no decomposition products and no bis-trichlorosilylmethane were produced.

In the best experiment with dichloromethane 150 milliliters were passed through the reactor in nine hours and twenty-five minutes at temperatures 350 - 390°C. This reactant contained some silicon tetrachloride. The products in the dry-ice trap were colorless liquids, those in both receivers were red-brown liquids. The flasks were stoppered and left overnight prior to distillation. In the morning, the liquids which had been red-brown in color turned black. Total yield of all products from the experiment was 63 grams. The products were distilled separately. All substances boiling above 130°C and all residues were collected. These high boiling liquids were mixed and fractionated through the Vigreux column. The fractions from 155°C to 181°C (41.5 grams) were refractionated through the glass-helix packed column. Two main fractions were obtained, 7.45 grams boiling at 160 - 167°C, Fraction

A, and 17.5 grams boiling at 178 - 181°C (most at 180.5 - 181°C), Fraction B.

Fraction A seemed to be impure as it was highly colored. It had 69.7 per cent chlorine and 20.0 per cent silicon.

Fraction B was found to have a specific gravity of 1.545 grams per milliliter at 17°C and 1.521 grams per milliliter at 23°C, as determined by weighing one milliliter delivered from a standardized pipette. Analysis of B for hydrolyzable chlorine gave values of 73.1, 74.4 and 74.6 per cent chlorine. $CSi_2H_2Cl_6$ requires 75.2 per cent chlorine.

Fraction B was a colorless, heavy liquid. It had a bright blue fluorescence when irradiated with ultra-violet light. It fumed in air and had a strong odor of hydrogen chloride.

In one experiment, the gaseous products from the furnace, which included white fumes, produced a curdy, white precipitate when bubbled through an alkaline solution. When a few drops of the liquid product were added to tenth normal aqueous sodium hydroxide there was an immediate reaction. A foul-smelling gas was given off, and a white curdy precipitate formed. When a few drops were added to dilute hydrochloric acid, a pungent-smelling gas was released and a grey curdy precipitate formed.

In all experiments, a large quantity of unreacted dichloromethane was recovered.

The first two experiments were performed with the furnace in a vertical position. Blocking of the reactor occurred frequently. Because of this trouble the furnace was dismounted and thoroughly cleaned. Most of the silicon-copper pellets had disintegrated. It was found that the blocking was due to partial disintegration of the pellets, producing a powder which formed a solid mass plugging the furnace. One pellet was found in

a most interesting condition. Apparently wherever there once was a particle of copper on the surface, pits were produced in the surface of the pellet by removal of silicon, as may be seen from the photograph, Figure 10.

One of the investigations of the products from the experiments was the measurement of refractive indices on an Abbe refractometer. After only ten refractive indices had been measured and although precautions were taken to exclude moisture, enough polymerization had taken place on the faces of the prisms to render the instrument useless and the prisms had to be reground.* Dr. M.C. Hunter (111) advised us that it was the experience of the Dow-Corning Corporation that no compound containing more than three silicon-halogen bonds should be placed in a prism refractometer.

From these experiments, two organo-silicon compounds were isolated, bis-dichlorosilylmethane and trichlorosilyldichlorosilylmethane. These are described separately below.

Bis-dichlorosilylmethane ($SiCl_3$-CH_2-$SiCl_3$)

This was a colorless, heavy liquid, which darkened quickly and smelled like hydrogen chloride. The compound discolored quickly when stored in a stoppered vial, going through many shades of yellow and red and finally turning black. It attacked rubber, cork and tin-foil quickly, turning the rubber hard and brittle, and disintegrating the cork and tin-foil. It had a refractive index at 22°C of 1.471 as determined on one sample and 1.472 on another. The density was determined to be 1.545 at 17°C and 1.521 at 23°C.

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* This was done free of charge by Taylor and Co., Montreal, to whom grateful acknowledgment is expressed.

The molecular weight cryoscopically in benzene was found to be 291. The theoretical value for $CSi_2H_2Cl_6$ is 283.

The boiling point was determined at several pressures, the temperatures corrected for stem and thermometer errors. The logarithm of the pressure and the reciprocal of the absolute temperature were calculated. The data are listed in Table VII .

TABLE VII

Pressure-Temperature Relations for

Bis-trichlorosilylmethane

p mm.	log p	t °C	T °K	$T^{-1} \times 10^3$ °K^{-1}
6	0.7782	55	328	3.049
10	1.0000	64	337	2.967
22	1.3424	78	351	2.842
38	1.5798	90	363	2.755
53	1.7243	96	369	2.710
70	1.8451	103	376	2.660
102	2.0086	114	387	2.584
143	2.1553	124	397	2.519
192	2.2833	132	405	2.469
255	2.4065	141	414	2.415
303	2.4814	147	420	2.381
366	2.5635	153	426	2.347
440	2.6435	159	432	2.315
489	2.6893	164	437	2.288
590	2.7709	171	444	2.252
644	2.8089	175	448	2.232
751	2.8756	180	453	2.208

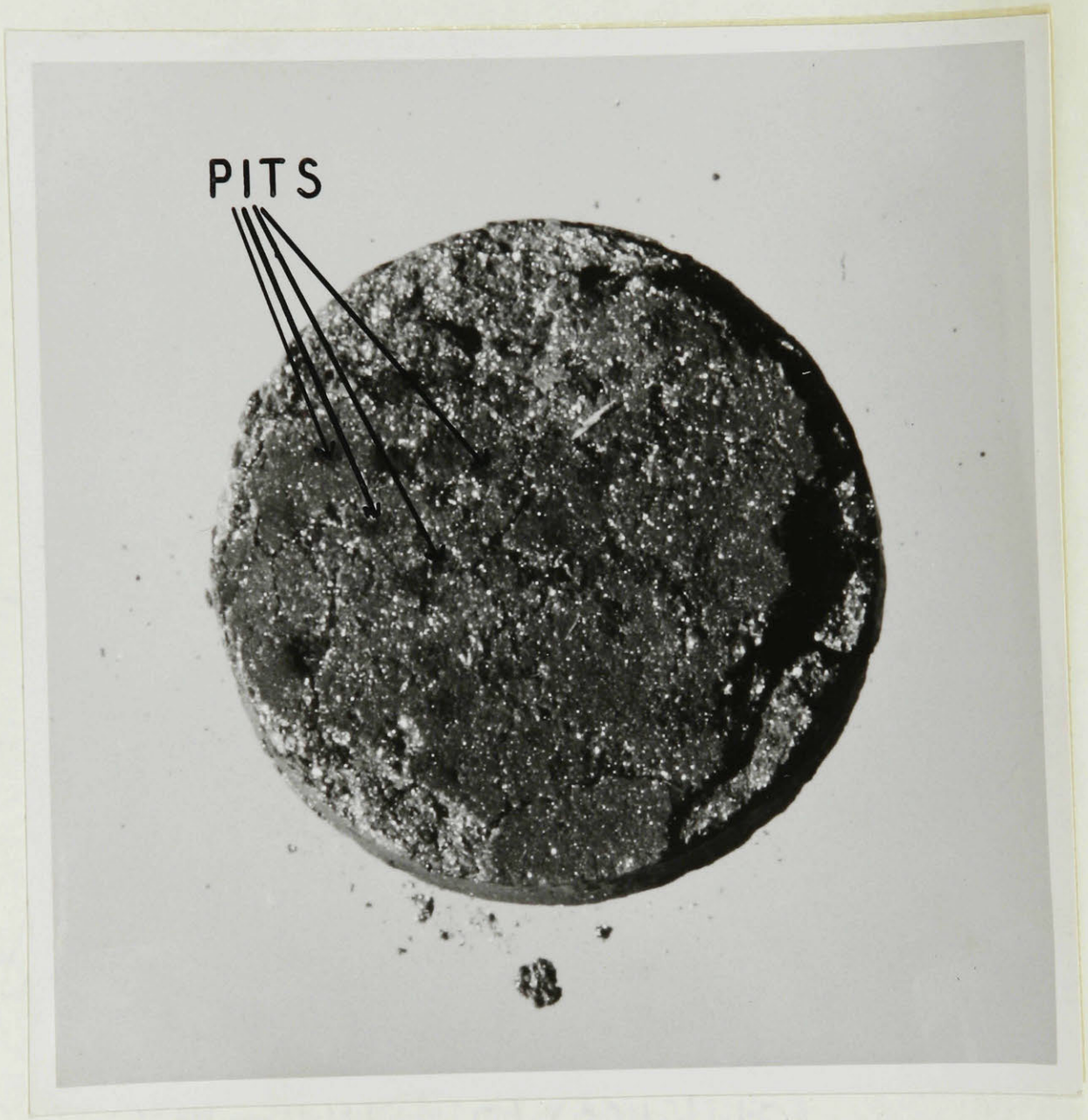
Graphs were plotted of pressure against boiling point and log pressure versus reciprocal of absolute temperature (Graphs 1 and 2). A smooth curve could be drawn through the first plot and a straight line through the points on the second. The equation of the straight line was calculated in the form of the "best-average straight line" (Ref. 3 Chap. 6) as outlined below. The equation of a straight line in general is

$$y = mx + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 2$$

and here

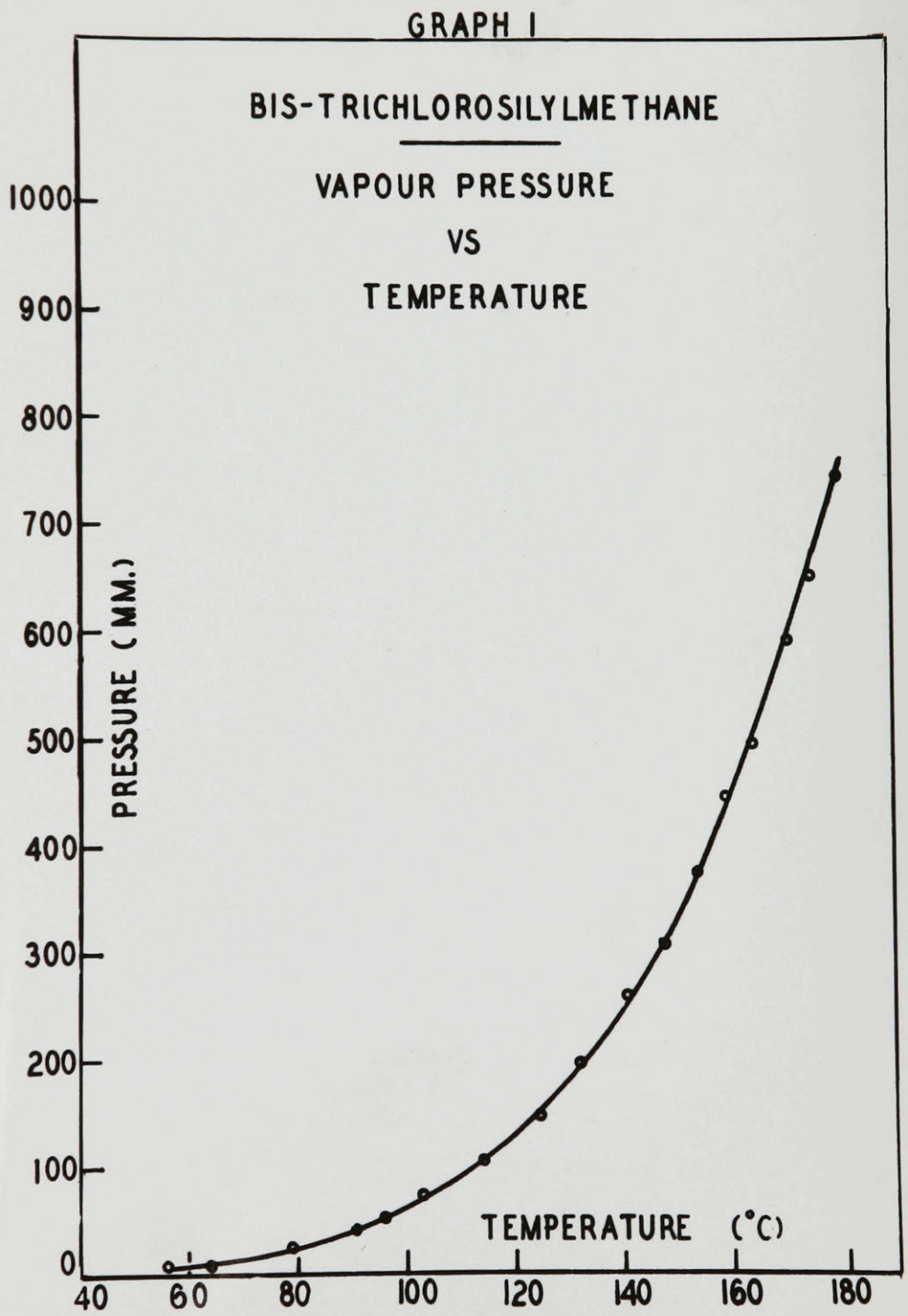
$$\log p = AT^{-1} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad 3$$

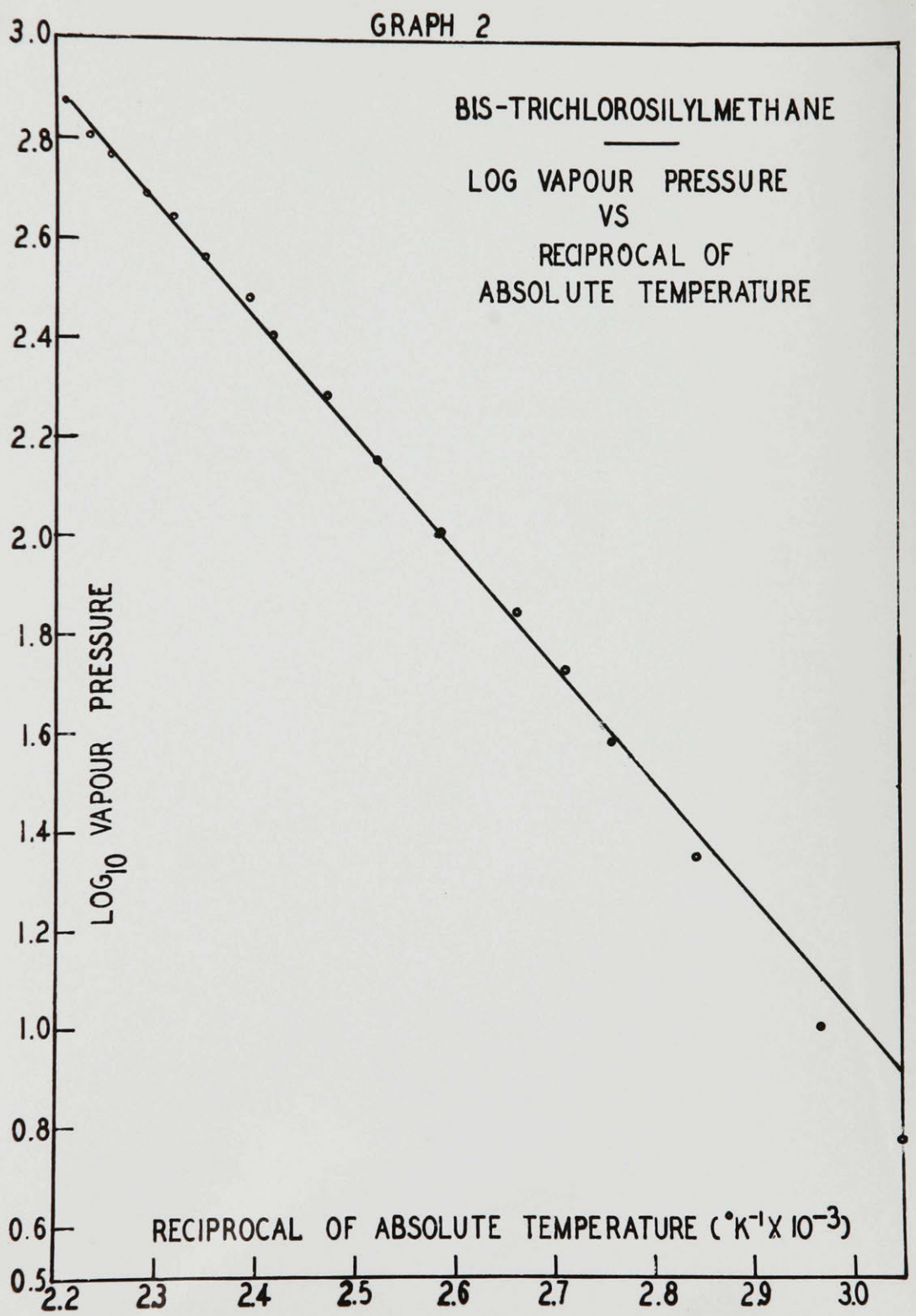
FIGURE 10



COPPER-SILICON PELLET AFTER USE
SHOWING DISINTEGRATION AND PITTING
6 X

Photographed by Mr. H. Coletta to whom grateful acknowledgment is expressed.


GRAPH I
BIS-TRICHLOROSILYLMETHANE
VAPOUR PRESSURE
VS
TEMPERATURE
PRESSURE (MM.)
1000
900
800
700
600
500
400
300
200
100
0
TEMPERATURE (°C)
40
60
80
100
120
140
160
180


GRAPH 2
BIS-TRICHLOROSILYLMETHANE
LOG VAPOUR PRESSURE
VS
RECIPROCAL OF
ABSOLUTE TEMPERATURE
LOG10 VAPOUR PRESSURE
RECIPROCAL OF ABSOLUTE TEMPERATURE (°K⁻¹ X 10⁻³)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.5
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0

For the sum of a set of values, equation 2 becomes

$$\Sigma y = m\Sigma x + nb \quad . \quad . \quad . \quad . \quad . \quad . \quad 4$$

where n is the number of the data in the set. Equation 3 is thus transformed to

$$\Sigma \log p = A\Sigma T^{-1} + nB \quad . \quad . \quad . \quad . \quad . \quad 5$$

The data for the straight line were broken into two sets of eight values and the sum of log p and of T^{-1} were obtained in each set. Two equations of the form of equation 5 were set up which were solved simultaneously for A and B. The calculation is presented below in Table VIII.

TABLE VIII

Calculation of Best-Average Straight Line

n = 8

log p		$T^{-1} \times 10^3$	
First Set	Second Set	First Set	Second Set
1.0000	2.4065	2.967	2.415
1.3424	2.4814	2.842	2.381
1.5798	2.5635	2.755	2.347
1.7243	2.6435	2.710	2.315
1.8451	2.6893	2.660	2.288
2.0086	2.7709	2.584	2.252
2.1553	2.8089	2.519	2.232
2.2833	2.8756	2.469	2.208
13.9388	21.2396	21.506($\times 10^{-3}$)	18.438($\times 10^{-3}$)

$$13.9388 = A \times 21.506 \times 10^{-3} + 8B \quad . \quad . \quad . \quad . \quad . \quad 6$$

$$21.2396 = A \times 18.438 \times 10^{-3} + 8B \quad . \quad . \quad . \quad . \quad . \quad 7$$

Solving equations 6 and 7 simultaneously

$$A = -2380$$

$$B = 8.1397$$

$$\log p = -2380T^{-1} + 8.1397 \quad . \quad . \quad . \quad . \quad . \quad 8$$

The boiling point at atmospheric pressure calculated from equation 8

is 180°C, observed 180 - 181°C. It is recorded in the literature as 184 to 185°C (32,47).

A comparison of observed and calculated boiling points at various pressures is given in Table IX. The mean deviation of the calculated from the observed values is ± 1.5°C.

From equation 8 the latent heat of evaporation may be calculated. The slope of equation 8 is multiplied by 2.303 R (R is the gas constant, and, in equation 3, A is the slope so that in equation 8 the slope is -2380).

$$L_v = 2.303\ R\ A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 9$$

$$L_v = 10{,}900 \text{ cal./ mole}$$

TABLE IX

Comparison of Calculated and Observed Boiling Points of Bis-trichlorosilylmethane

p mm.	t °C obs.	t °C calc.	$\delta t(t_{obs} - t_{calc})$
6	55	50	+5
10	64 *	60	+4
22	78	77	+1
38	90	90	0
53	96	98	-2
70	103	105	-2
102	114	115	-1
143	124	124	0
192	132	133	-1
255	141	142	-1
303	147	147	0
366	153	154	-1
440	159	160	-1
489	164	164	0
590	171	170	+1
644	175	173	+2
751	180	179	+1
760	184 **	180	+4

* $b.p._{10}$ = 64°C, Ref. 32.
** Refs. 32, 47.

Trouton's constant, a measure of the state of association of the liquid,

was obtained by dividing the latent heat of evaporation by the boiling point in ^{o}K. It was calculated to be 24.0 cal./mole/^{o}K.

Analysis of bis-trichlorosilylmethane:- Calculated for $CSi_2H_2Cl_6$:- chlorine = 75.2%, silicon = 18.8%, molecular refraction = 51.4, molecular weight = 283. Found: chlorine = 75.8, 73.1, 74.7, 74.6% silicon = 18.7%, molecular refraction = 51.5, molecular weight = 291.

Trichlorosilyldichlorosilylmethane ($SiHCl_2$-CH_2-$SiCl_3$)

This compound was found in the products from two experiments. It was a colorless liquid which turned yellow quickly and smelled like hydrogen chloride. The density at 27.5^{o}C was 1.464 as determined on the Fisher-Davidson gravitometer and the boiling point was 167 - 168°C corr. The molecular weight was determined by the depression in the freezing point of benzene and found to be 260.

Analysis of trichlorosilyldichlorosilylmethane:- calculated for $CSi_2H_3Cl_5$; chlorine = 71.2%, silicon = 22.5%, molecular weight = 249. Found; chlorine = 71.3, 70.3%, 69.7% (impure), silicon = 20.0% (impure), molecular weight = 260.

This compound has been reported only once (32). That was in a patent and the only datum was a boiling point at reduced pressure, $b.p._{10\ mm}$ = 51.0 - 52.5^{o}C.

REACTION OF 1,1-DICHLOROETHANE WITH COPPER-SILICON

Synthesis of 1,1-Bis-trichlorosilylethane

No correlation of the yield of the chlorosilyl alkane with either the rate of addition of the chloroethane or with the furnace temperature was observed in the several experiments performed.

The best experiment was done with the furnace at 360 - 380°C, rate of addition of 1,1-dichloroethane was 0.5 grams per minute. A yield of

7% 1,1-bis-trichlorosilylethane was obtained, calculated on the basis of unrecovered reactant (equation 10).

$$3\ C_2H_4Cl_2 + 2\ Si \longrightarrow C_2H_4(SiCl_3)_2 + \ldots \quad . \quad . \quad 10$$

In this experiment 55 milliliters of reactant were passed through the furnace in one and one-half hours. Sixteen grams of product condensed in the steam-heated trap. An unweighed amount of liquid in the dry-ice trap was volatile at room temperature and did not discolour bromine in carbon tetrachloride. When distilled, 13.3 grams of liquid were collected from 100°C to 211°C. Of this 4.4 grams (A) boiled at 191 - 194°C and after transfer to a smaller flask a further 0.7 grams (B) boiled at 190 - 204°C. Determination of chlorine in A showed 71.1 per cent. Silicon was found as 18.9 per cent. Density by gravitometer was 1.454 at 27.5°C. Sample A was 1,1-bis-trichlorosilylethane.

As in the experiments with dichloromethane, in several experiments a substance condensed in the dry-ice trap; it was volatile at room temperature and did not decolourize a bromine solution. Large quantities of silicon tetrachloride and trichlorosilane were again generated. In contrast to the results found with dichloromethane, in these experiments with 1,1-dichloroethane large quantities of decomposition products were formed even when yields of organo-silicon compounds were nil.

1,1-BIS-TRICHLOROSILYLETHANE ($\begin{matrix} SiCl_3 \\ SiCl_3 \end{matrix}\!\!>CH\text{-}CH_3$)

This compound had much the same properties as the other chlorinated disilyl alkanes prepared. It was a colourless, heavy liquid ($d^{27.5} = 1.454$) which turned yellow quickly. It fumed in moist air and smelled like hydrochloric acid. The boiling point found, 191°C, seemed consistent with the postulated structure.

The vapour pressure curve was investigated as outlined for bis-tri-

chlorosilylmethane. The resulting data are in Table X . Graphs were plotted of pressure versus temperature and log pressure versus reciprocal of absolute temperature (Graphs 3 and 4). Calculation of the best average straight line from the data for log pressure and reciprocal of absolute temperature gave the equation

$$\log p = -2425T^{-1} + 8.1089 \quad . \quad . \quad . \quad . \quad . \quad 11$$

TABLE X

Pressure-Temperature Relations for

1,1-Bis-trichlorosilylethane

p mm.	log p	t °C	T °K	$T^{-1} \times 10^3$ °K^{-1}
25	1.3979	90.3	363.5	2.75
50	1.6990	104.5	377.7	2.65
100	2.0000	122.3	395.5	2.52
150	2.1761	135.0	408.2	2.45
200	2.3010	144.2	417.4	2.40
250	2.3979	151.5	424.7	2.35
300	2.4771	157.4	430.6	2.32
350	2.5541	161.0	434.2	2.30
400	2.6021	168.2	441.4	2.26
450	2.6532	171.5	444.7	2.25
500	2.6990	173.2	446.4	2.24
600	2.7782	184.0	457.2	2.19
650	2.8129	186.5	459.7	2.18
700	2.8451	187.6	460.8	2.17
763	2.8825	194.9	468.1	2.14

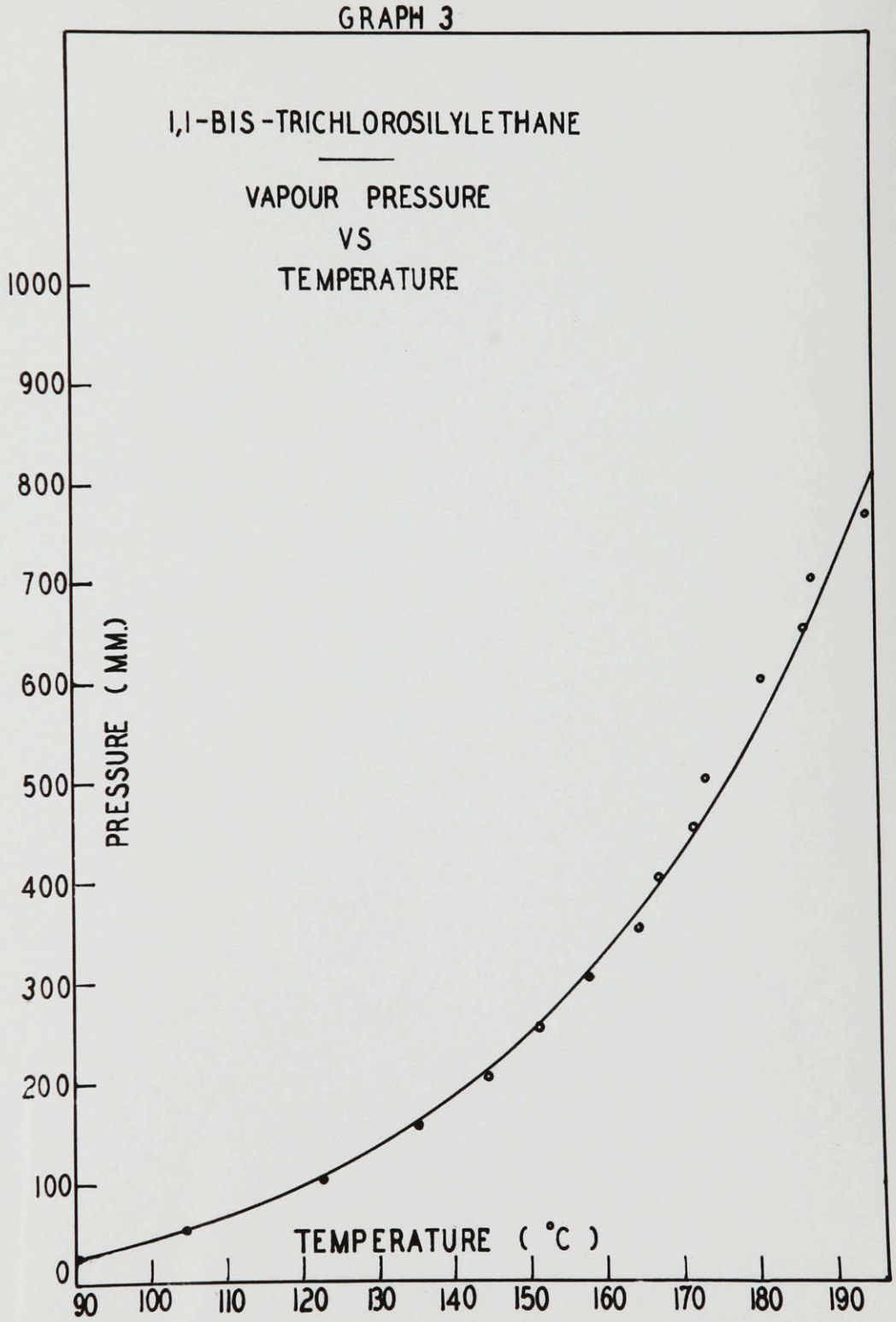
By calculation, L_v = 11,090 cal./mole and Trouton's constant L_v/T = 23.7 cal./mole/°K.

The boiling points calculated from equation 10 at various pressures are compared with the observed values in Table XI .

The average deviation of calculated from observed boiling points was ± 1.2°C. The boiling point of 1,1-bis-trichlorosilylethane at one atmosphere pressure calculated from equation 11 was 190.6°C.

Analysis of 1,1-bis-trichlorosilylethane:- Calculated for $C_2Si_2H_4Cl_6$: chlorine, 71.7%; silicon, 18.9%. Found: chlorine, 71.8, 70.3, 70.2, 71.1%; silicon, 18.7, 19.0, 18.9%.

GRAPH 3


1,1-BIS-TRICHLOROSILYLETHANE
VAPOUR PRESSURE
VS
TEMPERATURE
PRESSURE (MM.)
1000
900
800
700
600
500
400
300
200
100
0
TEMPERATURE (°C)
90
100
110
120
130
140
150
160
170
180
190

GRAPH 4

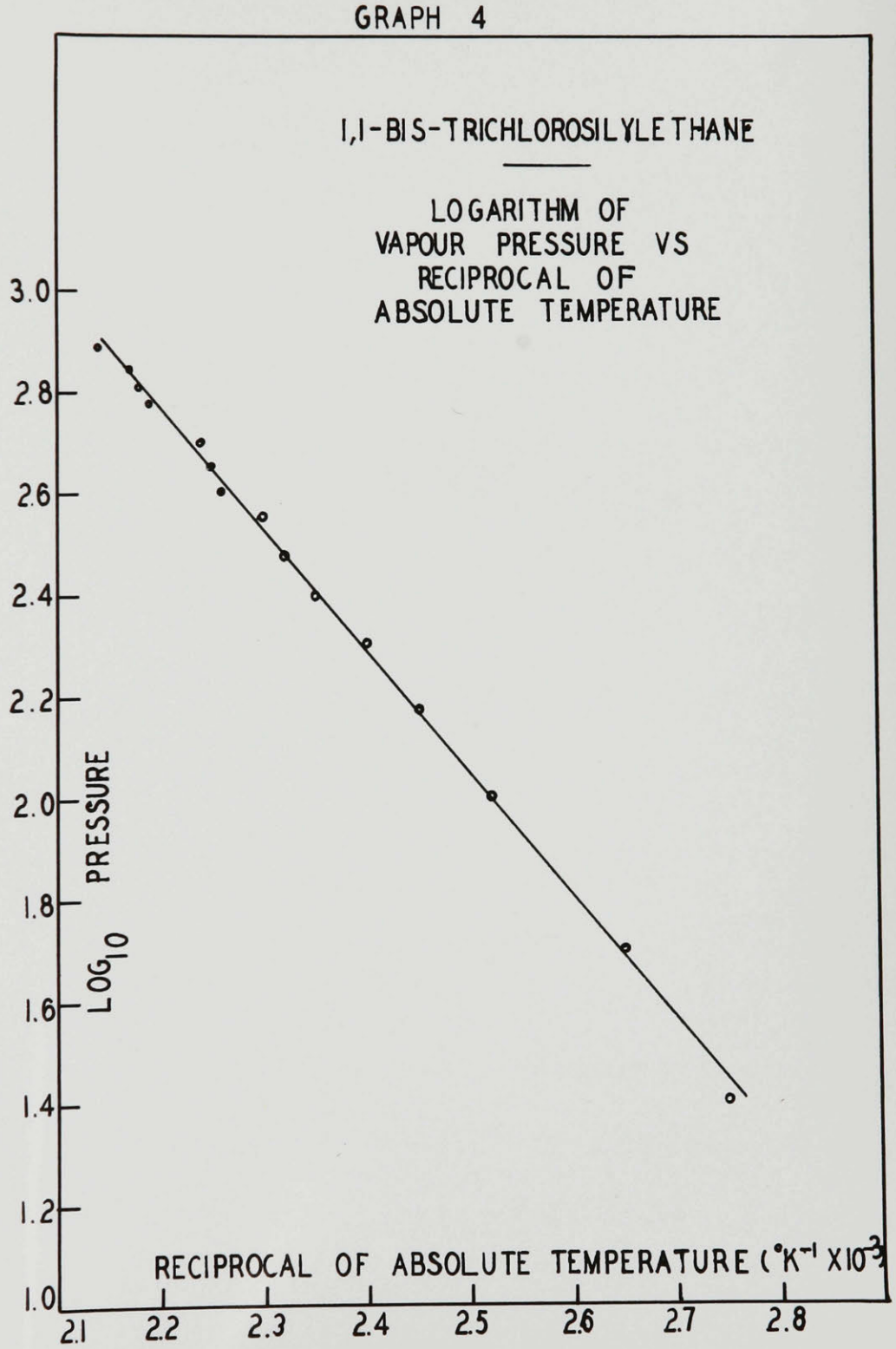

1,1-BIS-TRICHLOROSILYLETHANE
LOGARITHM OF
VAPOUR PRESSURE VS
RECIPROCAL OF
ABSOLUTE TEMPERATURE
LOG10 PRESSURE
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
RECIPROCAL OF ABSOLUTE TEMPERATURE (°K-1 X10-3)
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8

TABLE XI

Comparison of Calculated and Observed Boiling Points of

1,1-Bis-trichlorosilylethane

p mm.	t °C obs.	t °C calc.	δt ($t_{obs} - t_{calc}$)
25	90	88	+2
50	104	105	-1
100	122	123	-1
150	135	136	-1
200	144	144	0
250	152	152	0
300	157	157	0
350	161	163	-2
400	168	167	+1
450	172	171	+1
500	173	175	-2
600	184	182	+2
650	186	185	+1
700	188	188	0
763	195	191	+4

REACTION OF 1,2-DICHLOROETHANE WITH COPPER-SILICON

Synthesis of 1,2-Bis-trichlorosilylethane

The largest percentage yield of product was obtained when the furnace temperature was at 340 - 380°C and the rate of addition of the dichloroethane was two milliliters per minute. Slower rates and lower temperatures reduced the yield. If the temperature was below 330°C no organo-silicon products were obtained. Production of silicon tetrachloride, trichlorosilane and the volatile substance which did not decolourize a bromine solution took place but only at temperatures that produced appreciable quantities of the desired product.

In the best experiment, a yield of 1% of 1,2-bis-trichlorosilylethane was obtained. 400 milliliters of starting material were used. All substances boiling below 185°C were discarded and the remainder was distilled at reduced pressure. Five grams of a liquid boiling at 127° - 128°C at 100 millimeters pressure were collected, density, 1.467 at 28°C

(Fisher-Davidson gravitometer) and the molecular weight (cryoscopically in benzene) was 299. The theoretical value for $C_2Si_2H_4Cl_6$ is 297.

1,2-BIS-TRICHLOROSILYLETHANE ($SiCl_3-CH_2-CH_2-SiCl_3$)

This was a colourless liquid which turned yellow on standing and which smelled like hydrogen chloride. The density was 1.467 at 28°C.

The vapour pressure was measured at several temperatures in the apparatus previously described (Fig. 9). The data are outlined in Table XII. Graphs were plotted of vapour pressure versus temperature and log vapour pressure versus reciprocal of absolute temperature (Graphs 5 and 6).

TABLE XII

Pressure-Temperature Relations for

1,2-Bis-trichlorosilylethane

p mm.	log p	t °C	T °K	$T^{-1} \times 10^3$ °K^{-1}
100	2.0000	128	401	2.494
141	2.1492	140	412	2.427
227	2.3560	156	428	2.336
348	2.5416	170	441	2.268
509	2.7067	182	453	2.208
765	2.8837	201	472	2.119

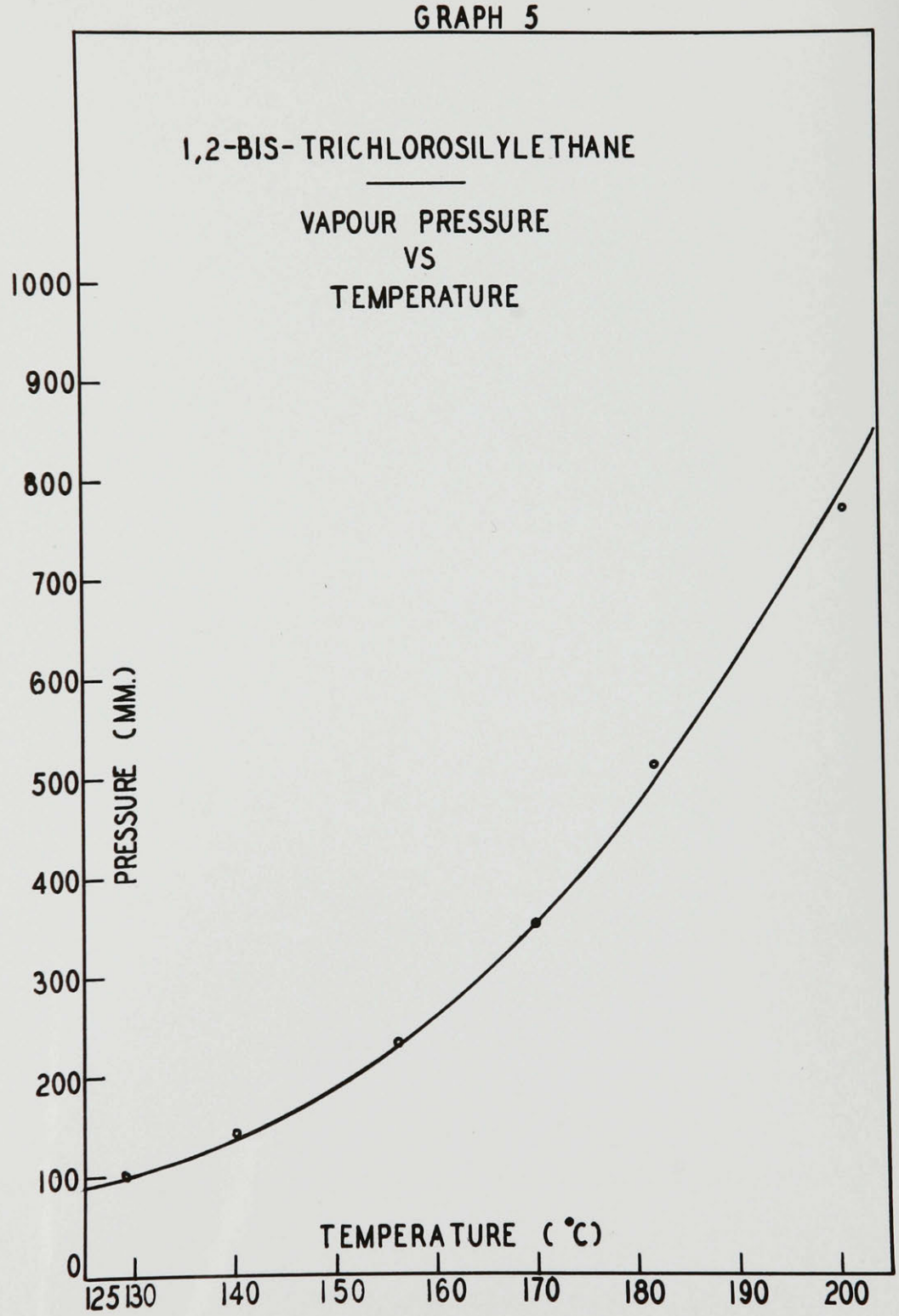
From the log p and inverse T data, the best average straight line was calculated to be

$$\log p = -2440\ T^{-1} + 8.059 \quad . \quad . \quad . \quad . \quad . \quad . \quad 12$$

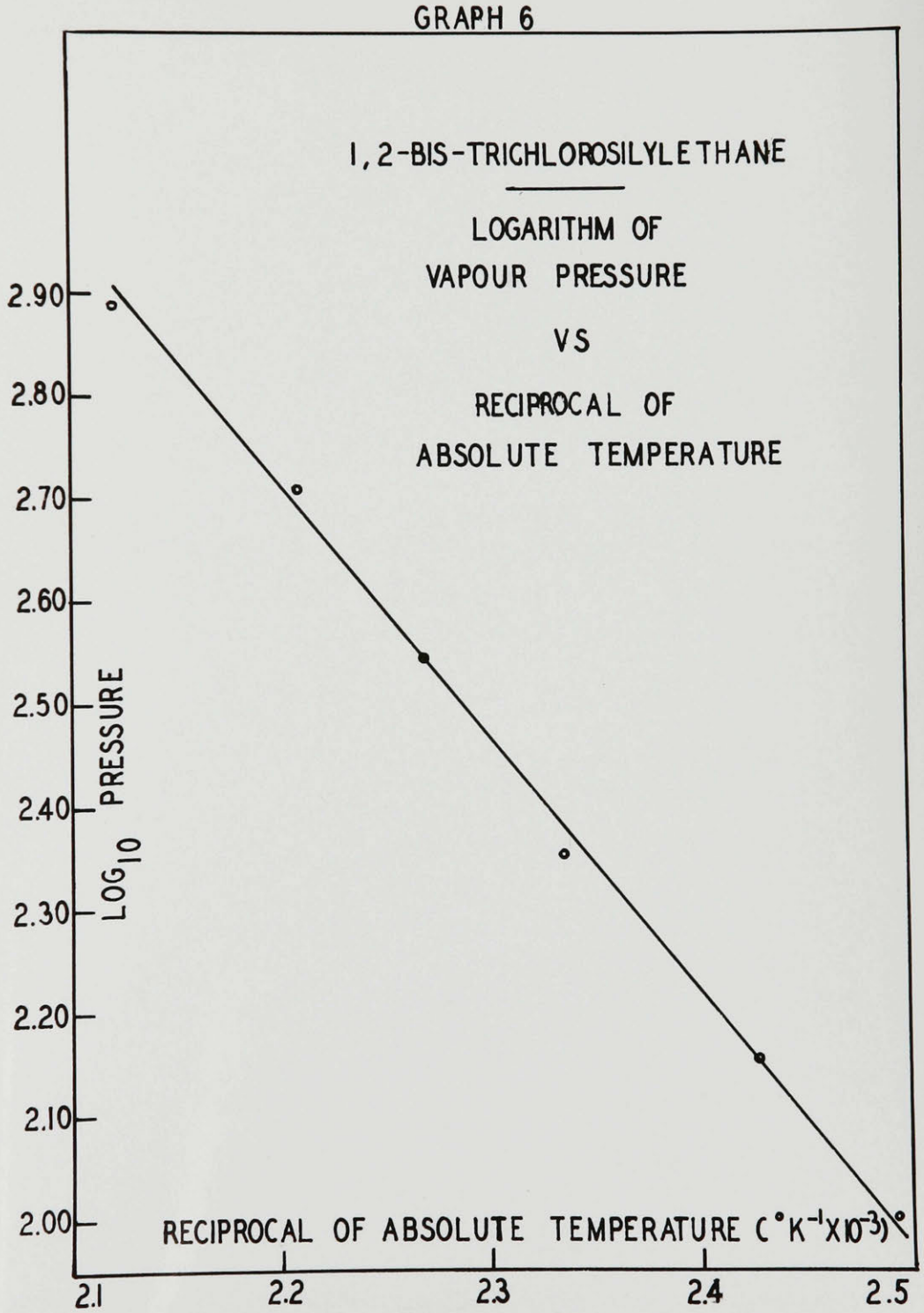
From the value of A (-2440) the latent heat of evaporation was calculated to be L_v = 11,180 cal./mole and Trouton's constant, L_v/T = 23.6 cal./mole/°K. The boiling points calculated from equation 12 are compared with the observed values in Table XIII.

The normal boiling point of 1,2-Bis-trichlorosilylethane calculated from equation 12 is 198°C. The value observed in this work was 200°C, and

GRAPH 5


1,2-BIS-TRICHLOROSILYLETHANE
VAPOUR PRESSURE
VS
TEMPERATURE
PRESSURE (MM.)
1000
900
800
700
600
500
400
300
200
100
0
TEMPERATURE (°C)
125
130
140
150
160
170
180
190
200

GRAPH 6


1,2-BIS-TRICHLOROSILYLETHANE
LOGARITHM OF
VAPOUR PRESSURE
VS
RECIPROCAL OF
ABSOLUTE TEMPERATURE
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
2.00
LOG10 PRESSURE
RECIPROCAL OF ABSOLUTE TEMPERATURE (°K-1X10-3)
2.1
2.2
2.3
2.4
2.5

it has been reported as 202°C (45). The average error found in the application of equation 12 was ± 1.2°C.

TABLE XIII

Comparison of Calculated and Observed Boiling Points of

1,2-Bis-trichlorosilylethane

p mm.	t °C obs.	t °C calc	$\delta t(t_{obs}-t_{calc})$
25	93 *	85	+8
100	128	130	-2
141	140	140	0
227	156	155	+1
348	170	169	+1
509	182	183	-1
765	201	199	+2

* Ref. 32. Not included in calculation of equation 12 or of average error.

Analysis of 1,2-bis-trichlorosilylethane:- calculated for $C_2Si_2H_4Cl_6$; 71.7% chlorine, 18.9% silicon, molecular weight = 297. Found; 71.8% chlorine, 19.0% silicon, molecular weight = 299.

REACTION OF 1,2-DICHLOROPROPANE WITH COPPER-SILICON

Synthesis of 1,2-Bis-trichlorosilylpropane

With this chloroalkane, the effect of temperature on the reaction with copper-silicon was opposite to that found with the previously described compounds. There was no production of organo-silicon compounds if the temperature was above 360°C, while the most successful experiment was done in the temperature range 300 - 320°C. In all experiments, whether successful or not, there was extensive production of decomposition products. More of the condensable gas was obtained at high temperature than at low.

In the most successful experiment, which yielded 1.6% 1,2-bis-trichlorosilylpropane, 510 milliliters of 1,2-dichloropropane was caused to react at a temperature of 300 - 320°C after being preheated to 350°C by

the half-heater at the upper end of the furnace. The time of reaction was six and one-half hours. A substance which condensed in the dry-ice trap but which was volatile at room temperature was bubbled through bromine in glacial acetic acid. The bromine was decolourized, but no identifiable product was obtained on distillation of the solution. 185 milliliters of the chloropropane was recovered. Three high boiling fractions were obtained which might have been the desired product, A boiling at 90-120°C at 50 millimeters, (2.3 grams); B at 91 - 100°C at 12 millimeters (1.8 grams) and C at 125 - 130°C at 12 millimeters (6.0 grams). Analyses of the three liquids showed that A had 65% chlorine, 17% silicon, B had 65% chlorine, 17% silicon, C had 68.5, 67.2% chlorine and 18.5% silicon. Theoretically $C_3Si_2H_6Cl_6$ has 68.5% chlorine, 18.1% silicon.

The three samples were combined and refractionated to yield 1.6 grams boiling at 147 - 178°C (80 mm.) and 0.9 grams at 175 - 180°C (80 mm.). The first fraction had 18.0% silicon, the second, 67.0% chlorine and 19.0% silicon.

1,2-BIS-TRICHLOROSILYLPROPANE $\left(\begin{matrix}CH_3\\SiCl_3\end{matrix}\!\!>CH\text{-}CH_2\text{-}SiCl_3\right)$

This compound was a colourless liquid which turned dark very quickly on exposure to air. It had an odour that was both musty and sharp. It was solid at the temperature of dry-ice (-78°C) and liquid at room temperature. The boiling point was measured at two pressures, $b.p._{12}$ = 125 - 130°C and $b.p._{80}$ = 175 - 180°C.

Analysis of 1,2-bis-trichlorosilylpropane:- calculated for $C_3Si_2H_6Cl_6$; chlorine, 68.5%, silicon, 18.1%. Found; chlorine, 68.5, 67.2, 67.0%, silicon, 18.5, 18.0%.

REACTION OF 1,4-DICHLOROBUTANE WITH COPPER-SILICON

Synthesis of 1,4-Bis-trichlorosilylbutane

Only one experiment was done with this reactant. 310 milliliters was passed into the reactor in five and one-half hours, the furnace being kept at 330 - 360°C. The condensing system included oil-heated traps at 200 ± 10°C between the furnace and the condenser (Fig. 7b). 200 milliliters of unreacted dichlorobutane was collected by distillation of the products from the experiment. Vacuum distillation of the residue yielded 12 grams boiling from 60°C at 4 millimeters to 132°C at 2 millimeters which contained 51% chlorine and 17% silicon. This was fractionated at reduced pressure. Only a small fraction could be isolated before extensive foaming made further distillation impossible. This small fraction boiled at 97 - 99°C at 5 millimeters pressure. There seemed to be more of the substance present boiling at the same temperature, but the foam climbed up through the helix-packed column and could not be broken.

1,4-BIS-TRICHLOROSILYLBUTANE ($SiCl_3$-$(CH_2)_4$-$SiCl_3$)

This compound was another colourless liquid with an odour both musty and sharp. Even though kept in a ground-glass stoppered vial, within five minutes of distillation a faint pink colour was noticeable and inside of an hour the liquid was bright red.

Analysis of 1,4-bis-trichlorosilylbutane:- calculated for $C_4Si_2H_8Cl_6$; chlorine, 65.6%, silicon, 17.2%. Found; chlorine, 65.5%, silicon, 17.2%.

REACTION OF CHLOROFORM WITH COPPER-SILICON

Chloroform, 240 milliliters, was passed through the furnace in four and one-half hours at 340 - 380°C. Aside from 100 grams of chloroform, no recognizable substances were found, except perhaps 1.2 grams which boiled at 140 - 150°C and which had completely decomposed in two days

even though kept in a stoppered vial. This substance may have been hexachlorodisilane, b.p., 140 - 142°C (2).

ATTEMPTED HYDROGENATION OF BIS-TRICHLOROSILYLMETHANE TO DISILYLMETHANE

In the first experiment, 15 grams of the chlorosilane was dissolved in 100 milliliters of anhydrous ether and this solution was placed in the flask (Fig. 8). Seven grams of lithium aluminum hydride* in 200 milliliters of ether was added slowly from the separatory funnel so that gentle reflux was maintained. The vapour temperature in the flask was 27°C. After all the hydride solution had been added the reaction mixture was distilled, but only ether was recovered.

In another experiment, 20 grams of lithium aluminum hydride dissolved in 300 milliliters of anhydrous ether was placed in the flask, and 42.5 grams of impure bis-trichlorosilylmethane in 100 milliliters of ether was placed in the separatory funnel. Nitrogen gas was bubbled through the solution in the flask, which was cooled in an ice-bath, and the chlorosilane solution was added over a period of one hour. Fractionation through the glass-helix packed column then yielded 10 grams boiling at 26 - 30°C. (Most came over at 26 - 27°C). During an attempt to refractionate the distillate, each bubble of vapour reaching the surface of the boiling liquid ignited with a click and a yellow-orange flash and gave clouds of white smoke. The heater was shut off and the system was flushed with nitrogen, but unfortunately when distillation was resumed there was nothing left but ether. It is believed that the 10 gram sample was disilylmethane as it boiled at the same temperature as a genuine sample prepared later.

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* Metal Hydrides Inc., Beverly, Mass.

HYDROGENATION OF TRICHLOROSILYLDICHLOROSILYLMETHANE TO DISILYLMETHANE

A solution of 24 grams of lithium aluminum hydride in 250 milliliters of ether was placed in the flask (Fig. 8) and 32 grams of the chlorosilane in 50 milliliters of ether was added through the separatory funnel. The mixture was distilled and fractionated as in the above experiment except that all systems were well flushed with nitrogen before use. Five grams were collected boiling at 26 - 27°C.

DISILYLMETHANE

The product was a colourless, mobile liquid with a musty smell, density, (Fisher-Davidson gravitometer) at 20°C, 0.754. Hydrolysis in aqueous alkali did not take place as quickly as hydrolysis of the corresponding chlorine-containing compound. During the experiments with this substance, at one time a small quantity was being transferred in the vapour state. The system had been flushed with nitrogen, but evidently not sufficiently, for when a part of the system was heated accidentally to about 70°C, an explosion took place. The glass apparatus was shattered and all except a very small quantity of the disilylmethane was lost.

The boiling point of this liquid was found at several pressures as recorded in Table XIV.

TABLE XIV

Pressure-Temperature Relations for Disilylmethane

p mm.	log p	t °C	T °K	$T^{-1} \times 10^3$ °K^{-1}
70	1.8451	-26	247	4.05
155	2.1909	-12	261	3.83
267	2.4265	+0.9	274	3.65
417	2.6201	13.5	287	3.48
760	2.8808	26	299	3.33

Graphs were plotted of pressure versus temperature (Graph 7) and log pressure versus reciprocal of absolute temperature (Graph 8). A

smooth curve was drawn joining the points in Graph 7, and the points in Graph 8 apparently fell on a straight line. The best average straight line through the points was calculated to be

$$\log p = -1370\ T^{-1} + 7.4190 \quad . \quad . \quad . \quad . \quad . \quad 13$$

Table XV compares the values calculated for the boiling points with those observed.

TABLE XV

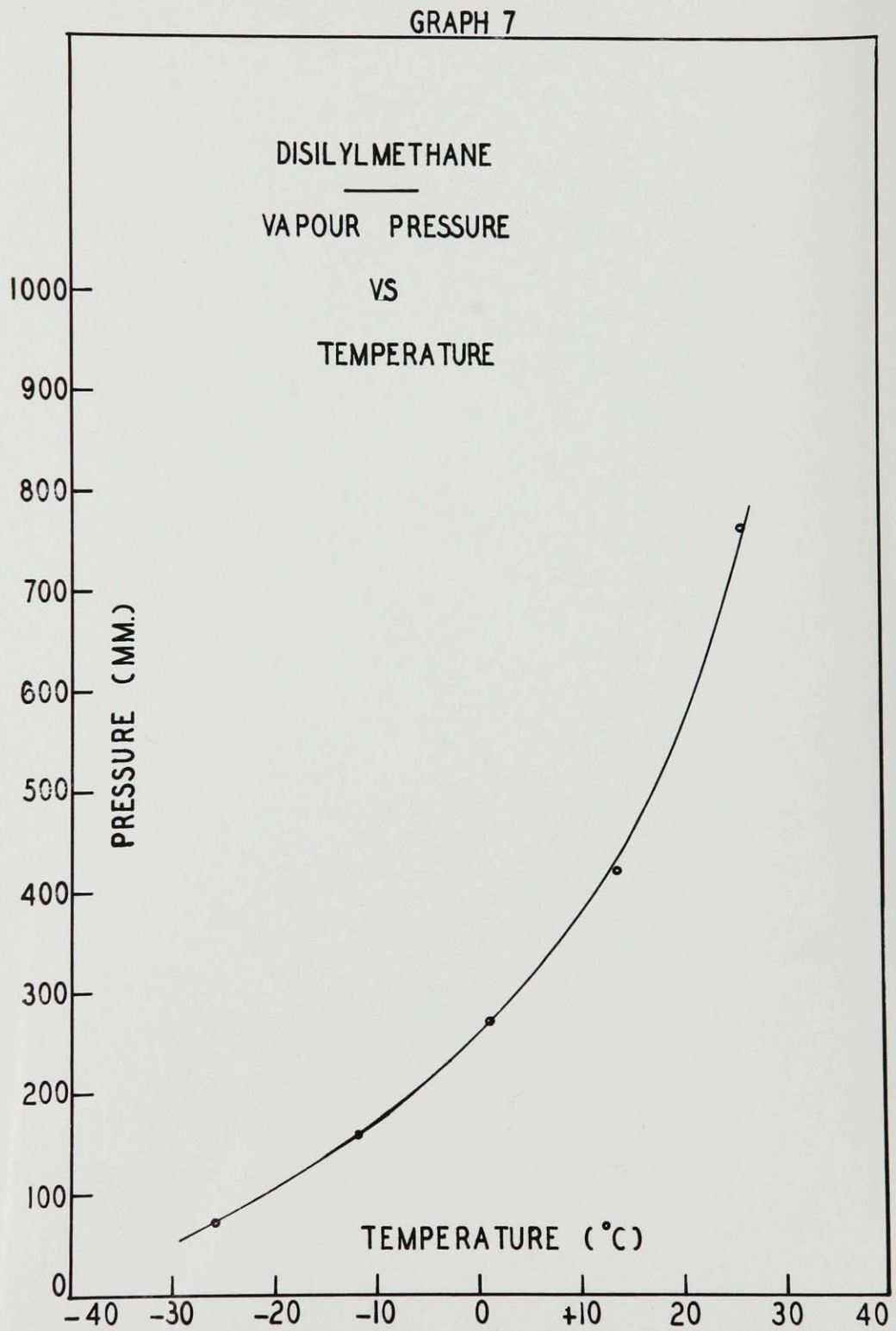
Comparison of Calculated and Observed Boiling Points of Disilylmethane

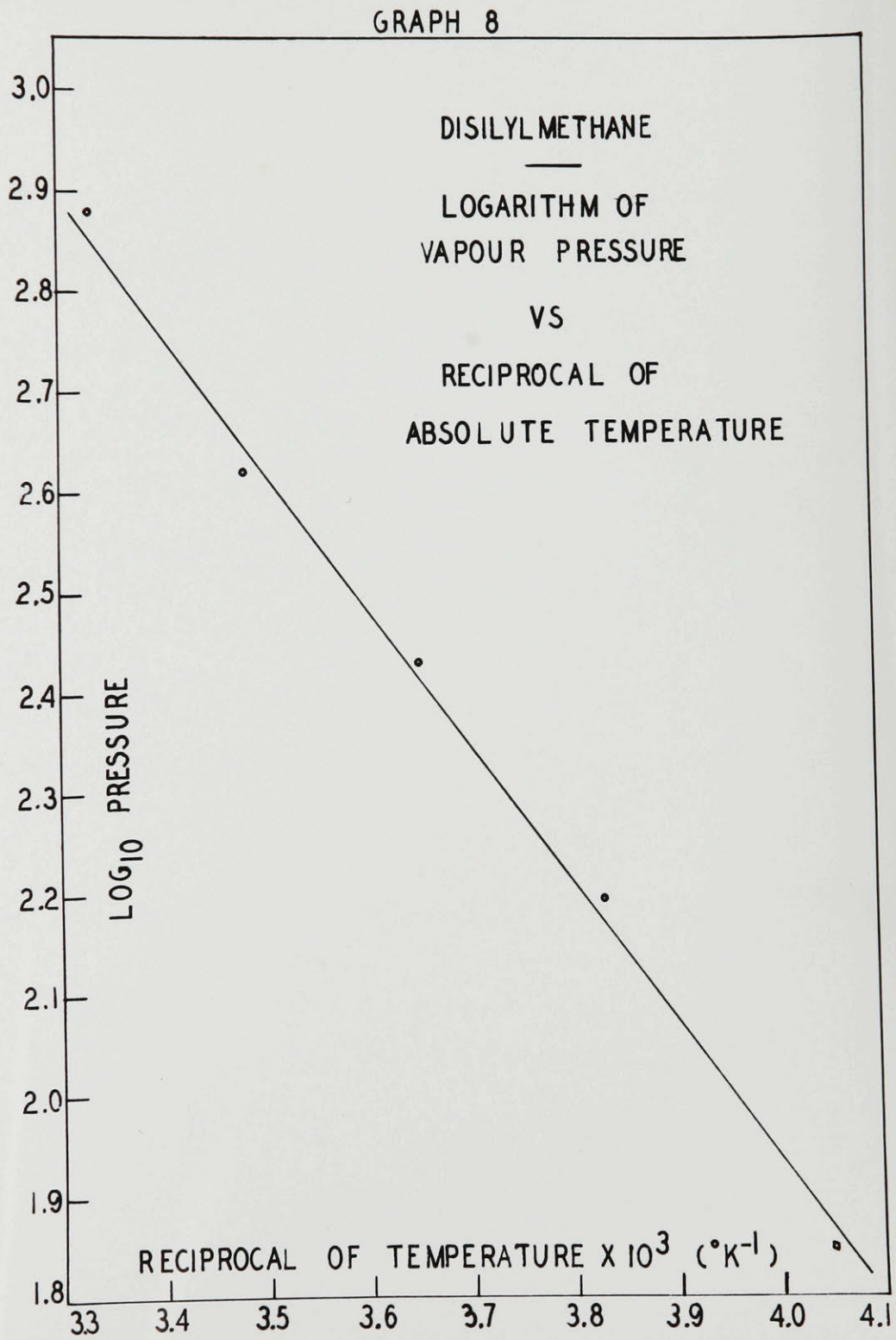
p mm.	t °C obs.	t °C calc.	$\delta t(t_{obs}-t_{calc})$
70	-26	-27	+1
155	-12	-13	+1
267	+0.9	+1.2	-0.3
417	13.5	13.2	+0.2
760	26	28	-2

The mean deviation of observed from calculated boiling points is $\pm$ 0.9°C. The latent heat of evaporation calculated from the value of A in equation 13 was L_v = 6240 cal./mole and Trouton's constant was calculated to be 20.8 cal./mole/°K.

For analysis, a small sample of the disilylmethane was weighed in a tared, sealed bulb which was then crushed below the surface of a saturated solution of potassium hydroxide contained in a closed system connected to a eudiometer. The volume of gas given off was measured, the solution was acidified with hydrochloric acid and the silicon content determined as usual.

From the 0.0219 gram sample used, 38.6 milliliters of hydrogen at N.T.P. should have been released. The amount actually measured (corrected to N.T.P.) was 19.5 milliliters or 0.504 of the theoretical amount. When the solution was removed from the system and acidified a further


GRAPH 7
DISILYLMETHANE
VAPOUR PRESSURE
VS
TEMPERATURE
PRESSURE (MM.)
1000
900
800
700
600
500
400
300
200
100
0
TEMPERATURE (°C)
-40
-30
-20
-10
0
+10
20
30
40


GRAPH 8
DISILYLMETHANE
LOGARITHM OF
VAPOUR PRESSURE
VS
RECIPROCAL OF
ABSOLUTE TEMPERATURE
LOG10 PRESSURE
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
RECIPROCAL OF TEMPERATURE X 10^3 (°K^-1)
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1

quantity of gas was evolved. It might be that the hydrolysis was incomplete or that some complex formed in such a concentrated alkaline solution. Stock (57) used 30% sodium hydroxide while saturated potassium hydroxide is about 60%. This interesting observation could not be repeated as the remainder of the disilylmethane had been lost in the explosion described above. No trouble was experienced in the silicon analysis.

Analysis of disilylmethane:- calculated for CSi_2H_8; silicon, 73.65%, hydrogen attached to silicon, 7.9%. Found; silicon, 73.6%, hydrogen attached to silicon, 4.0%.

HYDROGENATION OF 1,1-BIS-TRICHLOROSILYLETHANE TO 1,1-DISILYLETHANE

An excess (ca 10 grams) of lithium aluminum hydride dissolved in ether was placed in the reaction flask (Fig. 8) and 10 grams of impure 1,1-bis-trichlorosilylethane in 20 milliliters of anhydrous ether was added slowly. After heating under reflux for one hour, ca 20 milliliters of anhydrous benzene was added as a chaser. All liquid was distilled from the reaction flask and then fractionated. A fraction of 0.2 grams was collected boiling at 56 - 57°C.

1,1-DISILYLETHANE

This was a musty-smelling liquid which boiled at 56 - 57°C and melted at ca -50°C. It was less dense than the 30% sodium hydroxide (d_4^{20} = 1.33 (2)) solution used in its analysis.

Analysis of 1,1-disilylethane:- calculated for $C_2Si_2H_{10}$; hydrogen attached to silicon, 6.7%; Found, 6.6%.

HYDROGENATION OF 1,2-BIS-TRICHLOROSILYLETHANE TO 1,2-DISILYLETHANE

The reaction was done in the usual manner. Eight grams of impure chlorosilane in 50 milliliters of ether was added to an excess of lithium

aluminum hydride-ether solution during two hours, and the mixture was heated under reflux for an additional fifteen minutes. Sodium-dried benzene, 100 milliliters, was added and all the liquid was distilled from the flask. Fractionation gave 0.1 gram of a liquid boiling at 67.0-68.5°C.

1,2-DISILYLETHANE

This was a colourless, mobile liquid with a musty smell. It ignited very easily and burned with a luminous flame. It formed a white crystalline solid when cooled below the freezing point. It melted at -15 to -14°C and boiled at 67.0 - 68.5°C corr.

Analysis of 1,2-disilylethane*:- Calculated for $C_2Si_2H_{10}$; carbon, 26.6%, silicon, 62.2%, hydrogen, 11.2%. Found;

HYDROGENATION OF 1,2-BIS-TRICHLOROSILYLPROPANE TO 1,2-DISILYLPROPANE

Three grams of impure 1,2-bis-trichlorosilylpropane in 25 milliliters of ether was added to an excess of lithium aluminum hydride-ether solution in the hydrogenation apparatus. Addition took twenty-five minutes and the mixture was heated under reflux for a further half-hour. Dioxane was added as a chaser and all liquids were distilled from the reaction flask. The liquids were fractionated through the glass-helix packed column. No pure 1,2-disilylpropane was obtained. In the fraction boiling at 94 - 96°C corr (0.3 grams) there was 8.6% silicon. This amount corresponded to a content of 0.11 grams of 1,2-disilylpropane (98% yield). The boiling point of 1,2-disilylpropane calculated with the modified Egloff equation is 94°C (Table XXIX). The fractions boiling immediately on each side

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* The analysis was done by the National Research Council, Ottawa, to whom grateful acknowledgment is expressed.

of the above had only traces of silicon

ATTEMPTED HYDROGENATION OF 1,4-BIS-TRICHLOROSILYLBUTANE

An ether solution of 12 grams of impure 1,4-bis-trichlorosilylbutane was added slowly to an excess of lithium aluminum hydride in ether and the mixture heated under reflux for one-half hour. Thirty milliliters of redistilled anisole was added as a chaser, the liquid distilled from the reaction flask and then fractionated. No trace of a silicon-containing compound was found.

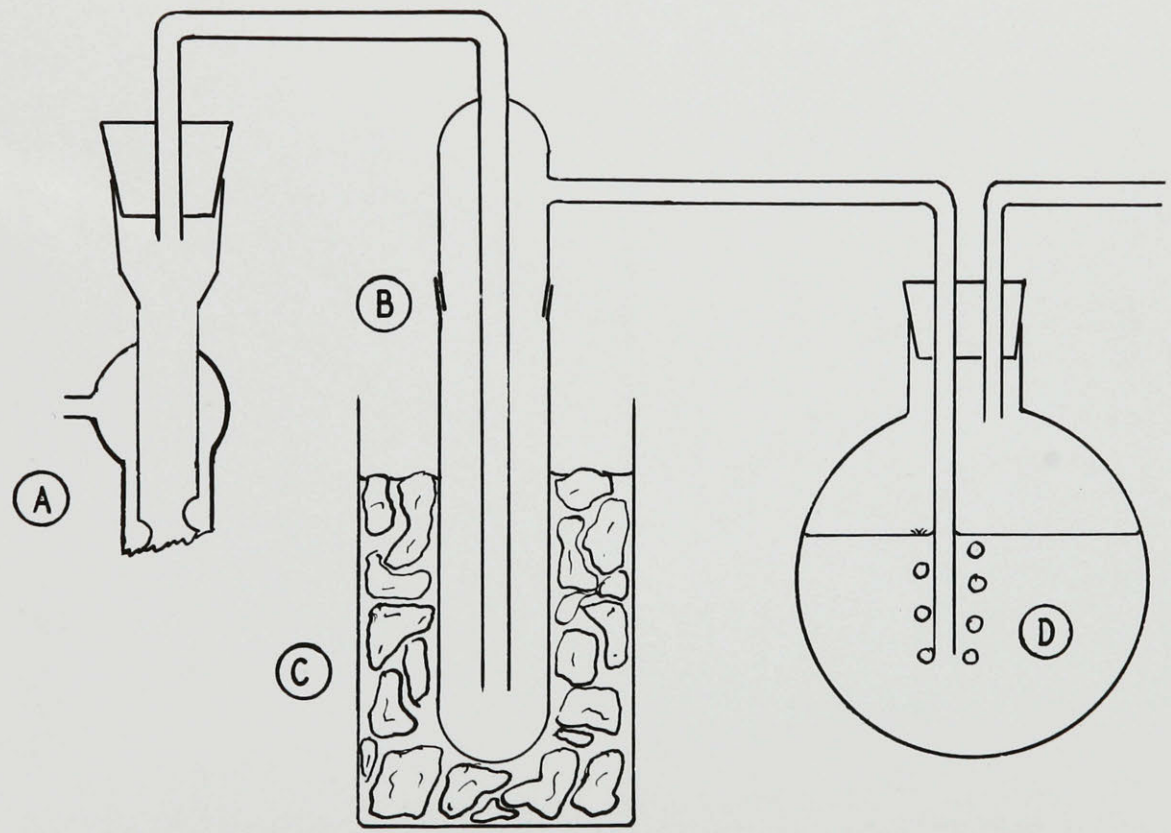
ATTEMPTED HYDROGENATION OF TITANIUM TETRACHLORIDE

The apparatus (Fig. 8) was adapted by connecting the top of the reflux condenser through a trap cooled in ice to an exit below the surface of a solution of ammonium hydroxide. An exhaust tube led from the flask containing the solution to the air (Fig. 11).

Two grams of lithium aluminum hydride was dissolved in 50 milliliters of ether contained in the flask and 17.3 milliliters of titanium tetrachloride dissolved in 150 milliliters of ether was added from the separatory funnel so as to produce gentle reflux. After complete addition reflux was maintained for two hours on a steam cone.

During addition of the titanium tetrachloride solution and for a short time thereafter a gas was evolved from the reaction mixture . This gas did not condense in the ice trap, did not dissolve in or react with the ammonium hydroxide solution, and burned with a non-luminous flame giving no deposit of solid material. No solid residue was found when the ammonia was evaporated. A trace of the tetrachloride plus a few milliliters of ether condensed in the ice trap. The solution in the reaction vessel deposited a red and then a black precipitate during the course of the reaction. In a word, no trace of a volatile product except hydrogen was found.

SYSTEM FOR DETECTION OF TiH_4



A:- WEST CONDENSER
B:- TRAP
C:- ICE BATH
D:- NH_4OH (dil)

FIGURE II

FITTING EGLOFF'S BOILING POINT EQUATION TO GROUP IV HYDRIDES

The closeness of fit of Egloff's equation

$$T = a' \log (N + b) + k \quad . \quad . \quad . \quad . \quad . \quad 1$$

or

$$T = a \ln (N + b) + k \quad . \quad . \quad . \quad . \quad . \quad 14$$

$$(a' = a \log_{10} e)$$

in the various hydrocarbon series as found by Egloff (101) led to an attempt to fit the equation to the hydrides of silicon. The compounds of this type recorded in the literature are silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8) and tetrasilane (n-Si_4H_{10}). No isomeric tetrasilane has been discovered. Higher hydrides have been prepared (112,113,114). They seemed to consist of several isomers (113, p 1700) that were never separated (112,115).

When the boiling points of the three higher silanes were substituted in equation 14, simultaneous solution for a, b and k yielded k with almost the same value as Egloff obtained from 143 hydrocarbons (Egloff k = -416.31, silane k = -415.8). When such a close approximation of values came from a tentative calculation it was decided to pursue the investigation. A search through the literature for all recorded boiling points for the silanes and the germanes yielded the data in Table XVI. A "best value" was calculated in each case where there were sufficient data to do so by weighting the values that seemed more accurate in the manner described by Egloff (116). These best values were substituted in equation 14 and the equations resulting were solved simultaneously. The value of k was assumed to be constant through both sets, but a and b were calculated separately for each element. The results of the calculation are in Table XVII.

TABLE XVI

Comparison of Boiling Points

Recorded in the Literature for Hydrides of Silicon and Germanium

Compound	Formula	Boiling Point Literature	Reference	Boiling Point "best value" °K
Silane	SiH_4	-116.0°C	117	161.6
		-112°C	112	
		-111.9°C	18	
		-111.8°C	118	
		161.95°K	119	
		-112°C	23	
		$-111.9°C_{781}$	50	
Disilane	Si_2H_6	-15°C	112	258.4
		-14.5°C	18	
		-19°C	118	
		259.0°K	119	
Trisilane	Si_3H_8	53°C	112	326.2
		52.9°C	18	
		$53.2°C_{766}$	113	
Tetrasilane	n-Si_4H_{10}	80-90°C d	112	381.2
		109°C	113	
		107.4°C	114	
		109°C	18	
Germane	GeH_4	-91 to -90°C	120	184.0
		-88.5°C *	121 *	
		184.80°K	122	Boiling point literature °K
Digermane	Ge_2H_6	29.0°C	123	302.2
Trigermane	Ge_3H_8	110.5°C	123	383.7

* This is a best value from work reported up to 1924.

TABLE XVII

Constants for the Equation $T = a \ln (N + b) + k$

Family	a	b	k
Silanes	395.8	3.5	-416.31
Germanes	446.1	3.0	-416.31

When these values were used in equation 14 to calculate the boiling points, the results were very close to those which were called the best values, except in the case of compounds with only one central atom. For these compounds the error was approximately constant, (Tables XVIII, XIX and XX), and could be compensated by introducing the new term $-\frac{18.0}{N^{\infty}}$ in equation 14. The new term is obviously equal to -18.0 if N has the value of unity but vanishes for any greater value. Thus equation 14 became

$$T = a \ln (N + b) + k - \frac{18.0}{N^{\infty}} \quad . \quad . \quad . \quad . \quad 15$$

The values of T for methane, silane and germane calculated by equation 15 are in Table XXI.

Table XVIII is abstracted from Table 2 in Egloff's paper (101) and is included for comparison. Compounds in parentheses in the tables were not used to calculate the constants.

TABLE XVIII

Calculated and Observed Boiling Points of

n-Alkanes*

$$T = 323.73 \ln (N + 4.4) - 416.31$$

Compound	No. central atoms	T obs. °K	T calc. °K	δT
(Methane)	(1)	(111.55)	(129.63)	(-18.08)
Ethane	2	184.6	184.6	0.0
Propane	3	230.9	231.6	-0.7
Butane	4	272.6	272.7	-0.1
Pentane	5	309.08	309.08	0.0

* Table 2, Ref. 101.

TABLE XIX

Calculated and Observed Boiling Points of

Silanes

$$T = 395.8 \ln (N + 3.5) - 416.31$$

Compound	No. central atoms	T obs.* °K	T calc. °K	δT
(Silane)	(1)	(161.6)	(179.0)	(-17.4)
Disilane	2	258.4	258.4	0.0
Trisilane	3	326.2	324.6	+1.6
Tetrasilane	4	381.2	381.2	0.0

* Best values, Table XVI.

TABLE XX

Calculated and Observed Boiling Points of

Germanes

$$T = 446.1 \ln (N + 3.0) - 416.31$$

Compound	No. central atoms	T obs.* °K	T calc. °K	δT
(Germane)	(1)	(184.0)	(202.1)	(-18.1)
Digermane	2	302.2	301.7	+0.5
Trigermane	3	383.7	383.0	+0.7

* Best values, Table XVI.

TABLE XXI

Calculated and Observed Values of the Boiling Points of

Compounds with One Central Atom from the Modified Equation

$$T = a \ln (1 + b) - 416.31 - \frac{18.0}{1^{\infty}}$$

Compound	a	b	T obs. °K	T calc. °K	δT
Methane	323.73	4.4	111.6	111.6	0
Silane	395.5	3.5	161.6 *	161.0	+0.6
Germane	447.8	3.0	184.0 *	184.1	-0.1

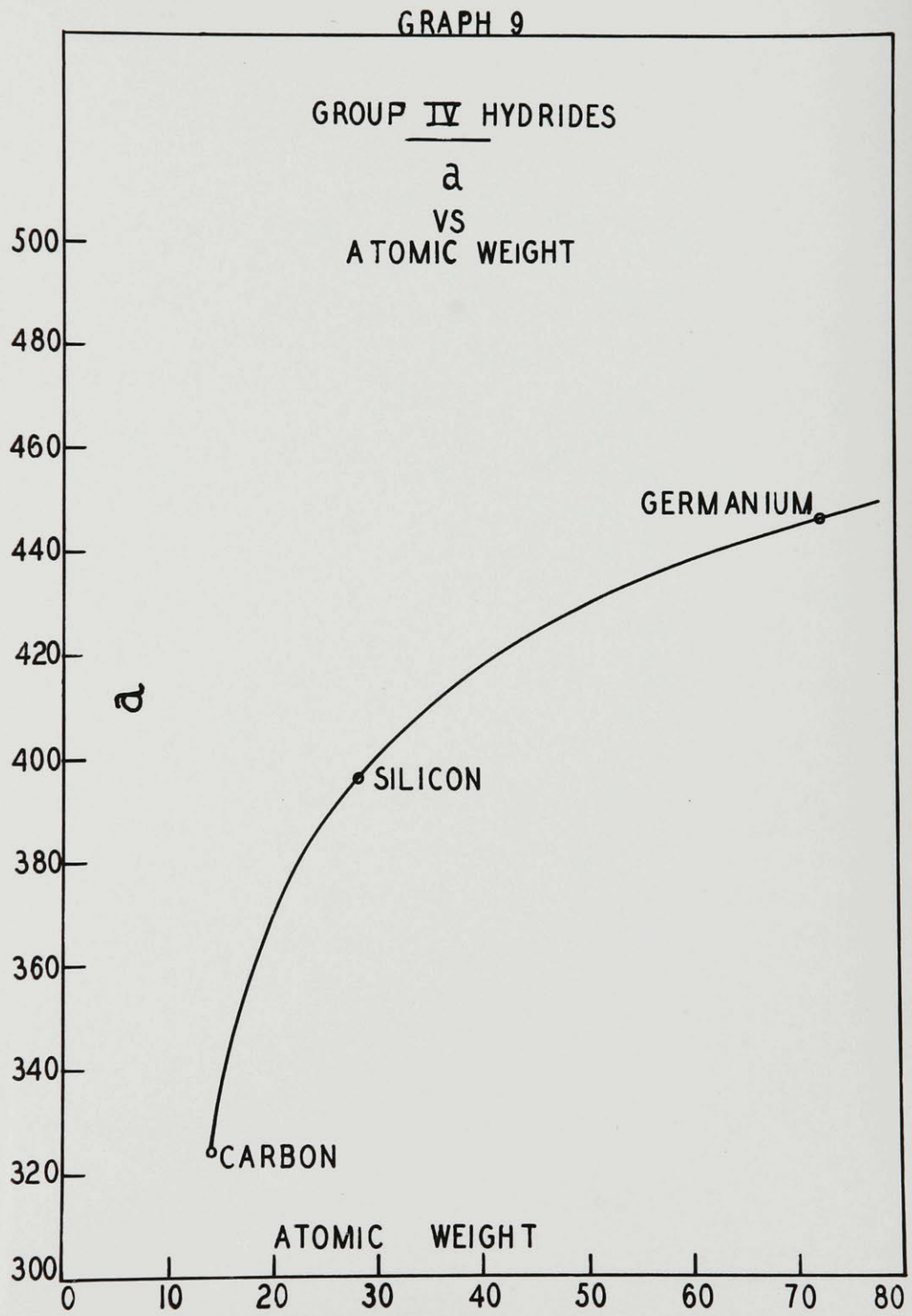
* Best values, Table XVI.

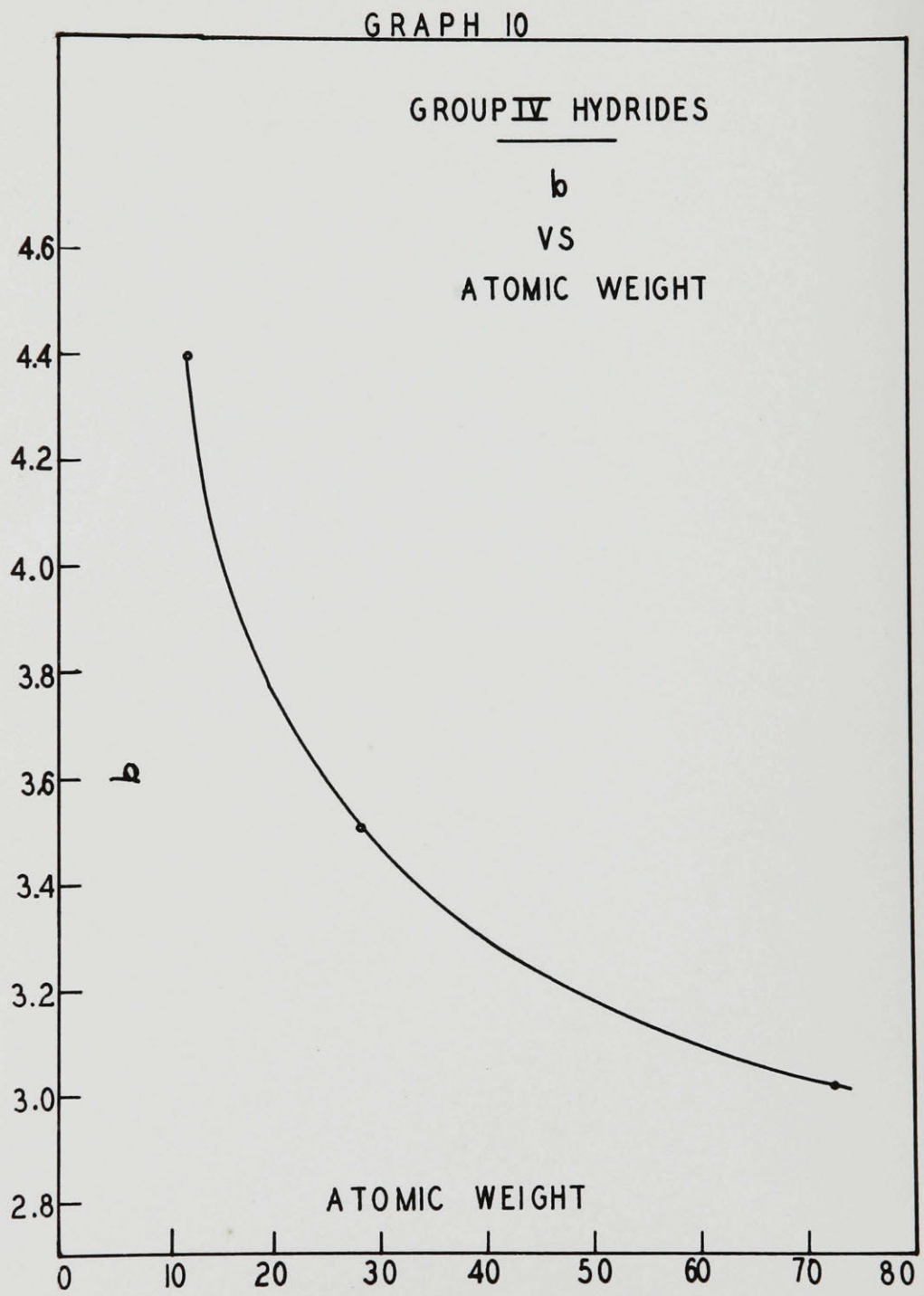
Graphs were plotted of the values of a and b against the atomic weight of the central atom for the alkanes, silanes and germanes (Graphs 9 and 10). Smooth curves were drawn through the points.

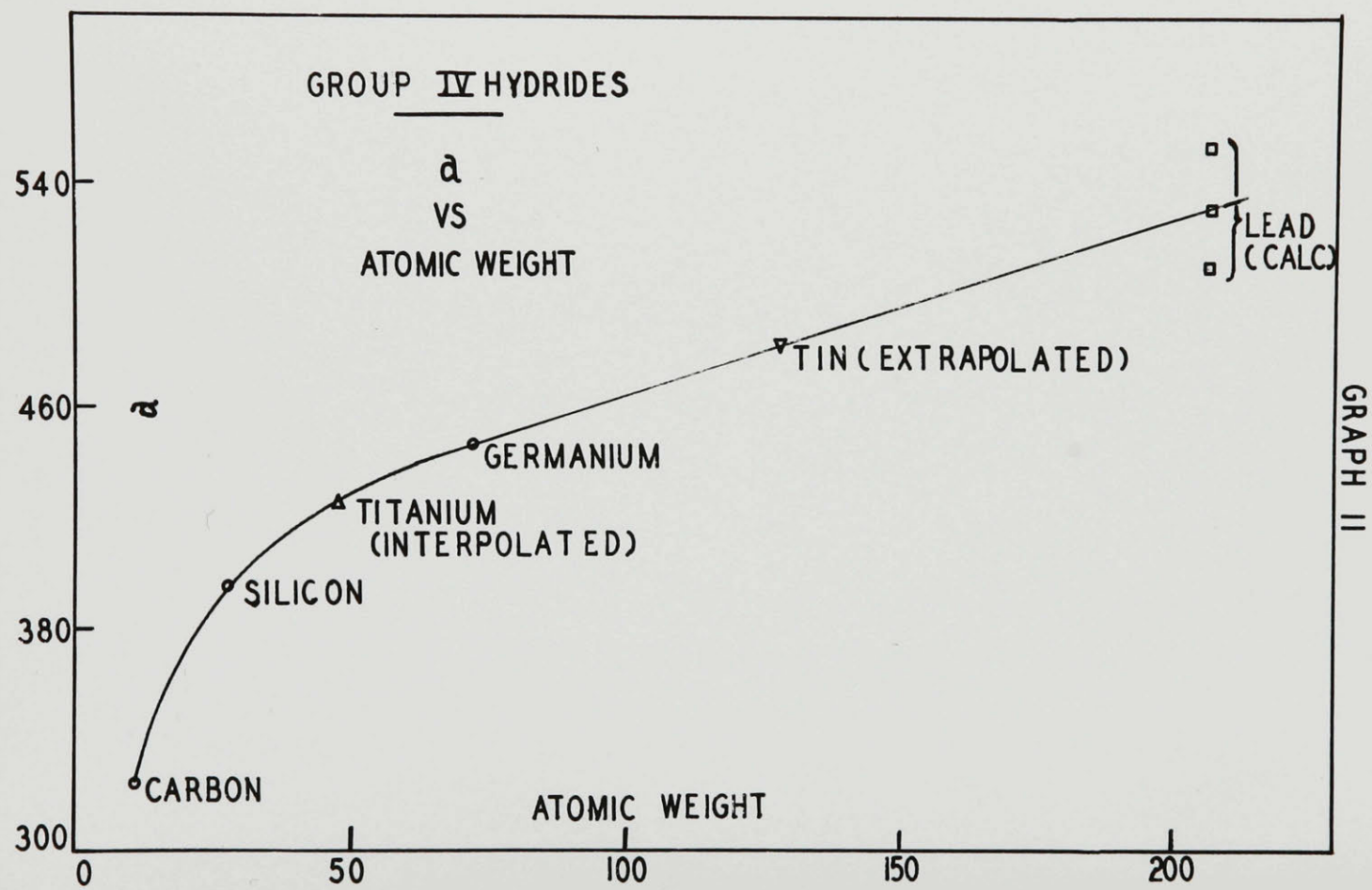
The same method of calculation of the constants for equation 15 was then used to calculate the parameters for various families of alkylsilanes. Because of the constancy of k already found, it was assumed that k = -416.31 for all normal molecules. The value that Egloff found (101) for iso alkanes (2-methyl alkanes) was used for the analagous compounds among the alkyl silanes, k = -424.51. The boiling points of the disilyl alkanes were not obtained from the literature, but from the research reported in this thesis. In both the polyalkyl silanes and disilyl alkane classes with structural isomerism, all compounds of each class were used together to calculate a and b, with whichever value of k was appropriate to the structure. The values obtained and the boiling points calculated with these values are in Tables XXII to XXVII. From the data in the last column in these tables, $\delta T = T_{obs} - T_{calc}$, the root mean square deviation of calculated from observed boiling points was obtained by squaring all the δT's, adding the squares, dividing the sum by the total number of compounds tested (including those with $\delta T = 0$) and taking the square root of the quotient. The root mean square deviation of calculated from observed boiling points is 0.71°C for the twenty-one compounds fitted to the modified form of the equation, equation 15.

Table XXV is abstracted from Table 3 in Egloff's paper (101) and is included for comparison.

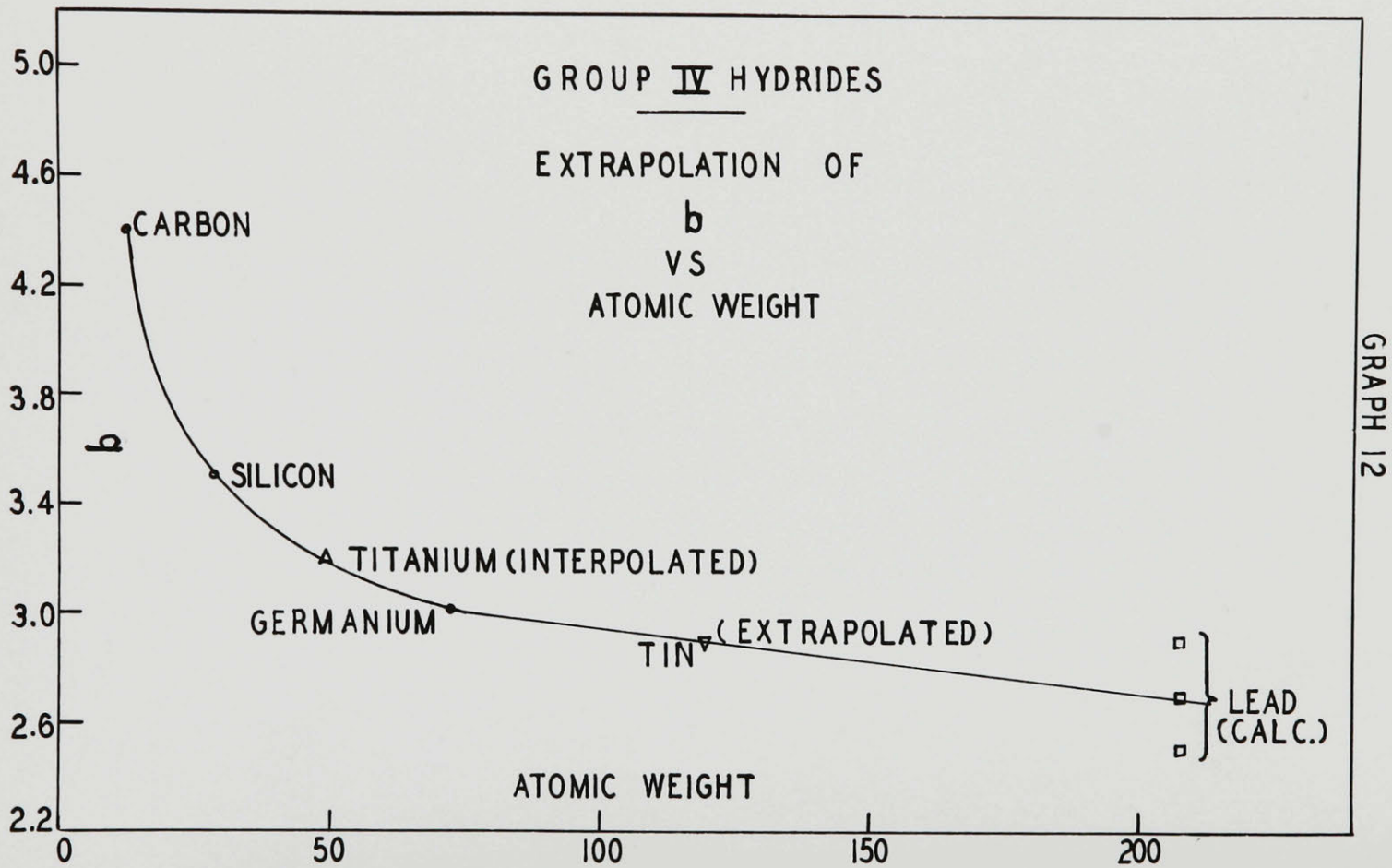
When the plots of a and b versus the atomic weight (Graphs 9 and 10) were extrapolated to the atomic weight of tin (A = 118.6) (Graphs 11 and 12), the values of a = 482, b = 2.9 were obtained. When these were substituted in equation 15 and N was taken as unity, the value of -51°C


GRAPH 9
GROUP IV HYDRIDES
a
VS
ATOMIC WEIGHT
500
480
460
440
420
400
380
360
340
320
300
a
GERMANIUM
SILICON
CARBON
ATOMIC WEIGHT
0
10
20
30
40
50
60
70
80


GRAPH 10
GROUP IV HYDRIDES
b
VS
ATOMIC WEIGHT
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
b
ATOMIC WEIGHT
0
10
20
30
40
50
60
70
80


GROUP IV HYDRIDES
a
VS
ATOMIC WEIGHT
540
460
380
300
a
LEAD
(CALC)
TIN (EXTRAPOLATED)
GERMANIUM
TITANIUM
(INTERPOLATED)
SILICON
CARBON
ATOMIC WEIGHT
0
50
100
150
200

GRAPH II


GROUP IV HYDRIDES
EXTRAPOLATION OF
b
VS
ATOMIC WEIGHT
b
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
CARBON
SILICON
TITANIUM (INTERPOLATED)
GERMANIUM
TIN
(EXTRAPOLATED)
LEAD
(CALC.)
ATOMIC WEIGHT
0
50
100
150
200

GRAPH 12

for the boiling point of stannane was obtained. According to Paneth (64), stannane boils at -52°C.

NORMAL COMPOUNDS

TABLE XXII

Calculated and Observed Boiling Points of

Mono-n-alkyl silanes

$$T = 321.1 \ln (N + 5.2) - 416.31 - \frac{18.0}{N^{\infty}}$$

Compound	No. central atoms	T obs. °K	Ref.	T calc. °K	δT
Methylsilane	2	216.3	16	216.4	-0.1
Ethylsilane	3	259	50	259	0
n-Propylsilane	4	296	50	296	0
n-Butylsilane	5	328	50	329	-1

TABLE XXIII

Calculated and Observed Boiling Points of

n-Polyalkyl silanes

$$T = 322.0 \ln (N + 5.0) - 416.3 - \frac{18.0}{N^{\infty}}$$

Compound	No. central atoms	T obs. °K	Ref.	T calc. °K	δT
Dimethylsilane	3	253	16	253	0
Diethylsilane	5	327	*	325	+2
Di-n-propylsilane	7	384	50	384	0

* $b.p._{741}$ = 56.0°C, Ref. 124; b.p. = 54°C, Ref. 50.

Extrapolation to the atomic weight of lead did not give values for a and b which would allow correct calculation of the boiling point of plumbane. This result was not surprising as the extrapolation covered almost as great a distance (A = 118 to 208) as the known curve (A =

12 to 118). In a different approach it was assumed that k = -416 and b was somewhere in the range 2.5 to 3.0. The boiling point of plumbane, (-13°C or 260°K (128)), the value of k, and values for b assumed at 0.2 intervals from 2.5 to 2.9 were substituted in equation 15 and the equation was solved for a. The resulting values of a and b (Table XXVIII) were plotted on Graphs 11 and 12 versus atomic weight. The values that gave the smoothest extrapolations were a = 531.2, b = 2.7. When the boiling points of plumbane were calculated from these with equation 15 a value of -13°C (260°K) was obtained.

TABLE XXIV

Calculated and Observed Boiling Points of

α,ω-Disilyl-n-alkanes

$$T = 342.2 \ln (N + 5.1) - 416.3 - \frac{18.0}{N^{\infty}}$$

Compound	No. central atoms	T obs. * °K	T calc. °K	δT
Disilylmethane	3	299	299	0
1,2-Disilylethane	4	340	339	+1

* This thesis.

ISO COMPOUNDS

TABLE XXV

Calculated and Observed Boiling Points of

2-Methyl alkanes *

$$T = 323.73 \ln (N + 4.4) - 424.51$$

Compound	No. central atoms	T obs. °K	T calc. °K	δT
(2-Methylpropane)	(4)	(260.9)	(264.5)	(-3.6)
2-Methylbutane	5	300.93	300.88	+0.05
2-Methylpentane	6	333.43	333.59	-0.16
2-Methylhexane	7	363.23	363.32	-0.09

* Table 3, Ref. 101

TABLE XXVI

Calculated and Observed Boiling Points of

Dimethyl-n-alkyl silanes

$$T = 322.0 \ln (N + 5.0) - 424.5 - \frac{18.0}{N^{\infty}}$$

Compound	No. central atoms	T obs. °K	Ref.	T calc. °K	δT
Trimethylsilane	4	283	125	283	0
Dimethyl-n-propylsilane	6	347	126	347	0

TABLE XXVII

Calculated and Observed Boiling Points of

α,ω-Disilyl-α-methyl-n-alkanes

$$T = 342.2 \ln (N + 5.1) - 424.5 - \frac{18.0}{N^{\infty}}$$

Compound	No. central atoms	T obs. * °K	T calc. °K	δT
1,1-Disilylethane	4	330	331	-1
1,2-Disilylpropane	5	(368 ?)**	367	+1

* This thesis. ** See Page 71.

TABLE XXVIII

Values of a for Plumbane from Various Values of b

b	a
2.5	554.0
2.7	531.2
2.9	510.7

Because of the attempt to synthesize a volatile titanium hydride (titane ?, TiH_4), we were interested in calculating its boiling point. When the values of a and b at the atomic weight of titanium were taken by interpolation from Graphs 11 and 12 and a boiling point was calculated, the value found was -98°C, from a = 425, b = 3.2 . This calculated value might be low as the boiling point of titanium tetrachloride lies above

the curve connecting the boiling points of the Group IVa tetrachlorides (Graph 13).

A comparison of the various values of a and b for all compounds investigated is given in Table XXIX.

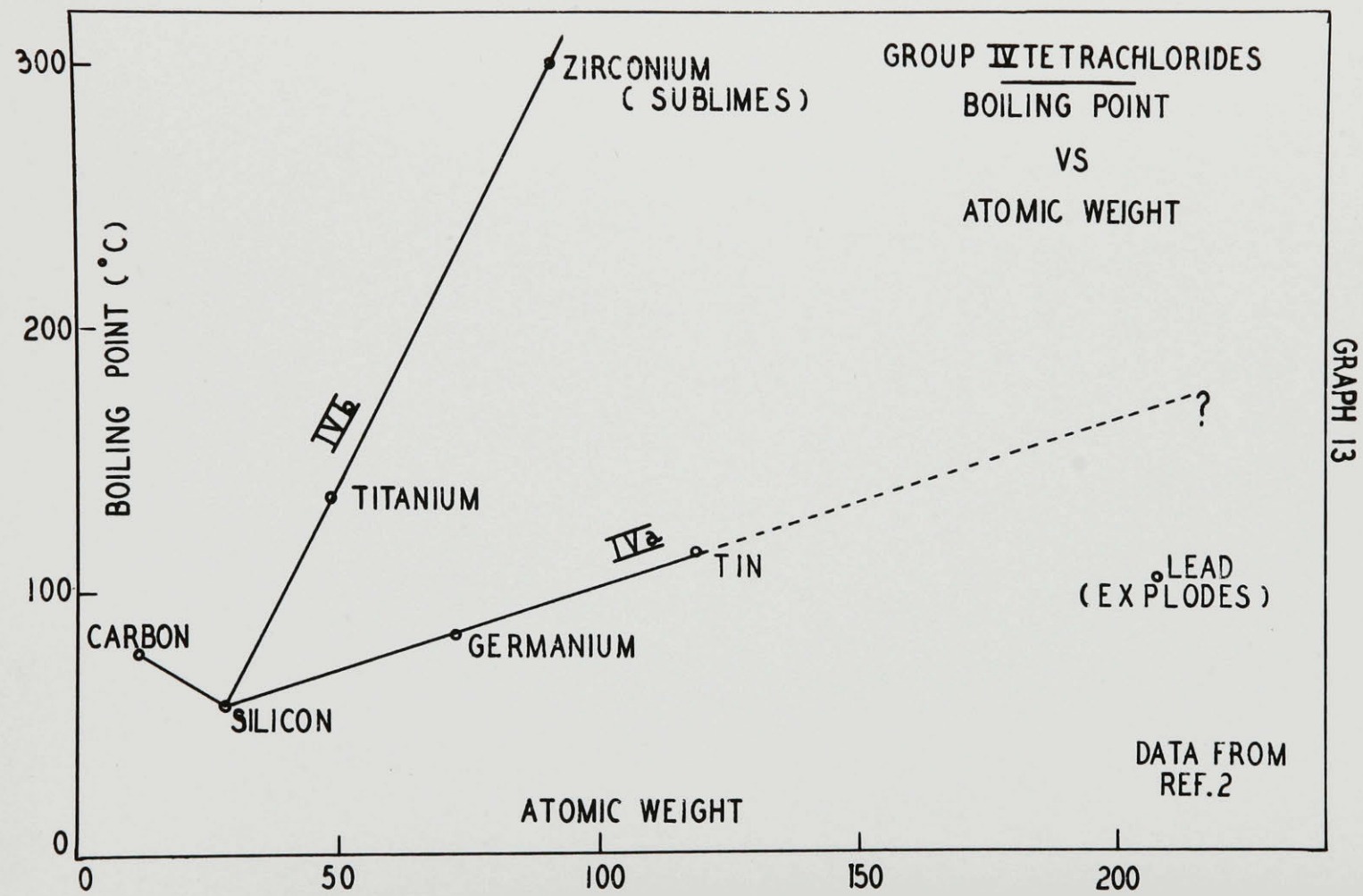
TABLE XXIX

Comparison of Constants for Equation 15

$$T = a \ln (N + b) + k - \frac{18.0}{N^{\infty}}$$

Type of Compound	a	b
NORMAL, k = -416.31		
n-Alkanes (1)	323.73	4.4
Silanes	395.8	3.5
Titane (?) (2)	425	3.2
Germanes	446.1	3.0
Stannane (3)	482	2.9
Plumbane (4)	520.6	2.8
Mono-n-alkyl silanes	321.1	5.2
n-Polyalkyl silanes	322.0	5.0
α,ω-Disilyl-n-alkanes	342.2	5.1
ISO, k = -424.51		
2-Methyl alkanes (1)	323.73	4.4
Dimethyl-n-alkyl silanes	322.0	5.0
α,ω-Disilyl-α-methyl-n-alkanes	342.2	5.1

(1) Ref. 101. (2) Interpolation of Graphs 11 and 12. (3) Extrapolation of Graphs 11 and 12. (4) See Pages 83 and 84.


GROUP IV TETRACHLORIDES
BOILING POINT
VS
ATOMIC WEIGHT
BOILING POINT (°C)
ATOMIC WEIGHT
300
200
100
0
0
50
100
150
200
ZIRCONIUM
(SUBLIMES)
IVb
TITANIUM
IVa
TIN
?
LEAD
(EXPLODES)
CARBON
SILICON
GERMANIUM
DATA FROM
REF. 2

GRAPH 13

DISCUSSION

THE ROCHOW SYNTHESIS

Synthesis of bis-trichlorosilyl alkanes by the reaction of alkyl dichlorides with silicon in the presence of copper was found to be a simple reaction to use. Temperature control was not important as long as the temperature was above a minimum in most cases. Except in the case of bis-trichlorosilylmethane yields were very low. Pretreating the copper-silicon mixture with hydrogen at high temperature was found to be unnecessary; it did not affect the yields. The rate at which reagent was passed into the furnace did not seem to affect the amount of product in any regular fashion. A similar finding in this reaction with monohalo alkanes was reported by Riccoboni and Zotta (128).

Using a vertical furnace filled with pellets turned out to be impractical; in a short time the furnace became blocked with powder as the pellets disintegrated under the influence of high temperatures and the reaction. Rochow (129) found that his pellets were very brittle and stated he knew no way to increase their tensile strength. He did not remark on any trouble caused by disintegration products. The difficulties experienced in this work may have been due to the vibration of a large motor which was nearby. The vibration may have caused the particles released by the pellets to pack together into the cake found. In a position 10° of arc from the horizontal and with the furnace half-filled with copper-silicon powder, no further trouble was experienced.

The amount of silicon tetrachloride and of trichlorosilane produced was generally much greater than the amount of the desired product.

No compounds that corresponded to products of incomplete reaction of the dichloro alkanes were recovered in any experiment, although such

products were searched for carefully. I.e. no products of the type $Cl-R-SiCl_3$ were found. This was surprising, and research as to the reason for this lack might elucidate further the actual course of the reaction.

BIS-TRICHLOROSILYL ALKANES

These compounds were all heavy, colourless liquids. They changed colour rapidly when stored, becoming black within two days, whether storage was in rubber-stoppered, cork-stoppered or tin-foil wrapped, cork-stoppered vials or in ground-glass-stoppered test-tubes. Another reaction that took place during storage was the production of compounds (unidentified) that caused foaming when the liquid was boiled. This was much more noticeable with the propane and butane compounds. It was probably due to a low molecular weight polymer.

All bis-trichlorosilyl alkanes had densities greater than 1.4 and Trouton's constant for those for which it was measured was well above 21 cal./mole/^{o}K, indicating association.

These substances fumed in moist air and smelled strongly of hydrogen chloride. They reacted very quickly with traces of moisture. Glass apparatus dried at 110°C for several hours still retained a sufficient amount of moisture on the surface to cause a film of polymer to form. The only efficient way to remove polymeric materials was found to be by soaking in concentrated alkali.

When the bis-trichlorosilyl alkanes were added to aqueous alkali, decomposition was immediate and vigorous and a white curdy, brittle mass formed. This was a highly cross-linked silica-like polymer.

REACTION OF DICHLOROMETHANE WITH COPPER-SILICON

The gas that condensed in the dry-ice trap but did not decolourize bromine in carbon tetrachloride may have been ethane or some homologue. Hydrocarbons are always found as by-products of the Rochow synthesis (130). If it was a hydrocarbon it must have been saturated as it did not add bromine. There is the possibility that it might have been methyl chloride (b.p. -24°C (2)). However, any appreciable yield of methyl chloride in the furnace should have led in turn to synthesis of trichlorosilylmethane (CH_3-$SiCl_3$) and none was found among the products.

The comparatively large yields of "hydrocarbon", chlorinated silanes and trichlorosilyldichlorosilylmethane and the low yields of bis-trichlorosilylmethane all point to extensive decomposition of the dichloromethane. This could not be avoided, at temperatures below 340°C where the decomposition was less almost none of the desired substance was produced.

BIS-TRICHLOROSILYLMETHANE ($SiCl_3$-CH_2-$SiCl_3$)

The blue fluorescence when exposed to ultra-violet light and faint phosphorescence which died quickly after such exposure that was noted for this compound was similar to the behaviour reported by Challenger and Kipping (131) for some of their alkylchloro silanes.

The high density (d^{23} = 1.521) is characteristic of chlorinated hydrocarbons and of alkylchloro silanes. For example, the density at 24°C of hexachloroethane (C_2Cl_6) is 2.04 (2), at 20°C of 1,1,1-trichloropropane ($C_3H_5Cl_3$) is 1.39 (2) and of trichlorosilylethane ($C_2H_5SiCl_3$) at 19.4°C is 1.2388 (132). However, the rate of change of density, $\delta d/\delta t$ = 0.04 grams /ml./°C, is higher than that usually found for alkylchloro silanes.

Comparison of the boiling points of bis-trichlorosilylmethane with values recorded in the literature showed that the compounds synthesized in this work boiled at a lower temperature at atmospheric pressure than compounds reported previously (Table XXX). At reduced pressure the same boiling point was observed in this work as in that previously reported.

TABLE XXX

Comparison of Boiling Points of

Bis-trichlorosilylmethane

Boiling Point °C	Pressure mm.	Source
180 - 181	760	observed, this work
180	760	calculated from eq'n 8
184 - 185	756	Ref. 47
185 - 186	764	Ref. 32
185.1 - 185.6	760	Ref. 32
64 - 65	10	observed, this work
60	10	calculated from eq'n 8
63.7 - 65	10	Ref. 47

Trouton's constant, 24.0 cal./mole/°K, showed a high degree of association of the liquid. Water has a Trouton's constant of 26, while unassociated liquids have $L_v/T \sim 21$. In comparison, the constant for methyltrifluorosilane (CH_3SiF_3) is 23.3 (133).

TRICHLOROSILYLDICHLOROSILYLMETHANE ($SiHCl_2-CH_2-SiCl_3$)

The density, $d^{27.5} = 1.464$, was slightly less than that of the fully chlorinated substance, bis-trichlorosilylmethane.

As already mentioned, the only reference to this compound in the literature (32) gave only one datum, the boiling point at 10 millimeters pressure, 51.0 - 52.5°C. In this work the boiling point was only measured at atmospheric pressure and found to be 165 - 167°C. Using the Ramsay-Young formula (139) one can calculate the boiling point of a substance at

any pressure if data are known on the boiling point of the substance at another pressure and the boiling points of a structurally similar substance are known at both pressures. The formula is

$$\frac{T_A'}{T_B'} = \frac{T_A''}{T_B''}$$

where T_A and T_B are the boiling points of the two liquids at two pressures represented by T' and T''. Using bis-trichlorosilylmethane as the reference substance, the boiling point of trichlorosilyldichlorosilylmethane at 10 millimeters pressure was calculated to be 51°C in good agreement with the recorded value of 51.0 - 52.5°C.

REACTION OF 1,1-DICHLOROETHANE WITH COPPER-SILICON

The substance which was condensed in the dry-ice trap but was volatile at room temperature was again probably a saturated hydrocarbon for similar reasons as outlined previously.

1,1-BIS-TRICHLOROSILYLETHANE $\left(\begin{matrix}SiCl_3\\SiCl_3\end{matrix}\!\!>CH\text{-}CH_3\right)$

Both Trouton's constant, 23.7, and the density, $d^{27.5} = 1.454$, were large, they were smaller than the values found for bis-trichlorosilylmethane, showing the increase in organic character with the introduction of a second carbon atom.

REACTION OF 1,2-DICHLOROETHANE WITH COPPER-SILICON

This was the only reactant for which the rate of addition to the furnace had any definite effect on the production of organo-silicon compounds. It was noted that a four-fold increase in addition rate increased the yield by 200%. This might be due to less decomposition of the product when it was forced out of the high temperature zone more quickly.

1,2-BIS-TRICHLOROSILYLETHANE ($SiCl_3$-$(CH_2)_2$-$SiCl_3$)

A comparison of various boiling points as found in this research and in the literature are given in Table XXXI. The boiling points found in this work are slightly below those previously reported.

TABLE XXXI

Comparison of Boiling Points of

1,2-Bis-trichlorosilylethane

Boiling Point °C	Pressure mm.	Source
200	765	observed, this work
198	760	calculated from eq'n 12
199 - 202	760	Ref. 42
202	760	Ref. 45
85	25	calculated from eq'n 12
92 - 93	25	Ref. 32

Trouton's constant was 23.6 cal./mole/°K, which was slightly lower than that for the 1,1- compound but it still indicated a highly associated liquid. The density was 1.467 at 28°C, denser than the 1,1- compound.

REACTION OF 1,2-DICHLOROPROPANE WITH COPPER-SILICON

With this compound, the temperature effect being opposite to that found in other cases, and the decolourization of a bromine solution by the gaseous products indicated that a different reaction was present. If the temperature became too high, the copper, instead of activating the dichloropropane by removal of one chlorine atom

$$CH_3\text{-}CHCl\text{-}CH_2Cl + Cu \longrightarrow (CH_3\text{-}CHCl\text{-}CH_2)^* + CuCl$$

removed both chlorines to produce an unsaturated compound.

$$CH_3\text{-}CHCl\text{-}CH_2Cl + Cu \longrightarrow CH_3\text{-}CH{=}CH_2 + CuCl_2$$

This is analagous to the removal of halogens with zinc which is a standard laboratory reaction.

$$R\text{-}CHCl\text{-}CH_2Cl + Zn \longrightarrow R\text{-}CH{=}CH_2 + ZnCl_2$$

1,2-BIS-TRICHLOROSILYLPROPANE & 1,4-BIS-TRICHLOROSILYLBUTANE

The odours of these two compounds were similar, and somewhat different from the odours of the lower bis-trichlorosilyl alkanes. In common with all of these compounds they smelled like hydrogen chloride, but in addition the propane and butane compounds had a musty odour like those of the disilyl alkanes. Neither of these compounds had been previously reported, but they may be compared with 1,3-bis-trichlorosilylpropane which was reported (45) to boil at 111°C at 20 millimeters pressure.

ATTEMPTED REACTION OF CHLOROFORM WITH COPPER-SILICON

The failure of chloroform to yield a silicon-substituted organic compound was not very surprising. While no attempted reactions with chloroform have been reported, it is known that if carbon tetrachloride is used in the Rochow reaction, the only identifiable products are silicon tetrachloride and hexachlorodisilane (134,135). This last compound was formed in small yields in the reaction with chloroform.

HYDROGENATION REACTIONS

Lithium aluminum hydride in ether proved to be an efficient reagent for replacing chlorine atoms with hydrogen. Reactions were completed in a short time and yields were generally good, varying from 50% to 100% in most cases. It was found better to add the chlorine compound in ether to the hydride solution than vice versa.

The yield could not be accurately calculated in most experiments as impure chlorosilyl alkanes were used. The impurities were introduced with the fractions from distillation on either side of the main fraction; these were added to the lithium aluminum hydride so as to use every trace of the

chlorosilyl alkane that could be obtained.

DISILYL ALKANES

These compounds were more stable than those containing chlorine attached to silicon. No changes were observed when samples were stored. When hydrolyzed in aqueous alkali the reaction was not quite as fast as with the bis-trichlorosilyl alkanes. The polymer formed had the same appearance. The disilyl alkanes burned with a luminous flame and gave clouds of silica. These compounds were less dense than water and had a musty odour.

SYNTHESIS OF DISILYLMETHANE (SiH_3-CH_3-SiH_3)

I) From Bis-trichlorosilylmethane

There was no product at all from the experiment when the lithium aluminum hydride solution was added to the chlorosilane while a yield of ca 100% was obtained when the chlorosilane was added to the hydride.

II) From Trichlorosilyldichlorosilylmethane

A yield of 55% of disilylmethane was obtained when the chlorosilane was added to the hydride solution. The reason for the lower yield when hydrogenation was already one-sixth complete cannot be explained with the limited data available.

DISILYLMETHANE

This compound had a density of 0.754 at 20°C which may be compared with methylsilane, d^{-57}= 0.62 (16), dimethylsilane, d^{-80}= 0.68 (16) and liquid n-propane, $d^{-44.5}$= 0.585 (2). The density of the hydrocarbon with molecular weight nearest disilylmethane (M. Wt. = 76), pentane (M. Wt. = 72) is d_4^{20} = 0.626 (2).

The amount of hydrogen released when disilylmethane was added to saturated potassium hydroxide was one-half of the theoretical amount.

More gas was released on neutralization of the resulting mixture. This reaction was not observed with other disilyl alkanes and more investigation is necessary before any reason can be given.

Disilylmethane appears to be normal and non-associated both in the liquid and the vapour states as Trouton's constant was calculated to be 20.8 cal./mole/^{o}K. Trouton's constant for ethylsilane ($CH_3-CH_2-SiH_3$) was reported as 21.0 (50).

HYDROGENATION OF 1,2-BIS-TRICHLOROSILYLPROPANE

An estimated yield of 100% was obtained but the product could not be separated from the dioxane used as a chaser as an azeotrope seemed to form. Dioxane is known to form azeotropes with hydrocarbons (136), while silicon compounds are noted for the number of azeotropes they form.(130). The azeotropes that dioxane forms with hydrocarbons boil less than 1°C below the boiling points of the pure hydrocarbons (136).

ATTEMPTED SYNTHESIS OF 1,4-DISILYLBUTANE

The reason why no product was obtained when 1,4-bis-trichlorosilylbutane was caused to react with lithium aluminum hydride is not understood. A possible explanation is that the impure liquid (that foamed when boiled) which was added to the hydride solution did not contain the chlorosilyl butane as believed. Instead, the small amount that had distilled ($<$0.1 gram) and had been used up in analytical procedures was all that had been produced in the furnace.

ATTEMPTED HYDROGENATION OF TITANIUM TETRACHLORIDE

It was assumed that the condensation temperature of a volatile hydride of titanium would not be as high as o^{o}C from the calculated boiling point of -98°C and allowing for an increment due to the different nature of Group IVb elements (Pages 85 and 86). Thus it should not have con-

densed in the ice-cooled trap. If formed, it would almost certainly have reacted with the dilute aqueous alkali, as do almost all co-valent compounds of the Group IV elements except carbon. If the hydride reacted invisibly with the alkali forming a soluble product, there would have been a deposit when the solution was evaporated. If any passed through the alkali unchanged it should have given a deposit when burned. If a volatile titanium hydride had condensed in the ice-trap it would probably have produced a colour change with the titanium tetrachloride that was known to have condensed there. It is known that lower hydrides of titanium (solids) reduce the tetrachloride to the brilliantly-coloured lower chlorides (137).

The highly coloured precipitates in the reaction flask were probably due to the formation of the lower chlorides ($TiCl_3$-violet, $TiCl_2$-glistening black (64)). Both lower chlorides are solids insoluble in organic solvents.

It was concluded that no volatile hydride of titanium had been produced. The reaction probably proceeded

$$TiCl_4,\ LiAlH_4 \longrightarrow TiCl_3,\ TiCl_2,\ LiCl,\ AlCl_3,\ H_2.$$

In view of the ease of preparation and large yields of stannane obtained from tin tetrachloride and lithium aluminum hydride (50) as compared with the low yield by the Paneth technique (138), it was surprising that no volatile titanium hydride was formed, since Krauber (62) reported that by the Paneth method he produced such a hydride.

As there are no reports in the literature disputing Krauber's claim (there are also none confirming it!), his work cannot be dismissed, but since no other methods of synthesis have yielded a volatile titanium hydride (62,63) his results should be viewed with suspicion.

EXTENDED APPLICATION FOR EGLOFF'S BOILING POINT EQUATION

The excellent predictions of the boiling points of various hydrides of Group IV elements, the root mean square deviation is only 0.78°C, show that the modified form of Egloff's equation is applicable to all compounds tested.

Why compounds with only one central atom should boil so much lower (18°C) than the original form of the equation predicted cannot be explained as being due to hydrogen bonding or increased symmetry allowing closer packing as these would cause deviation in the opposite direction. The most logical explanation is that MH_4 compounds should be considered to have a different structure than the rest of the n-alkanes, and so have a different value for k, k = -434.3 = -416.3 - 18.0 . Another compound where symmetry seems to cause a lowering of the boiling point below the calculated value is 2,2-Dimethylpropane which boils at 282.58°K while the calculated boiling point is 290.05°K (101).

That k should have the same value in all the normal series considered (disregarding MH_4 compounds) is a logical corollary of the observation by Egloff that k varied with the structure of the isomeric hydrocarbon series. The structures of all normal Group IV hydrides are similar and the same thing can be said of all the iso compounds where again k had a constant value both in the hydrocarbons and the alkyl silanes. In other words, this work has further proved Egloff's statement that the value of the parameter k depends on structure alone.

The finding that a and b were constant for all paraffin hydrocarbons (101) has also been extended. In the two series of compounds investigated which existed in more than one structural type (Table III), it was shown that both parameters had a constant value in the various structures.

A comparison of the various values of a calculated for the different series of compounds shows that organo-silicon hydrides containing one silicon atom have a value for a slightly less than that for the hydrocarbons. The presence of a second silicon atom in the molecule raises a to a value between that for hydrocarbons and that for silanes. The values of a for both the mono-n-alkyl silanes (terminal silicon atom) and the poly-n-alkyl silanes (internal silicon atom) are very close together, 321.1 and 322.0 respectively.

The value of b was found to be almost constant for all the alkyl silicon compounds, varying only from 5.0 to 5.2 regardless of the number of silicon atoms in the molecule. These values of b are all greater than that found by Egloff for the hydrocarbons, b = 4.4, even though for the silanes it is 3.5 .

Examination of the plots of a and b versus the atomic weight of the central atoms showed that smooth curves connect the points. a increases, and b decreases with atomic weight. That these are regular functions of atomic weight is proved by the extrapolation of the curves to the atomic weights of lead and tin which enabled the calculation of the boiling points of stannane and plumbane.

From consideration of the above four paragraphs it would seem that a is dependent on the intermolecular forces while b varies with the intramolecular forces. That intermolecular forces increase with atomic weight is well known. For instance, the constant b in van der Waals' equation of state, which is one measure of intermolecular attraction, is 0.001910 for methane and 0.002583 for silane (2). And that bond strength between atoms decreases with increasing atomic weight is amply evidenced by the decreasing stability of the hydrides of Group IV and Group V elements as

the atomic weight is increased.

That a should have almost the same value for all compounds of any grouping of a set of elements is logical, because the intermolecular forces will be about the same. The effective strength of the intermolecular forces will vary with changes in structure which change the closeness of packing of the molecules, but constant k varies for this. That a drops to less than the hydrocarbon value with the introduction of a silicon atom would mean that the gross dissimilarity of elements reduces the intermolecular attraction. A second silicon atom is no longer dissimilar so that the effect is only that of increasing atomic weight.

The increase of b caused by the introduction of a silicon atom into an alkane reflects the greater bond strength of a silicon-carbon bond as compared with a carbon-carbon or a silicon-silicon bond. As the number or position of silicon atoms has little effect on bond strength, the value of b should not change greatly, which was noted. It is predicted that a disilanyl radical (SiH_3-SiH_2-) in an organo-silicon molecule would lower the value of b to close to 4.4, the average of silicon-silicon and silicon-carbon values. If there is more than one alkyl group attached to the disilanyl radical, b will be between 4.4 and 5.0 .

This analysis makes changes in k qualitatively predictable. When molecules increase in symmetry, they can pack closer together and the intermolecular forces are more effective, thus the boiling point will be greater and k smaller. On the other hand, a decrease in symmetry causes the molecules to stay farther apart, lessening their interaction, which causes k to increase corresponding to a decrease in boiling point. For example, for normal compounds k = -416.3 while for 2-methyl compounds k = -424.5, or in other words, branching in the 2- position lowers the boiling point 8.2°C.

SUMMARY

1. Six bis-trichlorosilyl alkanes were prepared from the corresponding dichloroalkanes by means of the Rochow synthesis, of which three were not previously reported in the literature; 1,1-bis-trichlorosilylethane, 1,2-bis-trichlorosilylpropane and 1,4-bis-trichlorosilylbutane.

2. The physical properties of these compounds were investigated.

3. Chloroform did not yield any organo-silicon compounds when tried in the Rochow synthesis.

4. The bis-trichlorosilyl alkanes were hydrogenated to the corresponding disilyl alkanes by means of lithium aluminum hydride. Four were prepared, none of which had been previously reported; disilylmethane, 1,1-disilylethane, 1,2-disilylethane and 1,2-disilylpropane.

5. The physical properties of these compounds were investigated.

6. Titanium tetrachloride did not yield a volatile hydride when caused to react with lithium aluminum hydride.

7. The equation that Egloff derived to correlate the boiling points of hydrocarbons was fitted to the silanes, germanes, stannane and plumbane and to several series of alkyl silanes.

8. The parameter $\underline{k}$ in the equation was found to be the same for all compounds with similar structures, and to change when the structure changed. An increase in symmetry caused a decrease in $\underline{k}$ and vice versa.

9. The plot of $\underline{b}$ versus the atomic weight of the central atom was a smooth curve with $\underline{b}$ decreasing as the atomic weight increased.

10. $\underline{b}$ was found to be a measure of the bond forces inside the molecule. An increase in bond strength caused a corresponding increase in $\underline{b}$.

11. The plot of $\underline{a}$ versus the atomic weight of the central atom was a smooth curve with $\underline{a}$ increasing as the atomic weight increased.

12. *a* was found to be proportional to the intermolecular forces in the liquid. An increase in the intermolecular forces caused a corresponding increase in *a*.

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