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STUDIES IN GAS CHROMATOGRAPHY WITH REFERENCE TO VOLATILE INORGANIC COMPOUNDS.

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A Thesis Submitted for the Degree of

Doctor of Philosophy

March 1968

by

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ACKNOWLEDGEMENTS

This work was assisted by generous gifts of some high-purity germanium tetramethyl by The Organisch Chemisch Instituut, T.N.O., Utrecht, Holland, and some germanium by the Germanium Research Center, Kansas City, U.S.A., and the loan of two detectors by the Gow-Mac Instrument Company, Madison, New York, U.S.A.

The Author wishes to thank his supervisor, Dr. C.S.G. Phillips, for much advice and many fruitful discussions. He would also like to thank Dr. P. Powell (Acting supervisor during Dr. Phillips' sabbatical leave) for a continuity of supervision during a difficult stage of this work.

The Author is indebted to the Scientific Research Council for providing a maintenance grant for the first two and a half years of this work, and to the Committee of Advanced Studies and Exeter College for grants to enable the experimental work to be completed.

DESIGN AND CONSTRUCTIONAL WORK

The 'First Apparatus' described in Part 1 of this work was constructed jointly by the Author and P.L. Timms (then D.Phil. student) during the period of the Author's Part II work, and was subsequently modified by the Author in this work. All other apparatus described in Part 1 of this thesis was designed and constructed by the Author, with the following exceptions:

The stainless steel bombs, which were constructed by the Laboratory workshop staff.

Part of the Fraction Trapping Sequence shown on Plate 8, which was constructed by Mr. G. Wilkinson, Glassblower to the Laboratory.

The electronic timer (Section 2.43) and the temperature control unit (Appendix 1) which were constructed by the Electronics Staff of the Laboratory.

The Apparatus described in Part 3 of this thesis was designed by the Author, and constructed and operated in collaboration with M.M. Norgett and S.S. Blume (D.Phil. students).

ABBREVIATIONS USED IN THIS THESIS

In the interests of brevity in the text, and clarity in Tables and diagrams, the following abbreviations have been used in chemical formulae.

1/ Alkyl groups have been described by their first two letters with structural suffixes, thus: Methyl = Me, iso-Propyl = Pr^i (Phenyl = Ph).

2/ The chlorinated hydrocarbons obtained as products of the gold chloride reaction have been denoted by abbreviated structures with carbon and hydrogen not marked, thus:

$\begin{matrix} Cl \\ Cl \end{matrix}\!\!> = CH_2Cl_2$, $\begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!\!-\!\!< Cl = CHCl_2.CH_2Cl$, $\begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!\!= = CCl_2{:}CH_2$

3/ The permethyl silico-germanes, $Si_nGe_mMe_{2(n+m)+2}$, described in Chapter 6, have been denoted by abbreviated structures with methyl groups not marked, and silicon atoms as O and germanium atoms as ●. Thus: O-●-O = $SiMe_3.GeMe_2.SiMe_3$, O-O-●-● = $SiMe_3.SiMe_2.GeMe_2.GeMe_3$. An extension of this type of abbreviation has been used to describe the possible intermediates in the reactions leading to their preparation, where the terminal groups could be Cl or K, or the intermediates could be radicals; thus: O-●- = $SiMe_3.GeMe_2.Cl$ and/or $SiMe_3.GeMe_2.K$ and/or $SiMe_3.GeMe_2^{\bullet}$.

A B S T R A C T

ABSTRACT

The major part of the work described in this thesis is concerned with the development of the techniques of closed-circuit gas chromatography, as originally derived from conventional chromatography by Timms, for the separation and identification of certain volatile silicon and germanium compounds. These techniques were devised to extend the work, classically carried out in high-vacuum distillation systems, to more complex mixtures and smaller samples.

In addition to the development work on the basic method, development work was carried out on components and systems, in particular, detector circuitry, a cheap and simple method of temperature control for chromatographic columns, the deoxidisation of nitrogen supplies, and traps for high efficiency removal of volatiles from gas streams.

In its final form, the closed-circuit chromatographic apparatus consisted essentially of a preparative gas chromatograph, fitted with two columns and fraction collection traps, and equipped with facility for the recycling of samples, combined with an analytical system. The analytical system consisted of a two-column gas chromatograph equipped with a gas density detector for quantitative analysis of mixtures, provided the components could be identified. Analyses were either effected on products of reactions carried out in external apparatus, or on the products of the reaction of compounds, purified in the preparative system, passed in a nitrogen stream through a reactor containing anhydrous $AuCl_3$. This reactor with its ancilliary apparatus was fitted as part of the analytical system.

The system of a reactor containing gold chloride heated to 170°C effectively in series with a quantitative gas chromatograph was devised by Timms as a technique for the elucidation of the empirical formulae of the silicon-germanium hydrides, $Si_nGe_mH_{2(n+m)+2}$, which were quantitatively chlorinated to yield $SiCl_4$, $GeCl_4$ and HCl. In this work this technique was developed for the analysis of compounds of silicon and germanium with alkyl groups. Initially it was attempted to convert the tetramethyls and tetraethyls to the tetrachlorides and chlorinated hydrocarbons by reactions under severe conditions. Although this proved feasible, it was realised that partial chlorination under milder conditions should give structural information as well as empirical formulae, provided that all the products could be identified.

When the gold chloride reaction, under a variety of conditions, was carried out on $GeMe_4$ and the methyl germanium chlorides, it was discovered that chlorination of the methyl groups could occur without Ge-C bond fission. In particular, loss of methyl groups from $GeMe_2Cl_2$ and $GeMeCl_3$ mainly occurred after a stepwise chlorination to $CCl_3.GeMeCl_2$ and $CCl_3.GeCl_3$. All of the members of the series $CCl_nH_{3-n}.GeMe_mCl_{3-m}$ (n = 1 to 3, m = 0 to 3) were tentatively identified by their reactions and by gas chromatographic data.

In view of the large range of products obtained under these intermediate conditions, it was decided to attempt the reaction of gold chloride at temperatures only between 30° and 90°C, under which conditions no side chain chlorination would be expected to occur. As such, the technique was employed to determine the empirical formulae and, in particular, the structures of the permethyl silanes and permethyl germanes,

as the anticipated products of Si-Si and Ge-Ge fission only, the methyl silicon and germanium chlorides were not expected to react further to any great extent. Reactions under these conditions proved to be successful and the following compounds were identified:

Si_2Me_6, Ge_2Me_6, Si_3Me_8, Ge_3Me_8 and n-Si_4Me_{10}.

The permethyl silanes were prepared by the Wurtz-Fittig reaction of potassium on mixtures of $SiMe_3Cl$ and $SiMe_2Cl_2$ in stainless steel bombs at 125°C, as originally carried out (but using sodium) by Kumada. Fairly high yields, particularly of n-Si_4Me_{10}, were obtained. Although this type of coupling had already been carried out on $GeMe_3Cl$, it had not hitherto been carried out on mixtures of $GeMe_3Cl$ and $GeMe_2Cl_2$. This proved successful with potassium at 125°C for 24 hours, and reasonable yields of the permethyl germanes were obtained. The presence of $GeMeCl_3$ in the reaction mixtures did not apparently lead to the production of branched-chain volatile products. There was, however, strong evidence for the production of straight-chain compounds of both series with longer chains than those identified by the gold chloride technique. In common with most other true homologous series, plots of logarithmic retention volumes (or proportional values) against 'the number of atoms in the chain' of the known members of the two series were approximately linear. Extrapolation of these plots enabled values to be predicted for the next members of the series. These values were very close to the values actually obtained for compounds prepared in these reactions. In this way the following compounds were tentatively identified in the reaction products:

n-Ge_4Me_{10}, n-Si_5Me_{12}, n-Ge_5Me_{12} and n-Si_6Me_{12}.

This work was extended to the preparation and identification of a new series of compounds, the permethyl silico-germanes, $Si_nGe_mMe_{2(n+m)+2}$, only the first member of which had previously been prepared. Wurtz-Fittig coupling of mixtures of $SiMe_3Cl$, $SiMe_2Cl_2$, $GeMe_3Cl$ and $GeMe_2Cl_2$ by potassium at 130°C for 24 hours, yielded, in addition to the permethyl silanes and permethyl germanes, at least 12 new compounds in quantities (in terms of volatiles recovered) between 0.2% and 6.5%. Similar preparations, with $SiMe_3Cl$ or $SiMe_2Cl_2$ omitted, gave higher yields of specific members of this series of compounds and gave some indication of their structure. This information was conditioned, to an extent, by evidence that some rearrangement of groups at silicon and germanium was taking place under the reaction conditions.

The principal method employed for the identification of the permethyl silico-germanes was the gold chloride reaction carried out at temperatures between 30° and 50°C. It was found that samples of the order of 0.8 mg. were sufficient for three separate determinations of the empirical and structural formulae of these compounds. These determinations, under reasonably ideal conditions, gave results within 5% of the predicted values, and on larger samples, within 3%. In addition to this evidence, chromatographic retention data gave an indication as to their probable molecular formulae. Ultimately, a self-consistent hypothesis, confirmed to a large extent by a chromatographic determination of heats of solution, was devised for chromatographic prediction of their structures.

The following compounds were identified by the gold chloride technique and the other information as outlined above:

$SiMe_3.GeMe_3$

$SiMe_3.GeMe_2.SiMe_3$	$GeMe_3.SiMe_2.GeMe_3$
$SiMe_3.SiMe_2.GeMe_3$	$GeMe_3.GeMe_2.SiMe_3$
$SiMe_3.SiMe_2.SiMe_2.GeMe_3$	$GeMe_3.GeMe_2.GeMe_2.SiMe_3$
$SiMe_3.SiMe_2.GeMe_2.SiMe_3$	$GeMe_3.GeMe_2.SiMe_2.GeMe_3$
$SiMe_3.GeMe_2.GeMe_2.SiMe_3$	$GeMe_3.SiMe_2.SiMe_2.GeMe_3$
and $SiMe_3.SiMe_2.GeMe_2.GeMe_3$	and/or $SiMe_3.GeMe_2.SiMe_2.GeMe_3$

There was also chromatographic evidence for the presence of at least 10 isomeric forms of compounds with the following formulae:

$n\text{-}Si_4GeMe_{12}$, $n\text{-}Si_3Ge_2Me_{12}$, $n\text{-}Si_2Ge_3Me_{12}$ and $n\text{-}SiGe_4Me_{12}$

For the preparation of the permethyl germanes and the permethyl silico-germanes it was necessary to prepare $GeMe_3Cl$ and $GeMe_2Cl_2$ as reactants. Two methods for the preparation of these compounds were developed from existing techniques. The first of these was the 'rearrangement' reaction of $GeMe_4$ with $GeCl_4$, originally carried out with limited success in the presence of large amounts of $AlCl_3$. In this work the reaction was attempted with small amounts of catalyst, in some cases prepared in situ, e.g. by the slow reaction of aluminium with $GeCl_4$ in the presence of mercury. The reaction was found on occasion to work well with traces of $AlCl_3$ at 250°C, but was sometimes drastically, and rather unpredictably, inhibited, possibly by moisture. The reaction was shown to be either autocatalytic or catalysed by elemental germanium, to a small extent, at 250°C. Mercurous chloride was found to be a good catalyst for the primary reaction to $GeMe_3Cl$ and $GeMeCl_3$, but indifferent for further reaction to $GeMe_2Cl_2$. A mixture of aluminium and calomel was successfully used for the preparative work, presumably as it reacted

to form a mixture of both successful catalysts. With this catalyst it was shown that an equilibrium prevented the formation of high yields of $GeMe_2Cl_2$:

$$K = \frac{[GeMe_2Cl_2]^2}{[GeMe_3Cl][GeMeCl_3]} \simeq 22 \text{ at } 270^\circ C$$

The equivalent constant for the formation of $GeMe_3Cl$ was apparently much higher. The preparative work was carried out in stainless steel bombs but some of the experimental work was carried out in small sealed glass tubes which established that the stainless steel was also having some effect on the reaction.

The second preparative technique employed for the methyl germanium chlorides was the 'direct reaction' of methyl chloride with germanium in the presence of copper at 360°C. This reaction, normally carried out as a streaming method, was carried out in a stainless steel bomb. It appeared to take place almost quantitatively and in view of the presence of germanium, and the high temperature employed, it was presumed that equilibrium had been reached. The product ratio indicated that K (see above) for $GeMe_2Cl_2$ was approximately 53 at 360°C..

The last part of this work was concerned with the design, construction and operation of a chromatograph for operation at cryogenic temperatures. The principal feature of this apparatus was the temperature controlled air bath in which the chromatographic columns were mounted. This consisted of a long vertical glass tube, with an internally mounted wall heater, which was immersed in liquid nitrogen. The air bath was stirred by a series of fans powered by a small electric motor and the temperature was measured by a thermocouple. Temperature control was effected by merely

varying the current fed to the heater from a stabilised voltage A.C. supply. With this simple system control of the average air bath temperature within $\pm 0.5^{\circ}C$ was easily attained in the range -188° to $-90^{\circ}C$ with a maximum, but predictable temperature variation along a 2 X 25 cm. column of $2^{\circ}C$. This performance was better than any quoted in the literature. A conventional katharometer detection system was provided for the chromatograph.

This chromatograph was used for studies of the interaction of permanent gases and other low-boiling compounds with metallic ions. This was achieved by measuring the heats of adsorption of these gases on various solid phases with surfaces modified with salts containing a common cation. The initial success of this method has lead to its present use by other workers.

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T H E S I S

CHAPTER 1

INTRODUCTION

1.1 Chromatography

Chromatography has been defined as "A physical means of separation in which the components to be separated are distributed between two phases, one of which constitutes a stationary bed, usually packed as a column, of large surface area, the other being a fluid that percolates through the stationary bed".[1a] Chromatography defined in this way is distinguished from counter-current techniques such as distillation and static techniques such as liquid-liquid extraction, to which in many respects it bears a resemblance. It may be regarded as equivalent to a large number of small reversible steps, the 'Theoretical Plates', each one not necessarily being very efficient, occuring successively, the cumulative effect of which is, generally, a much higher efficiency than that obtained by other methods.

Chromatographic processes are classified according to the nature of the fixed phase which may be solid or liquid, and the moving phase which may be liquid or gas. This classification gives four basic types of chromatography:

1/ Liquid-Solid Chromatography (LSC)

2/ Liquid-Liquid Chromatography (LLC)

3/ Gas-Solid Chromatography (GSC)

4/ Gas-Liquid Chromatography (GLC)

All of these types of chromatography are currently in use, but only the last two are considered in this thesis.

Chromatographic processes are further subdivided according to the nature of the separation process under three basic headings:

1/ Elution Analysis, where the components of a small sample merely equilibrate between the two phases and are successively eluted from the end of the column, or retained as separated bands within the column.

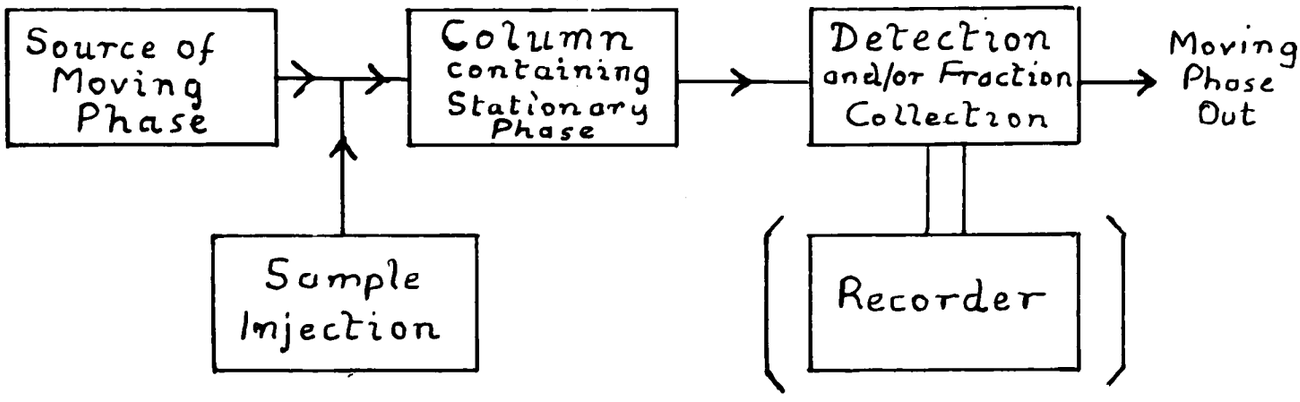
2/ Frontal Analysis, where each sample is continuously fed onto the column and the components successively appear at the other end until the final mixture is the same as the initial mixture.

3/ Displacement Analysis, where there is competition for the stationary phase between the components of the sample, or the sample and a more strongly retained substance continuously fed onto the column after injection of the sample. Components are eluted as a succession of bands.

Of these three processes, the first is in widest use and is the only one considered in this thesis. In fact 'Chromatography' commonly implies elution analysis, and the term will be used in this sense in this work.

The schematic arrangement of a chromatograph (i.e. a chromatographic apparatus) is shown in Fig.1. The output of such an apparatus, either as a recorder trace, or an actual physical separation, is called a chromatogram.

Fig.1. Schematic Chromatograph



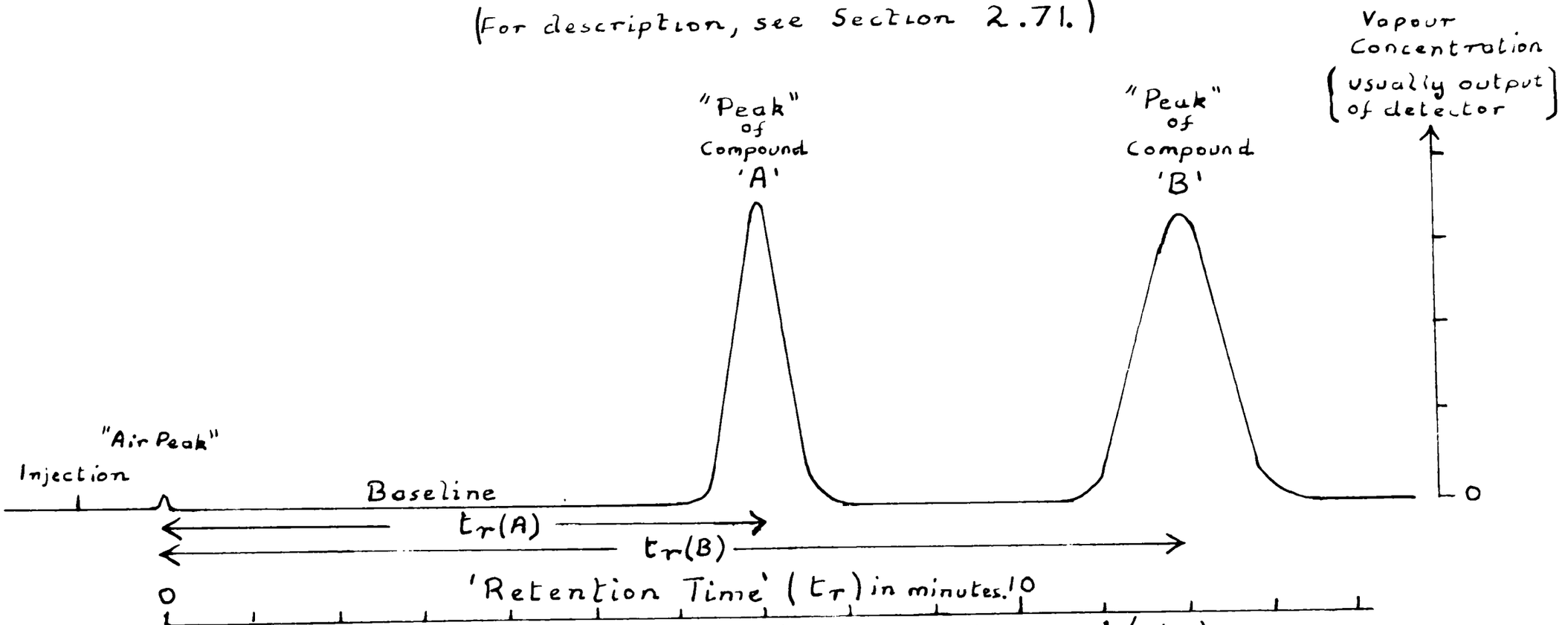
1.11 Evolution of Gas-Liquid and Gas-Solid Elution Chromatography

Although processes essentially chromatographic in principle are widespread in nature, and similar techniques such as distillation had been known for some considerable time (Aristotle 384 - 322 B.C. described the distillation of sea water), chromatography is usually traced back to 1906[2], when LSC was employed to separate plant pigments. This work was then forgotten until 1931[3]. A major breakthrough, both practically and theoretically, was the work of Martin and Synge in 1941[4], when they pointed out that the isotherms were more linear between two liquids (LLC) than a liquid and a solid (LSC), using $CHCL_3$ as moving phase and water on silicagel as stationary phase. They stated that "The mobile phase need not be a liquid but could be a vapour" (GLC) and saw that greater separating power should be possible using this method, as, in particular, diffusion effects, which give rise to a lowering of efficiency, would be less. They also gave a good

FIG. 2

A Typical Chromatogram

(For description, see Section 2.71.)



Alternatively represented as 'Retention Distance' (d_R)
or as 'Retention Volume' (V_R) = Retention Time × Gas Flowrate.

'Relative Retention Times' (t_R) are calculated thus:

if $t_R(A) = 1$, $t_R(B) = \dfrac{t_r(B)}{t_r(A)} = \dfrac{V_R(B)}{V_R(A)} = \dfrac{d_R(B)}{d_R(A)}$.

theoretical account of the Chromatogram and effectively applied the 'Theoretical Plate' concept to chromatography. From this work the significant field of paper chromatography was developed.

It was not until 1952 that the first work on GLC was published: James and Martin[5] achieved good separation of the fatty acids on a column packed with silicone oil containing stearic acid on an inert solid support, using automatic titration as a detector. Differentiation of the titration curves yielded the now familiar differential chromatogram (Fig.2). At the same time their theoretical treatment is adequate for most practical purposes to this day. They made use of 'Relative Retention Times (t_R)' for comparison between compounds, and found that if the log (t_R) values for the n-fatty acids were plotted against the number of carbon atoms a virtually straight line graph was obtained. They found that the efficiency of the columns was dependent on gas flowrate, and in particular on increasing the flowrate from zero that the efficiency went through a maximum. They derived a compressibility factor for the carrier gas (moving phase) for determining the average theoretical flowrate, and calculated the theoretical plate equation, based on measurements from recorder charts, for estimating the efficiency of the column. In a subsequent paper[6] they showed an awareness of the specificity of different compounds on stationary phases, where such factors as hydrogen bonding between solute and solvent could be used to obtain selectivity.

The linear nature of the log (t_R) plots was shown to be general, for true homologous series, by subsequent workers[7, 8]. In particular at any given column temperature the n-paraffins, 2-methyl paraffins,

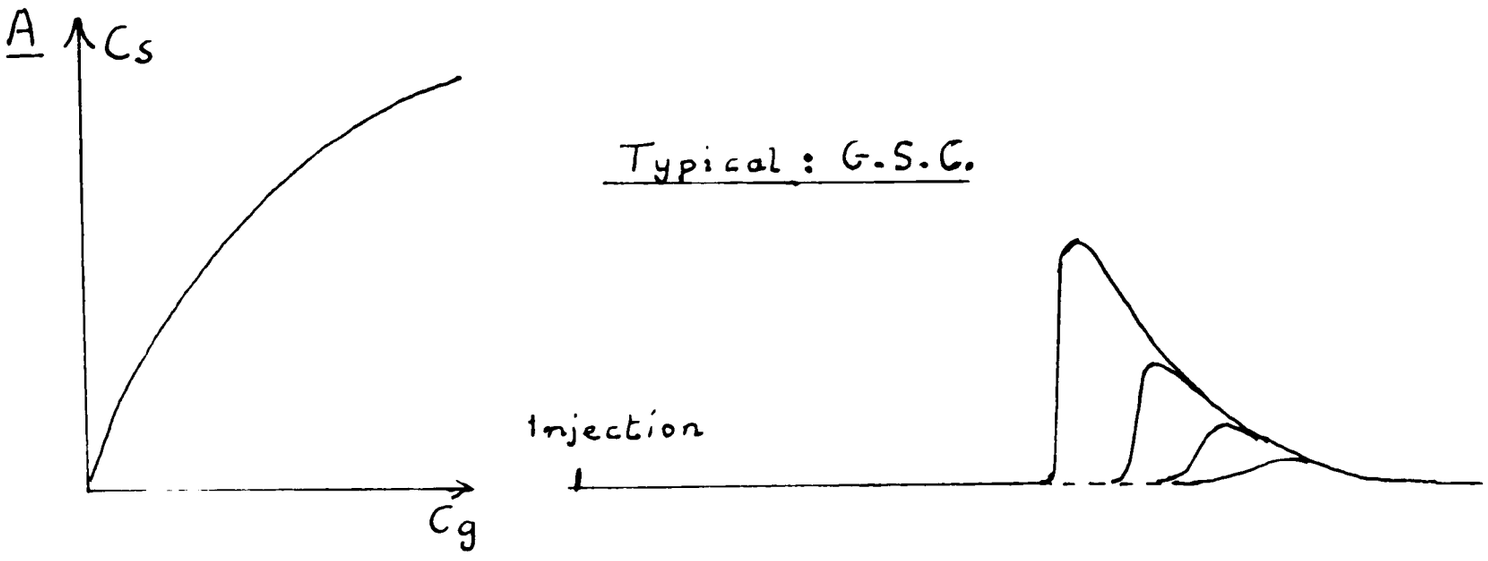
3-methyl paraffins, 2,2-dimethyl paraffins and alkyl benzenes formed a series of nearly parallel straight lines, with the branched chain compounds nearer the carbon number axis than the n-paraffins on each of the stationary phases, and the alkyl benzenes varying in position depending on the polarity of the stationary phase[9]. This and later work clearly showed that chromatographic functions were additive and that therefore retention times of compounds could be predicted fairly accurately provided that the retention times of at least two of their homologues were known. In addition, identification of compounds could, within limits, be made, particularly if two or more columns, of different selectivities, were employed.

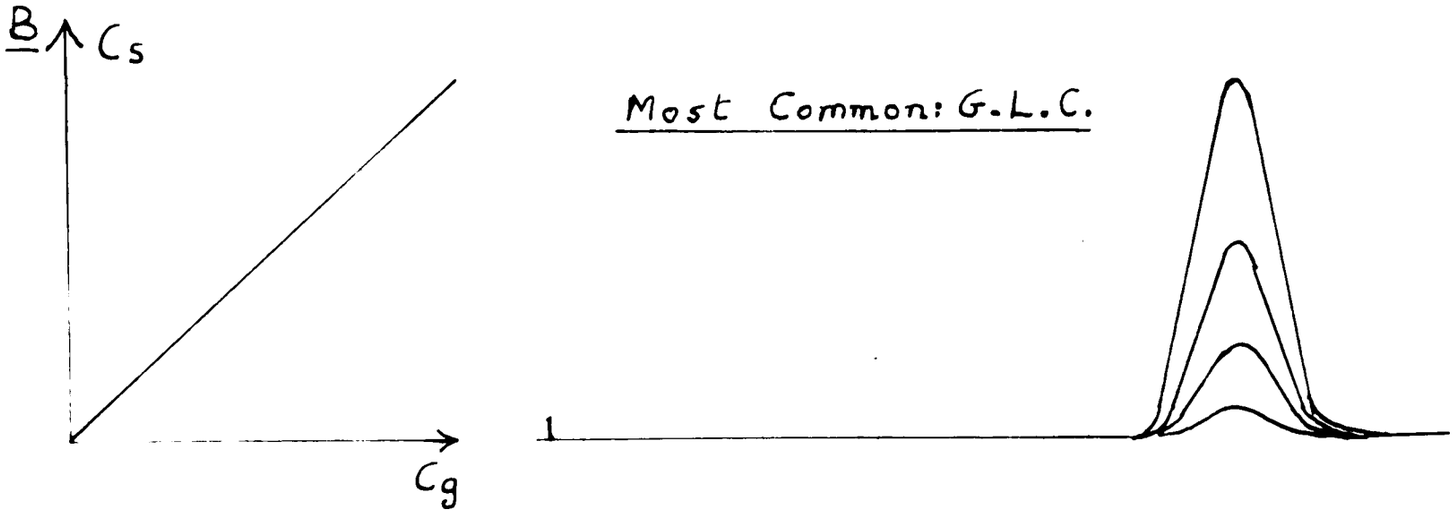
Retention times are related to the partition coefficients of the solutes between gas and liquid phases and, hence, to the free energies of solution[10]. Thus the reason for the linearity of the $\log(t_R)$ plots is the regular increment of the free energy of solution of members of homologous series.

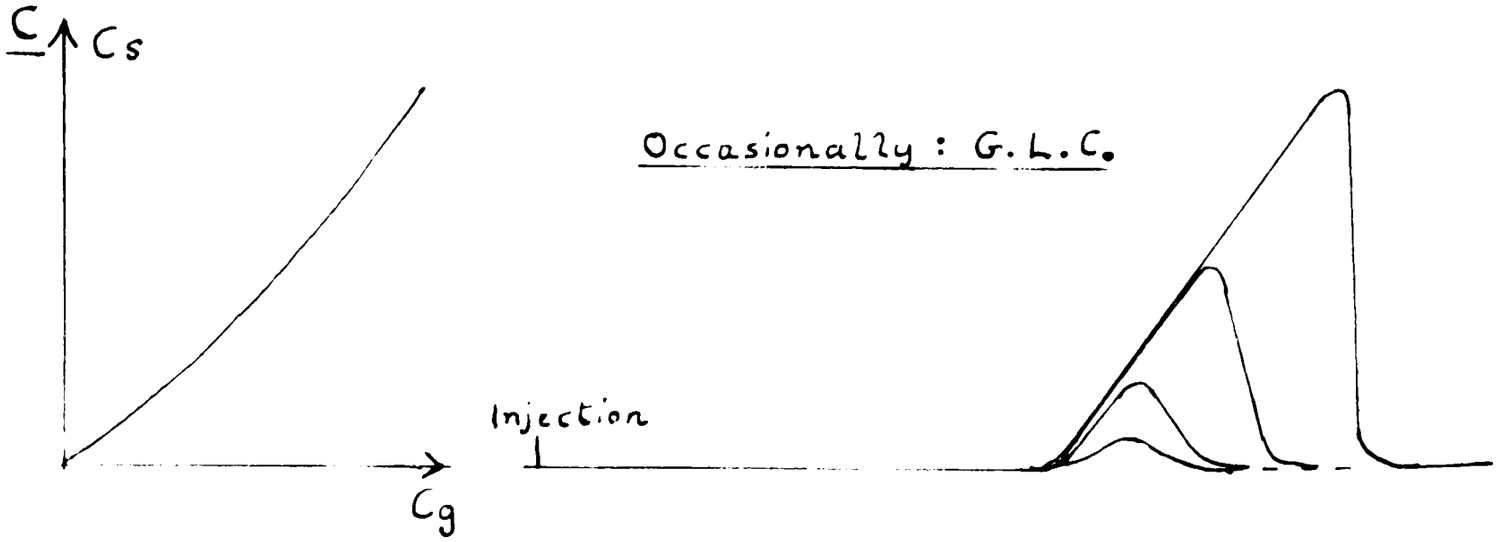
Gas-Solid Chromatography was originally developed somewhat earlier than GLC. The basic method was almost discovered in adsorption-desorption studies in 1924[11], but the first recognisable experiments were not published until 1942[12] when benzene and cyclohexane were separated on a silicagel column using a variety of gases as carriers. This type of analysis (together with other chromatographic techniques) was further developed by Claesson[13], Phillips[14] and Cremer et al.[15]. In the latter case both silicagel and active carbon were used to achieve separation of some permanent gases as well as low-boiling hydrocarbons. These studies were used to calculate the differences in adsorption

FIG. 3 **Typical Adsorption/Absorption Isotherms of Solutes and their effect on Peak Shape with Variations in Sample Size (G.L.C. and G.S.C.)**

C_s - Concentration of solute in Stationary Phase
C_g = Concentration of solute in Gas Phase







energies, but it was realised[15b] that the apparent elution time decreased with increasing sample size, only the 'tails' of the peaks occurring at the same elution time.

Extensions of this work to permanent and rare gases were carried out in particular by Janak[16(a-i)] who found the additional drawbacks that carbon could not be used above 90°C with hydrocarbon vapours as they tended to react[16c], and irreversible adsorptions occurred which necessitated pre-flushing with the compounds to be analysed[16d]. Janak suggested a 2 column technique for the analysis of all gas mixtures[16e]. The comparisons between GSC and GLC by James and Phillips[17] and Ray[18] concluded that the highly curved isotherms of most vapours on solid phases, leading to the highly 'tailing' peaks which, therefore, tended to overlap (see Fig.3), made GSC unsuitable for most separations, but very suitable for displacement analysis. As a result they suggested that Gas-Solid partition chromatography should only be employed for gases since the low heats of solution of such compounds made GLC impracticable, and that for compounds of greater complexity than propane GLC should be employed. For some considerable time these remained the general lines along which the two techniques have been developed. Recently most of the drawbacks of GSC have been overcome, for very small samples at least, by the use of adsorbents, usually alumina, modified with such materials as inorganic salts[19]. It may be concluded that now, for many purposes, there is not much to choose between the two methods but that GLC, by virtue of being the first method developed in a practical form, and possessing a higher repeatability, will continue

to be used for routine analysis, whereas GSC with its wide range of application and selectivity will be increasingly used for research.

1.12 Advantages and Application of Gas Chromatography

Gas chromatographic techniques offer several distinct advantages as methods for analysis and separation of mixtures of volatiles over the classical fractional condensation, distillation and high vacuum techniques:

1/ Chromatographic systems are capable of resolving more complex mixtures.

2/ Retention data may be used as a means of identification, particularly as more than one chromatographic column can be used; as opposed to a single invariable boiling point (which may be that of an azeotrope).

3/ Very small samples may be used; microgram samples may be easily handled.

4/ Chromatographic systems may be used to handle compounds with a wide range of boiling points (GLC from about -50°C to 400°C and GSC over a wider range still).

5/ Faster separation times than those attainable by other methods are possible if required.

6/ Compounds sensitive to moisture or oxygen are easily handled, as inert gases may be used as carrier, although some difficulty may be encountered in the introduction of such samples, unless they are prepared in situ.

7/ The techniques may be used for quantitative as well as

qualitative analysis of mixtures without their prior separation. In this respect, the gas density detector, originally devised by Martin[20], and described in section 2.45, is of particular use.

8/ Separation and recovery of individual components of a mixture, in a substantially pure state is possible in the microgram to gram scale.

9/ Chromatography may be used as a research technique for following the course of reactions, calculation of thermodynamic quantities etc..

These properties made the technique very suitable for investigations in the chemistry of inorganic volatiles such as hydrides, halides and organometallics, and, in particular, to the investigation of reactions where large numbers of products are formed.

It has been found that all the principal features of the chromatography of organic chemistry were duplicated with volatile inorganic and organometallic compounds. Special precautions had to be taken in many cases, which included selection of sufficiently inert column materials and removal of oxygen and water vapour to a very large extent from the carrier gases. Of particular significance was the fact that linear $\log.(t_R)$ plots were obtained with the straight and branch chain hydrides of silicon Si_nH_{2n+2}[21,22], and germanium Ge_nH_{2n+2}[21-23], methyls of silicon Si_nMe_{2n+2}[24,27], and germanium Ge_nMe_{2m+2}[28], and the genuinely mixed homologous series (i.e. all possible homologous series within the general series) the silicon-germanium hydrides $Si_nGe_mH_{2(m+n)+2}$, (see section 6.3)[29-31]. These last results were used to predict and identify more complex members of the same

series [32]. The later experiments [29-32] were carried out using modifications to basic chromatographic techniques, usually in conjunction with micro reactors, which gradually evolved into the closed-circuit technique described in part 1 of this thesis.

It has also proved possible to predict retention values with a fair degree of accuracy for inorganic compounds that are not, strictly speaking, homologues by adding theoretical retention values for different parts of the molecules, e.g. $=Si=$, CH_3-, $-CH_2-$. In particular, predictions have been made for alkyl silanes and germanes of the form $SiRR'R''R'''$ where R, R', R'', R''' may be the same or different alkyl groups[33,34], alkyl digermanes Ge_2R_6 and B- and N- alkyl borazoles $B_3N_3R_6$, where R represents the same or different alkyl groups or hydrogen[33]. The deviations from the predicted values, except for the borazoles, were never greater than 15%, and were usually within the range ± 0 - 8%[33].

1.2 Scope of this Thesis

Part 1 of this thesis describes work carried out in the development of closed-circuit gas chromatographic techniques and apparatus suitable for the study of silicon and germanium volatiles. In addition it describes the principal features of all experimental work carried out and the methods of calculation of results.

Part 2 of this thesis describes the chemistry involved in the preparation and identification of a new series of compounds, the permethyl silico-germanes, $Si_nGe_mMe_{2(n+m)+2}$, the first of which was

described, but not positively identified, by Mironov and Kravchenko in 1965[35]. This work included the development of methods of preparation of the methyl germanium chlorides which were required as starting materials, the application of the Wurtz-Fittig coupling reaction to mixed methyl germanium chlorides, for the preparation of the permethyl germanes, as this method had previously only been employed for the permethyl silanes[24, 27, 32], and the application of this reaction to mixtures of methyl silicon and germanium chlorides. In addition, it was necessary to develop an analytical method and establish its validity and application by trials on silicon and germanium tetra-alkyls and the permethyl silanes and germanes.

Part 3 of this thesis is concerned with the design, construction and operation of a gas-solid chromatograph for operation at cryogenic temperatures (-188° to -90°C), for the study of the interaction of gases with metallic ions.

1.3 Chemistry of certain Silicon and Germanium Volatiles

1.31 Preparation of compounds with Si-Si, Ge-Ge and Si-Ge bonds

Compounds of silicon and germanium with Si-Si and Ge-Ge bonds were among the first compounds of these elements to be prepared[36, 37]. By 1932, disilane, Si_2H_6[38], digermane, Ge_2H_6[37] and some of their alkyl[39, 40], aryl[41, 42] and halogen (of silicon only[36]) derivatives had been prepared, as well as longer-chain hydrides of both elements[37,38] and some aryl derivatives[43,44].

Typically, it was found that the Si-Si and Ge-Ge bonds in such compounds possessed a reasonable thermal stability, having a comparatively high resistance to homolytic fission, but were fairly reactive to heterolytic fission. In both types of reaction the hydrides were more reactive than the alkyls and aryls. In particular, the alkyls and aryls were found to be stable to air and moisture but the hydrides were unstable to air and to moisture, particularly if alkaline, and thus special handling techniques had to be developed for these compounds[37, 38].

A variety of preparative methods have been used for the formation of compounds with Si-Si and Ge-Ge bonds, only the more important ones being mentioned here.

The hydrides have been most commonly prepared by the acid hydrolysis of alloys of silicon and germanium with certain A Group metals, preferably magnesium[37, 38]. With the improvement in separation, afforded by gas chromatography over distillation methods, it has been shown[21, 22] that both straight and branched-chain isomers up to Si_8H_{18} and Ge_5H_{12} are prepared, in progressively decreasing amounts, by this method. A similar hydrolysis of Mg/Si/Ge alloys was shown to yield a series of compounds with Si-Ge, as well as Si-Si and Ge-Ge bonds; the silicon-germanium hydrides $Si_nGe_mH_{2(n+m)+2}$, together with the silicon and germanium hydrides[29-31]. Straight and branched-chain compounds up to $n+m = 6$ were identified. Treatment of magnesium silicide with chlorine has yielded the series Si_nCl_{2n+2}[45], and derivatives of disilane and trisilane have been identified as biproducts in high temperature direct syntheses of monosilane

derivatives from silicon, usually with a copper catalyst, with e.g. chlorine[45], hydrogen chloride[45] and methyl chloride[46].

Pyrolytic and electrical discharge reactions have been used for both decomposition and synthesis of hydrides and halides of silicon and germanium: Pyrolysis of $SiCl_4$ in various gases, and of Si_2Cl_6 in NMe_3, yields a variety of the higher chlorosilanes[45]. Similarly the methyl chloro disilanes, $Si_2Me_nCl_{6-n}$, with Me_4NCl catalyst will yield similar derivatives of tri- and tetrasilane[47]. Pyrolysis of germanium hydrides over germanium metal at 450°C (1 second) yields higher and lower members of the same series, and this has been extended to the decomposition and the synthesis, by 'cracking' mixtures of silanes and germanes, of the silicon-germanium hydrides. In each case the silicon skeleton remained intact and thus the methods were used for identification[29-31]. Electrical discharge techniques have been used in a similar way on the germanium hydrides[48] where the series up to Ge_8H_{18} was prepared, and the silicon and silicon-germanium hydrides[32, 49, 50].

The hexaalkyl disilanes were originally prepared by the action of various organometallic reagents on hexahalyl disilanes; Si_2Et_6 by Et_2Zn on Si_2I_6[39] and Si_2Me_6 by MeMgBr on Si_2Cl_6[51]. Aryl Grignard reagents[52] and phenyl-sodium[53] have been similarly used, but modified techniques were necessary to prevent fission of the Si-Si bond. Alkyl Grignard reagents have also been used to prepare peralkyl di-,tri- and tetra-silanes from their methyl chloro- derivatives obtained from the 'Direct' reaction[46, 47, 54]. In addition, the methyl Grignard reagent has been used to prepare the lower permethyl

germanes from GeI_2[55].

Analogous to the formation of Si-C and Ge-C bonds by the reaction of organometallic reagents with silicon or germanium halides, is the formation of Si-Si, Ge-Ge and Si-Ge bonds by the action of silyl or germyl metallics on the halides. This method has been mainly used for the preparation of unsymmetrical compounds, in particular:

$$Ph_3GeNa + Et_3SiBr = Ph_3GeSiEt_3$$ [56]

$$Ph_3SiK + Ph_3GeCl = Ph_3SiGePh_3$$ [57]

Which were the first Si-Ge compounds prepared. Asymmetrical disilane and digermane derivatives have also been prepared in this way. The reaction of two parts of Ph_3GeNa with one of Ph_2GeCl_2 yielded the first trigermane derivative to be prepared, Ge_3Ph_8[44], and a similar reaction of the silicon equivalents gave the first trisilane derivative, Si_3Ph_8[58]. A technique based on this method was employed in one of the two original preparations of the higher permethyl silanes, Si_nMe_{2n+2} (n = 5-7) when the mixture of potassium-methyl-silicon derivatives, obtained by fission of $(SiMe_2)_6$ by sodium-potassium, was treated with Me_3SiCl[25].

Aryl[59] and alkyl[60] digermanes have been prepared by the reaction of excess Grignard reagents with germanium tetrachloride. Yields of up to 70% of hexaaryl digermanes are possible[61], but maximum yields of hexaalkyl digermanes are usually less than 10%[28, 60]. It was subsequently shown that using the alkyl Grignard reagents in this way, smaller amounts of alkyl-trigermanes, and probably tetragermanes, are also prepared[28]. When $GeHCl_3$ was reacted in the same way with the methyl Grignard reagent, straight chain and cyclic

permethyl germanes with up to 7 Ge atoms were obtained[55]. A similar reaction of organo-lithium compounds with excess of Ph_3GeH[62] or $GeHCl_3$[55] was developed at the same time. It was subsequently shown that the higher permethyl germanes could be similarly prepared in the reaction of organo-lithiums on $GeCl_4$[28,60]. In general, higher yields of the peralkyl di- and tri-germanes were obtained using organo-lithiums rather than Grignard reagents on $GeCl_4$[28]. It has been shown that these reactions do not succeed directly with the equivalent silicon compounds[63].

The most general method used for the preparation of Si-Si[36,41], Ge-Ge[42] and Si-Ge[35, 64] bonds (as well as Si-C[65] and Ge-C[66] bonds) has been the Wurtz-Fittig coupling of compounds with Si-, Ge- (or C-) -halogen bonds, usually by alkali metals. Si_2Ph_6[41] and Ge_2Ph_6[42] were first prepared respectively from Ph_3SiCl and Ph_3GeBr by the action of sodium in xylene under reflux. Very high yields of both products have been obtained using this basic method[42, 67]. Other alkali metals and solvents have been tried with success, but excess of the metals, particularly in such solvents as NH_3, $EtNH_2$, dioxan and tetrahydrofuran, results in Si-Si and Ge-Ge bond fission and the formation of metallic silyls and germyls[68-71]. However, in the earlier experiments on the Wurtz-Fittig method applied to the hexa-alkyls of silicon[56] and germanium[40] it was found that solvents totally impeded the reaction of sodium, although the metal would react directly with the bromides to give the expected products. The yields were low, particularly if coupling of chlorides was attempted[72, 73]. More reactive metals such as potassium[72] and sodium-potassium[74], however, gave yields of over 90% in the absence

of solvent even with the chlorides, although the yields using potassium in solvents were lower[72]. Lithium in T.H.F, was also satisfactory for germanium coupling, but resulted in butoxy- derivative formation with silicon compounds[64]. Wurtz-Fittig coupling was used in 1963 to prepare the first silicon-germanium alkyl compound, $SiEt_3.GeEt_3$, when a mixture of Et_3SiCl and Et_3GeCl was coupled using sodium at 180°C in a sealed tube, (Si_2Et_6 and Ge_2Et_6 were also produced)[64]. The parent permethyl silico-germane, $SiMe_3GeMe_3$ was prepared in 1965 by a similar mixed reaction, using potassium for coupling[35]. Wurtz-Fittig coupling has also been used to couple silicon-containing compounds of greater complexity, in particular Ph_5Si_2Cl[58], Et_5Si_2Br[75] and Me_5Si_2Cl[24, 74].

The dialkyl and diaryl dihalides of silicon and germanium are also successfully coupled by alkali metals to give polymeric and cyclic products. Early experiments indicated that the cyclic products from Ph_2SiCl_2[43] and Ph_2GeCl_2[44] both had 4-membered rings. More recent experiments on the methyls of both elements showed that the volatile cyclic products were $(SiMe_2)_6$[76] and $(GeMe_2)_6$[77]. Coupling, using lithium under reflux in tetrahydrofuran in the case of germanium[77], and with sodium-potassium at low temperatures in the case of silicon[25] enabled yields of the volatile cyclic compounds of 60-80% to be obtained. The Wurtz-Fittig coupling of Me_3SiCl with Me_2SiCl_2 to give the permethyl silanes was first successfully achieved by Kumada et al.. Initially they found that the straight chain products up to Si_7Me_{16}[24] could be prepared, and more recently they have obtained the entire series up to $Si_{12}Me_{26}$[27]. Andrews[32]

has shown a small amount of $(SiMe_2)_6$ is also prepared in this reaction.

Thus, provided that this last method would also work with a mixture of Me_3GeCl and Me_2GeCl_2 to prepare the permethyl germanes, Wurtz-Fittig reactions on mixtures of Me_3SiCl, Me_2SiCl_2, Me_3GeCl and Me_2GeCl_2 would be expected to produce a mixture of the permethyl silanes and germanes together with a new family of compounds, the permethyl silico-germanes, $Si_nGe_mMe_{2(n+m)+2}$. Moreover, omission of one or more of the reactants should lead to the production of specific sub-series within the general series.

1.32 Preparation of the Methyl Germanium Halides

For the possible method of preparation of the permethyl silico-germanes mentioned in the previous section, of the reactants, the methyl silicon chlorides were commercially available, but it was necessary to prepare the methyl germanium chlorides.

Several methods for the preparation of the alkyl germanium halides have already been developed[78-80]. Most of the general methods described have started from germanium tetrachloride, germanium alkyls or elemental germanium.

Alkyl Grignard reagents were first used on $GeCl_4$ to prepare germanium tetraalkyls[81] and it was soon considered that this was the best method for their preparation[66]. However, there were reasonable amounts of biproducts which must have included the alkyl germanium halides. If the reaction is carried out by addition of limited amounts of Grignard reagents to $GeCl_4$ the intermediate compounds can be prepared as mixtures[78].

The analogous reverse reaction, fission of germanium-alkyl bonds by halogenating agents, was in fact the first method used for the deliberate production of Me_3GeBr[82]. Several halogenating agents have been used: Bromine reacts slowly with germanium tetraalkyls under reflux in such solvents as CCl_4[40], resulting in the loss of only one alkyl group. Yields of Me_3GeBr as high as 98% have been achieved in this way[35]. Aluminium halides catalyse the action of hydrogen halides[82] and alkyl halides, particularly iso-propyl halides[75,83], resulting in the fission of one alkyl group, and will also catalyse the reaction of the halogens, particularly iodine[84] which does not react on its own[35]. Fission of two alkyl groups is possible[85] with yields, e.g. of Me_2GeBr_2, as high as 80%[35]. Aluminium halides in larger quantities can themselves cause fission of tetraalkyl germanes[86].

In addition to these methods, two more elegant methods for the preparation of the methyl germanium halides are available. Neither requires the use of solvents, a minimal amount of by-products are formed, and therefore, with slight modifications to the basic techniques, simple distillation is required for working up.

Redistribution of groups in organometallic compounds is a very common reaction, being formally similar to such reactions as those of Grignard reagents on $SiCl_4$ and $GeCl_4$. The earliest example of rearrangement of groups at the same element was:

$$2\ EtZnI \xrightarrow{120^\circ C} ZnEt_2 + ZnI_2$$ [87],

and in Group IVB, exchange of ethoxy groups with chlorine or hydrogen at silicon, thus:

$$SiCl_4 + 3Si(OEt)_4 \longrightarrow 4\ SiCl(OEt)_3$$ [88],

$$4\ SiH(OEt)_3 \xrightarrow{(OEt^-)} SiH_4 + 3\ Si(OEt)_4$$ [89].

This type of reaction with the autocatalytic alkyl lead chlorides was investigated and was compared with the statistical rearrangement of different alkyl groups at Pb, Hg, Si and Sn when catalysed by aluminium chloride[92]. Attempts at rearrangement of alkyl and halogen groups at Ge initially met with failure[40, 86, 93], although a mixture of $GePh_4$ and $GeCl_4$ in the absence of catalyst at 350° had rearranged to yield 75% of $PhGeCl_3$[90,91]. Finally, successful rearrangement was achieved with aluminium halide catalysts at elevated temperatures with the reactants in sealed tubes[94], the rates of reaction increasing with increasing alkyl group length unless sterically impeded. The rearrangement of $GeCl_4$ with $GeBu^n_4$ was subsequently studied in detail[95, 96], mechanisms and kinetics being discussed. Reaction only took place in the presence of $AlCl_3$ at temperatures above 150°C. Redistribution, in the presence of rather large (7 - 10%) amounts of aluminium trichloride, of $GeCl_4$ with the tetraalkyl germanes from methyl to n-heptyl and with $GePh_4$ was subsequently described[97]. It was concluded that the redistribution of $GeMe_4$ with $GeCl_4$ was the least satisfactory rearrangement that was carried out, largely on the grounds of the high pressures involved and the slow rate of reaction[97]. In principle, however, there was no real reason given why this method should not work with the methyl compounds with more appropriate techniques.

Direct preparation, from elements and alkyl halides, of mixtures of alkyls and halides or alkyl-halogeno compounds is a fairly general

reaction[98]. Solvents are sometimes required, and catalysts (usually the IB metals) are required with the less reactive metals. This type of reaction was first applied to silicon[99, 100] and germanium[101] by Rochow, using copper as catalyst and a variety of the lower alkyl halides. Reaction took place at reasonable rates at temperatures in the range 315-360°C.. It was found that, with methyl chloride, the main product was $GeMe_2Cl_2$[101], but with higher alkyl chlorides than ethyl chloride, alkyl germanium trichlorides were the principal products[102, 103]. It was subsequently found that with higher reaction temperatures, even methyl chloride tends to produce $GeMeCl_3$ in large quantities[104], and that this also occurs if large amounts of copper are used[105]. These trends tend to be more pronounced if bromides are used[105], and also occur with the equivalent reactions of silicon[45, 100].

1.33 Methods of Analysis

Although the classical oxidation techniques[106] were successfully employed for the analysis of some of the first silicon-germanium compounds prepared[56, 64], they are not suitable for the analysis of small samples purified on a chromatograph, particularly if the compounds contain both silicon and germanium.

Timms and the Author[29-31] developed a method for the analysis of the silicon germanium hydrides, where small samples, purified by gas chromatography, were chlorinated by passage in a stream of nitrogen through a heated reactor containing slowly decomposing $AuCl_3$, thence through a tube, heated to around 350°C. The products were

trapped out of the gas stream and subsequently simultaneously injected onto a chromatograph fitted with a density detector[20]. The products, principally HCl, $SiCl_4$ and $GeCl_4$, were identified by their retention times and their relative amounts were calculated from the detector signal. In this way empirical formulae could be discovered, but no structural evidence was obtained. This method would be a general one provided:

1/ The compounds concerned could be chlorinated in this way

2/ All the products were volatile and thermally stable

3/ All the products could be identified by gas chromatography.

This method could also yield structural information if certain bonds were selectively chlorinated under suitable conditions.

As has been mentioned in the previous section, bromination of silicon and germanium tetraalkyls gets progressively more difficult as alkyl groups are replaced, and even with catalysis is extremely slow beyond the second stage[85]. However, since chlorine is more reactive than bromine and since very high reaction temperatures could be employed, it was expected that complete fission of alkyl groups from silicon and germanium would be possible. Therefore, provided that no deposition of such products as silicon, carbon, germanium or silicon carbide occurred, the gold chloride method should be applicable for the analysis of silicon and germanium alkyls.

Selective cleavage of the Si-Si and Ge-Ge bonds in both alkyl[40, 70] and aryl[44, 71], disilanes and digermanes has been shown to take place smoothly with bromine in various solvents at room temperature or below. The alkyl compounds were cleaved more readily than the aryl

compounds, and very high yields of the trialkyl bromides, considering that traditional working up methods were used, have been obtained in this way[54, 70]. The conditions required for this cleavage were much milder than those for cleavage of alkyl groups from tetraalkyl silanes[45] or germanes[40]. Since subsequent cleavage of the trialkyl bromides required even more rigorous conditions, very little side reaction would be expected in Si-Si or Ge-Ge fission. Thus halogen cleavage has successfully been used on a macro scale for structural analysis of disilane, digermane and silico-germane derivatives, in particular, $Et_3SiGePh_3$[56], $Ph_3SiGePh_3$[57], the series $Si_2Me_nEt_{(6-n)}$[54, 107, 108] and digermanes with more than one type of alkyl group[28]. In addition to bromine, chlorine in CCl_4 at low temperatures and iodine at slightly elevated temperatures have been used for Si-Si fission[54].

The rate of cleavage of disilanes is reduced by the replacement of methyl groups by electron-withdrawing groups, such as chlorine[108], but attack is still on the Si-Si bond, the remaining Si-C bonds presumably being protected by chlorine at silicon. Thus the structural analysis of such compounds as Si_3Me_8 and Si_4Me_{10} (where Si_2Me_5Br and similar products were produced by primary fission) has been successfully carried out[109]; the ratios of $SiMe_3Br$ to $SiMe_2Br_2$ indicating the chain lengths. This method was first attempted, with limited success, on Si_3Ph_8[44] and has been recently employed on several alkyl trigermanes[28].

Thus at the outset of this work it appeared that the gold chloride method could be satisfactorily employed, once suitable reaction

conditions had been determined, on methyl silanes, methyl germanes and methyl silico-germanes.

PART I

E X P E R I M E N T A L

This Part is concerned with the design and construction of apparatus, experimental techniques and methods of interpretation of results as used for the chemical investigations described in Part II.

CHAPTER 2

DESIGN OF APPARATUS, EXPERIMENTAL TECHNIQUES AND INTERPRETATION OF RESULTS.

2.1 Closed Circuit Gas Chromatography

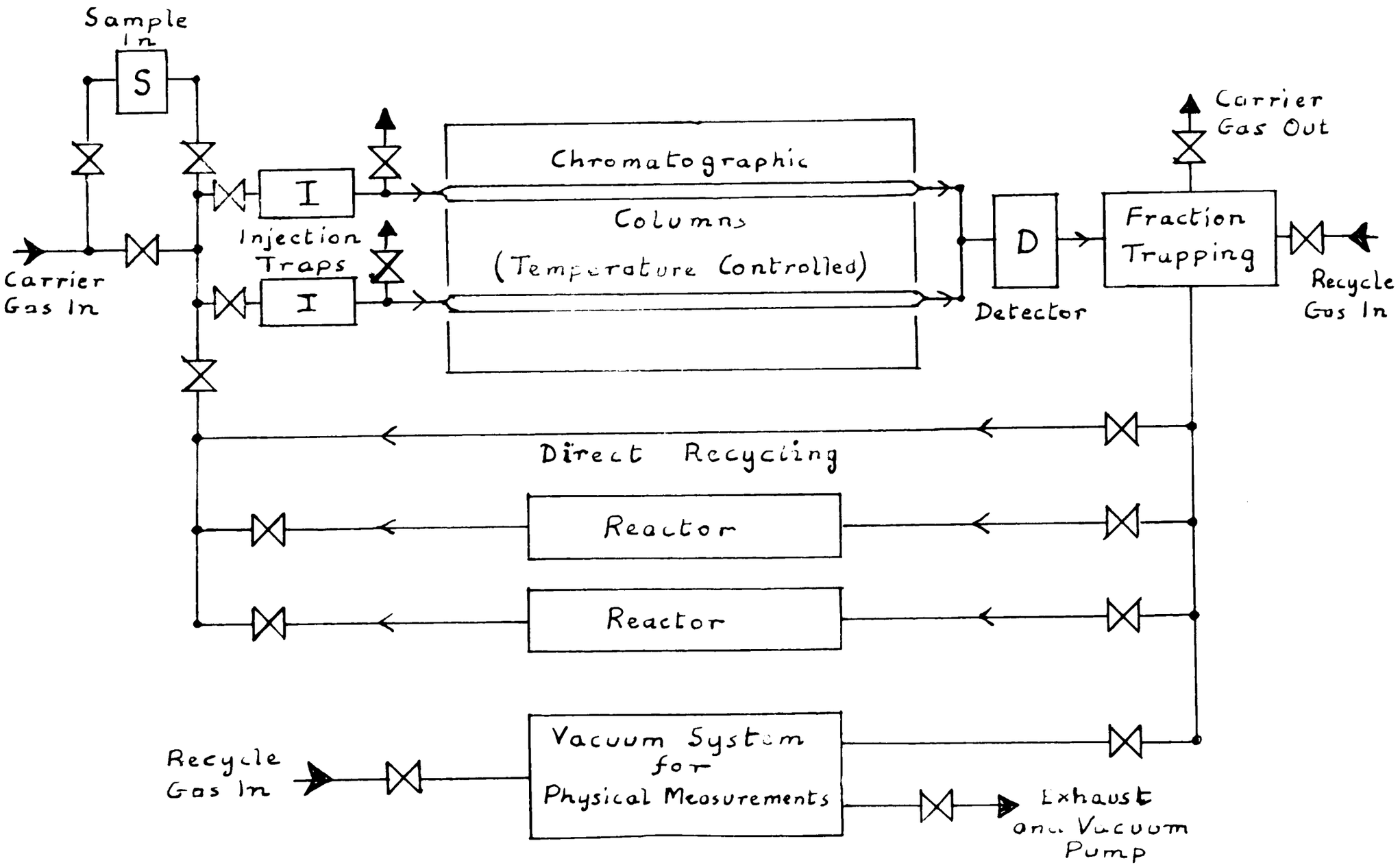
2.11 Introduction

As gas chromatography extends the degree and complexity of the practical separation of volatiles previously attained by fractional distillation, so closed circuit gas chromatography extends the complexity of problems that can be solved when compared with the classical high-vacuum fractional distillation techniques. These latter techniques are particularly desirable in the chemistry of volatile inorganic compounds, where the compounds are often sensitive to oxygen or moisture. Classical vacuum techniques in inorganic chemistry were used in particular by Stock[38] and by Dennis[37] in their work on hydrides, the corresponding chromatographic work being developed from the work of Borer[21, 22] by Timms[29], Andrews[32] and the Author[30].

2.12 General Principles

In closed circuit work, samples of volatiles, in the gram to microgram range, are moved from trap to trap through the apparatus in non-reactive gas streams. The traps are constructed so that,

FIG. 4 Block Diagram of Closed-Circuit Gas Chromatographic Apparatus



when cooled by such refrigerants as liquid oxygen or nitrogen, they will remove a very high proportion of the volatiles in the gas stream, and when warmed they will allow all the volatiles they contain to evaporate so that they can be removed by the gas stream. Separation, purification and identification of individual compounds is carried out by chromatographs integral with the rest of the apparatus. Gas phase reactions may be carried out in micro-reactors within the apparatus, on individual compounds or mixtures, for preparative or analytical purposes, and the products of such reactions may be identified or isolated by chromatography. A high-vacuum system may be provided for making physical measurements. Initial samples may either be prepared in situ or introduced in a variety of ways. A block diagram of such an apparatus is shown on Fig.4.

In practice it proved best[29] to construct at least two chromatographic systems for handling the different sized samples involved: a large scale chromatograph was desirable for the separation of individual components from reaction mixtures, capable of handling total samples of up to ½ gm., and one or more smaller scale systems, of higher sensitivity, were desirable for analytical work on the purified components.

The value of having at least two chromatographic columns with different separating chracteristics in the large scale preparative system was appreciated at an early stage, as in many of the complex systems investigated there were examples of compounds that were coincident chromatographically on any one stationary phase and were therefore impossible to separate. In the majority of these cases

the multiple peaks obtained with the one column could be resolved, individually at least, on another column of a more, or less, polar nature. If this method of multiple peak separation failed, then it was indicative of a considerable similarity in physico-chemical nature of the compounds concerned.

2.13 Development

The development of a closed circuit apparatus, constructed (with the exception of the detectors) entirely of glass, has taken place in three major stages culminating in the apparatus employed for the latter, and greater, part of the work described in this thesis. The first stage was the construction by Timms[29] of a preparative system connected directly to an analytical system and, in this apparatus, the early work on the silicon-germanium hydrides was carried out. The preparative system was a single-column chromatograph with a four-way fraction trapping sequence. The column operated at ambient temperature, limiting separations to the lower members of the series, and thus the relative difficulty of recycling in this system was not a grave drawback as multiple peaks were rare. The analytical system consisted of the prototype gold chloride reactor and its accompanying chromatograph, a pyrolysis tube and chromatograph, and a molecular weight apparatus[110].

The next stage was carried out when the Author collaborated with Timms. It was realised that higher-boiling compounds than those already investigated were also prepared in the silico-germane reaction mixtures. As the amounts of these compounds were small,

larger preparations were necessary in order to obtain reasonable samples of these compounds. This meant that a larger scale preparative apparatus was required, fitted with two different columns, as multiple peaks were anticipated, with facility for operation at elevated temperatures. A six-way fraction trapping sequence was deemed necessary, and adequate recycling facility was also required. In addition, a large scale pyrolysis tube was desirable for preparative purposes. In view of the hazardous nature of the preparation of the silicon and germanium hydrides (see section 2.52) it was suggested that a small scale apparatus was included in the system for pilot experiments. The analytical system of the original apparatus was considered adequate in its existing form. An apparatus with these features was jointly designed and constructed by Timms and the Author during the latter's B.A. Part II work, and this is shown in diagram form in Fig.5.

This apparatus was subsequently employed, with some modification and reconstruction by the Author, in the earlier part of the work described in this thesis. In the interests of clarity, this will henceforth be described as the 'First Apparatus'. The subsequent development of this apparatus culminated in the construction of a completely new apparatus which was used in the latter part of this work and which will be called the 'New Apparatus'. Both apparatuses were constructed inside a large fume cupboard occupying the entire height of the laboratory, and were supported on a scaffolding made of slotted steel and steel rods. They were operated from within the fume cupboard.

FIG. 5

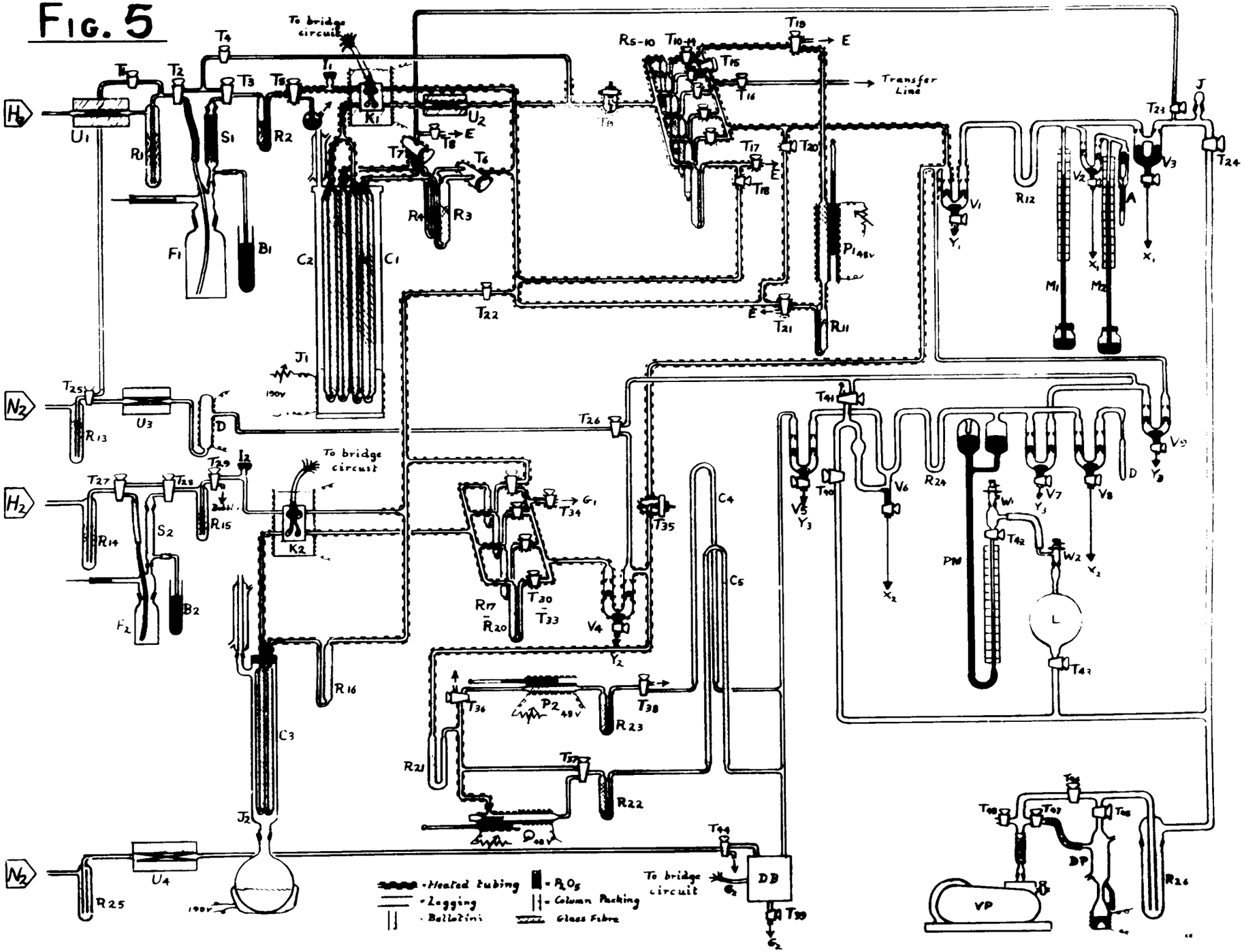
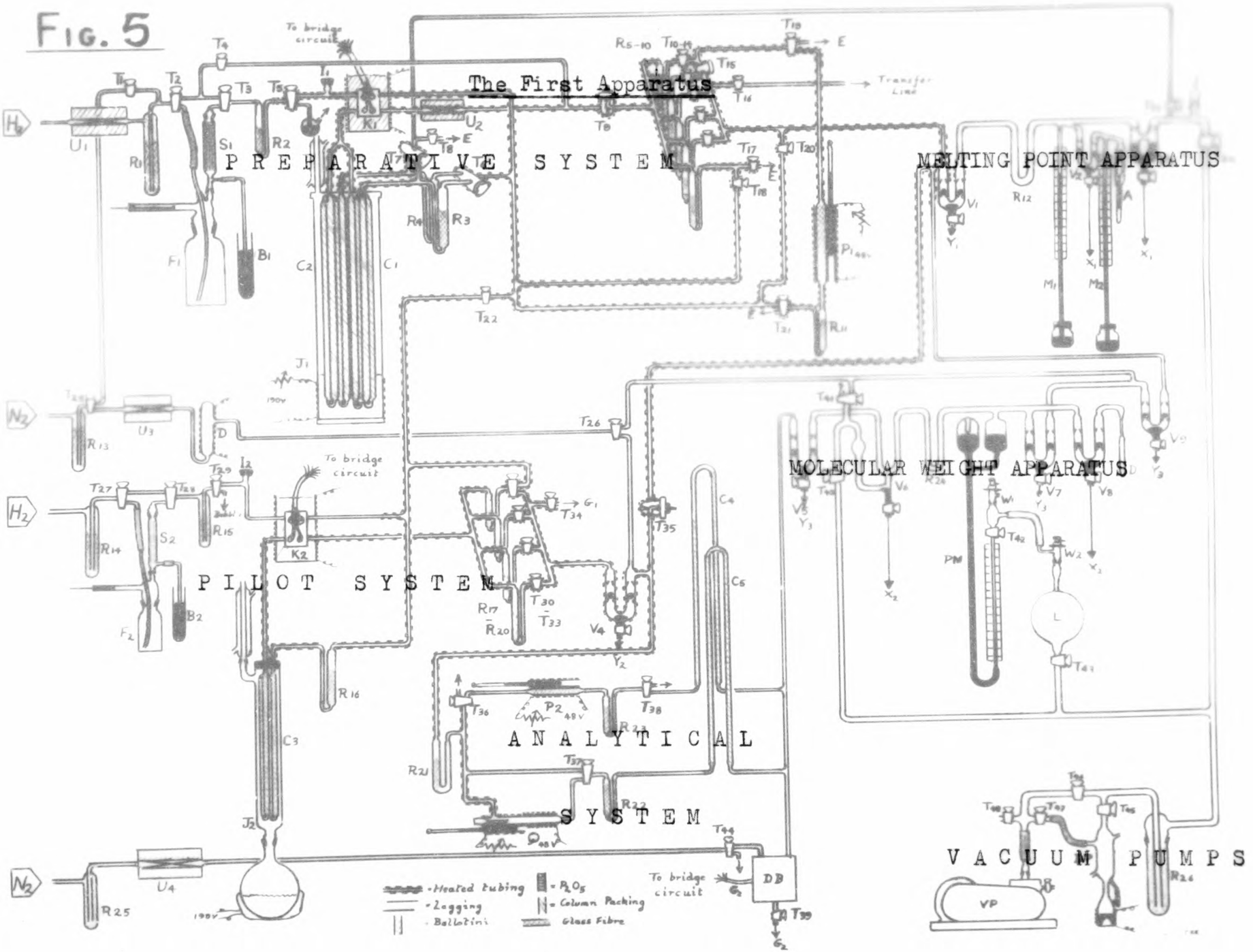

H2
N2
H2
N2
To bridge circuit
To bridge circuit
To bridge circuit
Transfer Line
E
U1
U2
U3
U4
K1
K2
R1
R2
R3
R4
R5-10
R11
R12
R13
R14
R15
R16
R17
R20
R21
R22
R23
R24
R25
R26
S1
S2
F1
F2
B1
B2
C1
C2
C3
C4
C5
J1
J2
P1 48V
P2 48V
D 90V
100V
T1
T2
T3
T4
T5
T6
T7
T8
T10-11
T15
T16
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T48
V1
V2
V3
V4
V5
V6
V7
V8
V9
Y1
Y2
Y3
X1
X2
M1
M2
A
D
PM
W1
W2
L
DB
DP
VP
G1
G2
Heated tubing
Lagging
Ballotini
P2O5
Column Packing
Glass Fibre

Fig. 5


FIG. 5
The First Apparatus
PREPARATIVE SYSTEM
MELTING POINT APPARATUS
MOLECULAR WEIGHT APPARATUS
PILOT SYSTEM
ANALYTICAL SYSTEM
VACUUM PUMPS
To bridge circuit
Transfer Line
H2
N2
VP
DB
Heated tubing
Lagging
Ballotini
P2O5
Column Packing
Glass Fibre

2.2 The First Apparatus - Design and Construction (Letters refer to Fig.5).

The First Apparatus was constructed almost entirely of Pyrex glassware, assembly being effected by in situ glass blowing. Metal-glass joints had to be made to the detectors and were originally made with Araldite adhesive (Ciba A.R.L.) as sealant on sleeve joints. These tended to crack when heated and so subsequently a mixture of glass wool and Araldite was cast around the joints, and no further trouble was encountered. In the chromatographic systems, semi-capillary tubing (i.d.2mm.) was used for all interconnections to minimise the volume. All taps in these systems had solid keys of 1 - 2 mm. bore and were sprung to withstand 15 psig.. In order to minimise grease absorption effects the keys of the taps were only sparingly lubricated with a silicone high vacuum grease (Edwards). Since heated columns were being employed, all taps and tubes had to be heated and this was achieved electrically (see Section 2.41). The tubes were heated to approximately 10° above the maximum column temperature and the taps to a somewhat higher temperature. Despite the tap heating, grease absorption was still a major problem, and in order to guarantee the purity of an individual compound, all the taps concerned with the particular experiments had to be 'conditioned' by that compound.

The columns in the preparative chromatograph (C1, C2) were packed with Silicone '702' (Midland Silicones) 10% and tri-tolyl phosphate (tri p-cresyl phosphate) 10%; both on a support of 'Embacel' (May and Baker). The columns in the analytical system (C4, C5) were

packed with 10% Silicone 702, and the column in the pilot system (C3) was packed with 10% tritolyl phosphate. The columns in the preparative and pilot apparatuses were installed in vapour jackets so that they could be operated at ambient or 64.5°C (boiling methanol). A subsequent modification to the preparative system permitted the liquid to be changed, and operation at 100°C was attempted, but this resulted in mechanical failure of the top manifold of the vapour jacket. The analytical columns were initially operated at ambient, but that on the gold chloride system was subsequently modified for operation at higher temperatures (see Section 2.41).

The preparative system and the pilot system used hydrogen as carrier gas and Gow-Mac hot wire katharometers (K1, K2) as detectors (see Section 2.45). All outlets were connected to a common scavenge system fitted with a pin-hole burner for normal operation. Subsequently the burner was fitted with a pilot light as a safety precaution.

Special reaction flasks (F1, F2) were fitted to the preparative and pilot apparatuses for hydride preparations (see Section 2.52).

The analytical system consisted of four different apparatuses, three sharing a common gas density detector (see Section 2.45) for quantitative measurements: The detector was used to determine molecular proportions of products from pyrolysis reactions carried out in a reactor (P2) and also from the gold chloride reaction carried out in the cell (Q) (see Section 2.6). The detector was also used, in conjunction with pressure measurements obtained by a Pearson Amplifying Manometer on samples in a fixed volume between mercury seals, for molecular weight determinations on the lower

hydrides[110]. As this last technique was effectively limited to compounds boiling below 150°C, it was not used in the work described in this thesis.

The analytical system was completed with a vacuum system which enabled vapour pressure and melting point determinations to be carried out (see Section 2.46). It was also provided with cone and socket fittings so that samples could be removed from the system. Vacuum was provided by a mercury diffusion pump backed up by a rotary vacuum pump.

Hydrogen for the system had residual oxygen removed by a catalytic cartridge and the stream was then dried by passage through a trap cooled by liquid nitrogen. Nitrogen for the analytical system was dried by passage through a trap cooled in liquid oxygen and then passed through a sodium deoxidiser (see Section 2.42). Gas flow was controlled by standard pressure heads (B.O.C.), and flow impedances (see Section 2.42) were used to obtain greater precision (U1 - U4).

The complete apparatus required little routine maintenance apart from regreasing the taps, re-activating the deoxidisers and clearing the drying traps of water. The purification traps had, however, to be filled up with refrigerant at least every 18 hours and it took a day to re-commission the apparatus if this was not done.

2.3 Shortcomings of the First Apparatus - Design of the New Apparatus

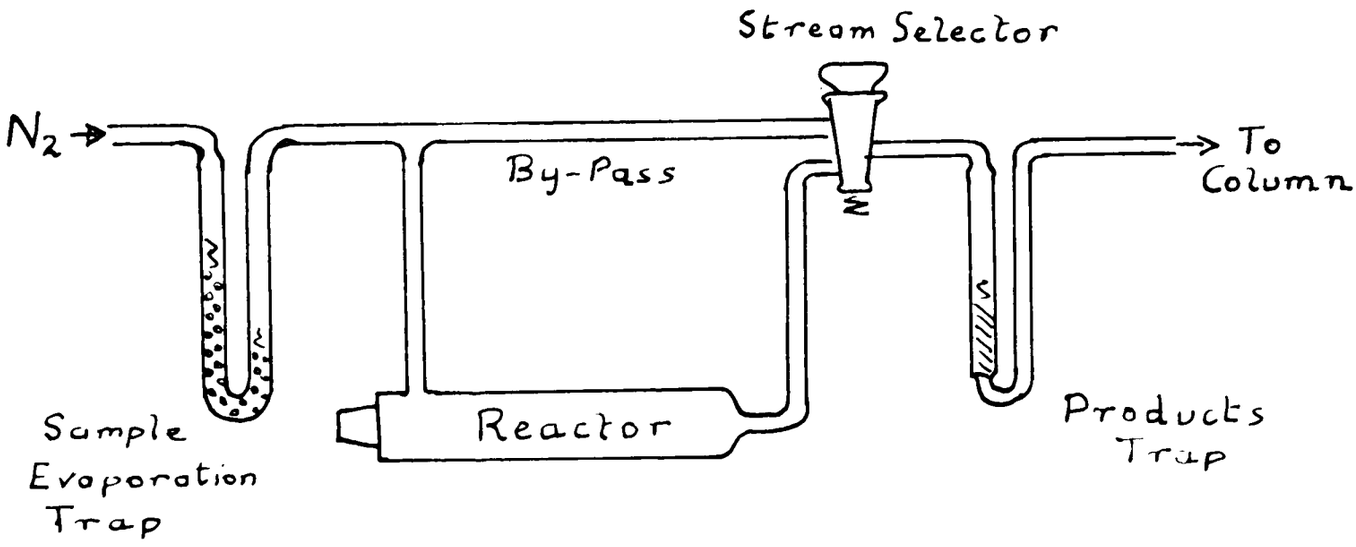
As the First Apparatus manifested several operational shortcomings and was damaged by vibration due to building work on the laboratory roof (in particular caused by a pneumatic drill, operated less than

12 feet vertically from the apparatus over a period of around 8 months), it was decided to design and construct a completely new apparatus of similar scope but on slightly different principles, for the later part of this work.

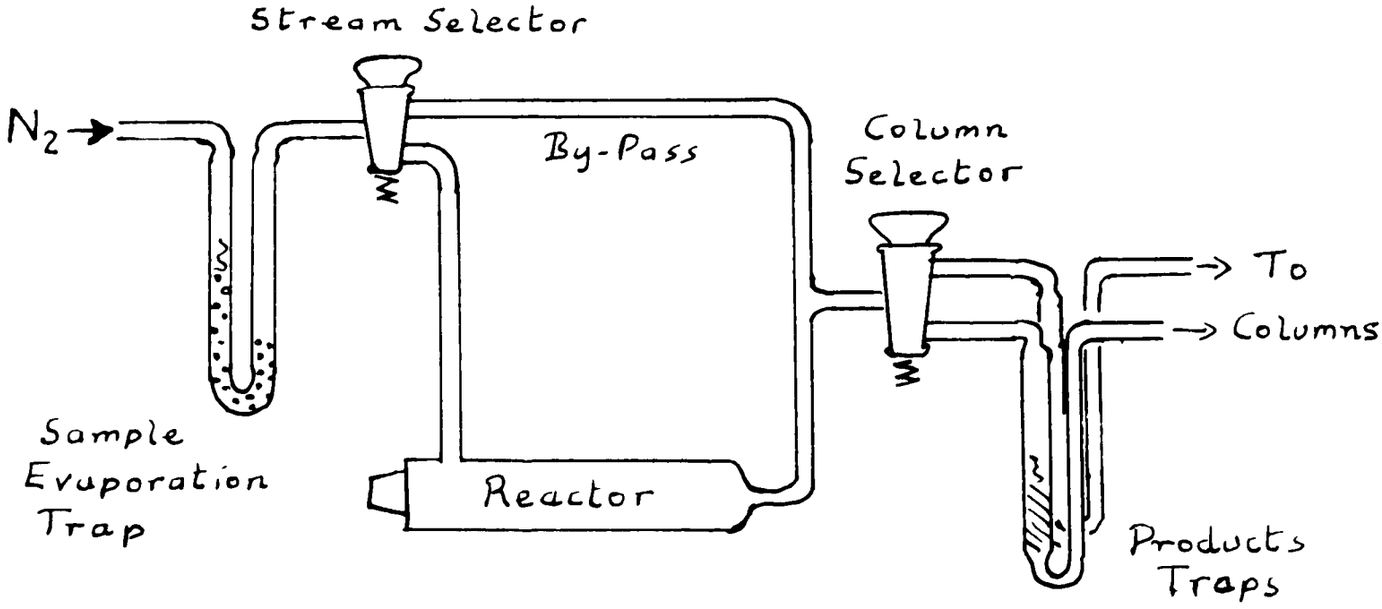
The major shortcoming of the First Apparatus was due to the large number of taps in the 'working' section (the parts of the apparatus through which samples actually passed) as absorption by grease was very significant. This was of particular significance when only small samples of compounds were obtainable, and sizeable samples were required for conditioning. Thus it was desirable to reduce the number of taps in the working section. This was achieved by altering the principle of the apparatus by reducing the working section in size and complexity and providing a more complicated peripheral system of gas supplies. Wherever possible, in particular in the fraction trapping sequences, the design was such that on recycling operations, samples left traps through the same side as they entered, the taps associated with the traps being merely used as controllable carrier gas inlets or outlets. One trap in each sequence was used, in conjunction with its tap, as a scavenge system for allowing unwanted sample to leave the apparatus and be burnt. None of the other taps associated with the trapping sequences were ever deliberately contaminated with samples, thus greatly reducing the number of operations required for their purification. The various recycling and transfer systems in the First Apparatus were replaced by a single manifold with valves and 'T' joints connected to different parts of the apparatus. Facility was made for pre-flushing

Fig. 6 The Gold Chloride Apparatus

A/ Original Design



B/ Modified Design (Simplified)



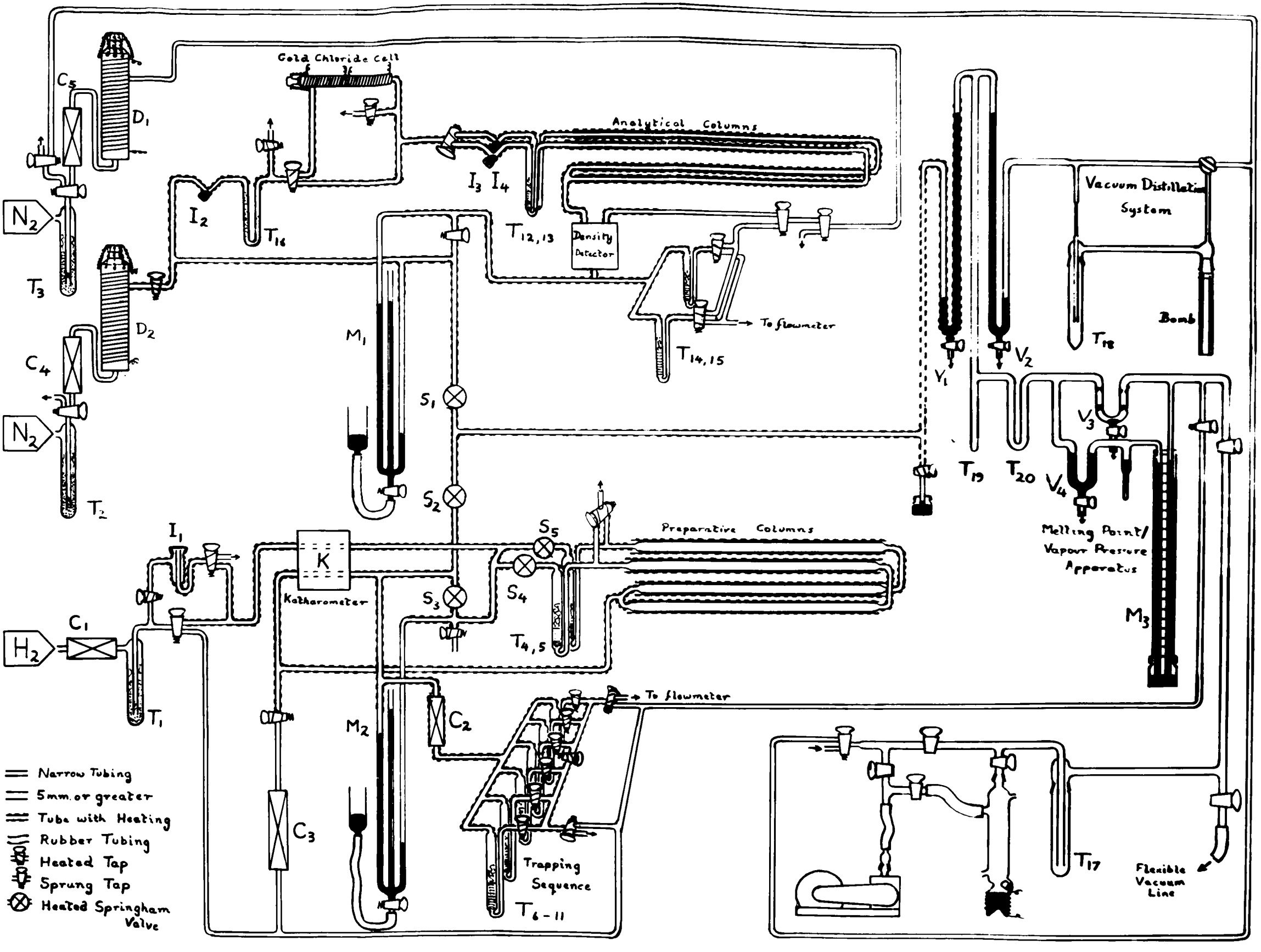
all recycling operations, thus reducing the chance of contamination of samples. As the reference supply of nitrogen for the density detector was to be used for recycling operations and the detector outlet was sealed into the system, this supply was also fitted with a deoxidiser. Taps on the recycling system were replaced as far as possible by diaphragm valves (Springham), and the column selecting tap in the preparative system was replaced by two of these valves. Ideally the other taps in the working section should have been replaced by Springham valves, but economic considerations dictated otherwise. Where the use of sprung glass taps was inevitable in the working section, care in defining their precise position and function could lead to a considerable reduction in undesirable effects of the absorption by grease. An example of this can be demonstrated in the system associated with the gold chloride reactor: The original system is shown in Fig. 6A in a somewhat simplified form. In this system the part of the stream selector that connected the reactor to the products trap was only purged when in the reaction mode. As the gas stream at this point consisted of a mixture of products and chlorine in nitrogen, certain components tended to be selectively absorbed on the tap grease. This meant that excessive purge times through the cell were required, resulting in large amounts of chlorine passing into the chromatograph. At least three conditioning runs under identical reaction conditions were required before consistent results were obtained. The modification, shown in Fig. 6B, limited the absorption in the stream selector to a single sample compound, which remained the same in a set of experiments. The fact that a

column selector tap was fitted was not so critical as this could be purged in the by-pass mode for 10-20 minutes if necessary, without detriment to the results, prior to injection of the products onto the columns.

All taps in the narrow bore part of the New Apparatus were of the 'Interkey' variety with 2mm. bore solid keys. Use of these taps simplified maintenance and provided easy replacement in the event of damage.

The analytical system was simplified by deletion of the pyrolysis apparatus, since this was not required, and the molecular weight apparatus was also omitted as the anticipated boiling points of the compounds to be investigated were too high for this technique. The functions of the pilot apparatus and the gold chloride apparatus were combined in a system fitted with two columns with similar packings to those used in the preparative system. This offered several advantages: The analytical system could be used for obtaining all retention data, thus rendering precise measurements on the preparative system unnecessary. Secondly, as the density detector was employed, the analytical system could be used for quantitative analysis of all reaction mixtures where the products could be identified. Thirdly, when the gold chloride reaction was applied to the alkyls, rather than the hydrides, many more products could be formed, and some of these formed 'multiple' peaks on the chromatograms (see Section 2.65). These could only be resolved by two-column techniques. Fourthly, by reducing the amount of apparatus from which numerical results were obtained, to a single two-column chromatograph, the

FIG. 7 NEW APPARATUS - SIMPLIFIED SCHEMATIC DIAGRAM



number of 'apparatus constants' was reduced, allowing easier comparison of results. There was, however, a potential drawback to this rationalisation: The requirement for quantitative analysis was that the areas of the 'peaks' on the chromatograms had to be easily measurable and, therefore, fairly broad. In addition, the density detector, in order to be truly quantitative, must measure slow changes of concentration on account of its volume. Thus in order to carry out analysis in a reasonably short time, reasonably low column efficiencies were required. On the other hand, the requirement for accurate retention data is high column efficiency. These conflicting requirements were met to a large extent by making the Silicone 702 column of moderate efficiency only so that this could be used as the primary column for the gold chloride analyses, and making the tritolyl phosphate column of higher efficiency for use as the primary column for retention data. In each case the secondary column could be used for cross checking and resolution of multiple peaks.

As it was intended to investigate compounds with higher boiling points than those for which the First Apparatus was originally designed, all the columns in the New Apparatus were electrically heated (see Section 2.41) so that any temperature from ambient to 160°C could be attained. It was also considered desirable to equip both the preparative and analytical systems with permanent manometers. These were constructed with three arms, one being open to air and the other arms being connected to the upstream and downstream ends of the columns. The functions of the manometers were threefold: They would provide a visual check on chromatograph performance, they

could be employed for detection of leaks and, since the open arms were equipped with a catchment reservoir, they would act as safety valves.

The vacuum system (see Section 2.46) was equipped with a melting point/vapour pressure apparatus similar to that in the First Apparatus, and was also fitted with a vacuum distillation system for extraction of products from the stainless steel bombs used for the majority of the preparations described in this work (see Section 2.51). The distillation unit had the advantage that direct transfer of products of reactions into the preparative system was possible.

The First Apparatus had proved difficult to repair and, for certain manipulations, difficult to operate due to its rather cramped arrangement. Accordingly, spatial arrangement was made a specific design feature of the New Apparatus. The following principles were observed in the design and construction of the New Apparatus:

1/ The frontal layout of the apparatus was, as far as possible, logical operationally and all taps were easily accessible.

2/ Ample spacing was allowed between tubes so that each was easily accessible for assembly and repair. Joints to be blown in situ were located in general in the most accessible spaces, and were removed as far as possible from other components so that damage to these was not done during assembly.

3/ Adequate clearance was allowed below traps, and any glassware below them was protected against damage by metal shelving.

4/ The apparatus was constructed, as far as possible, in large sub-assemblies, on a specially designed glass-blowing frame.

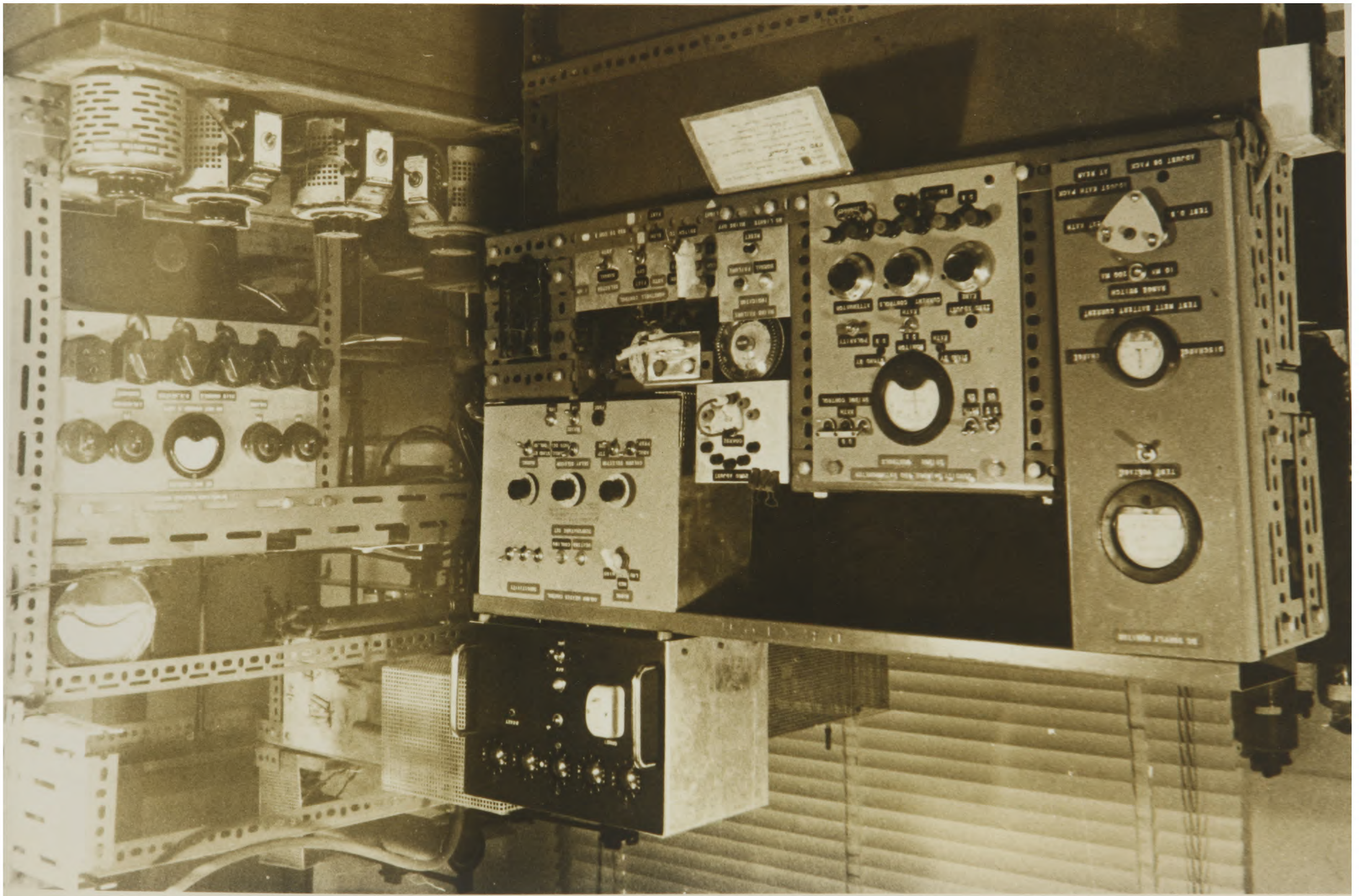
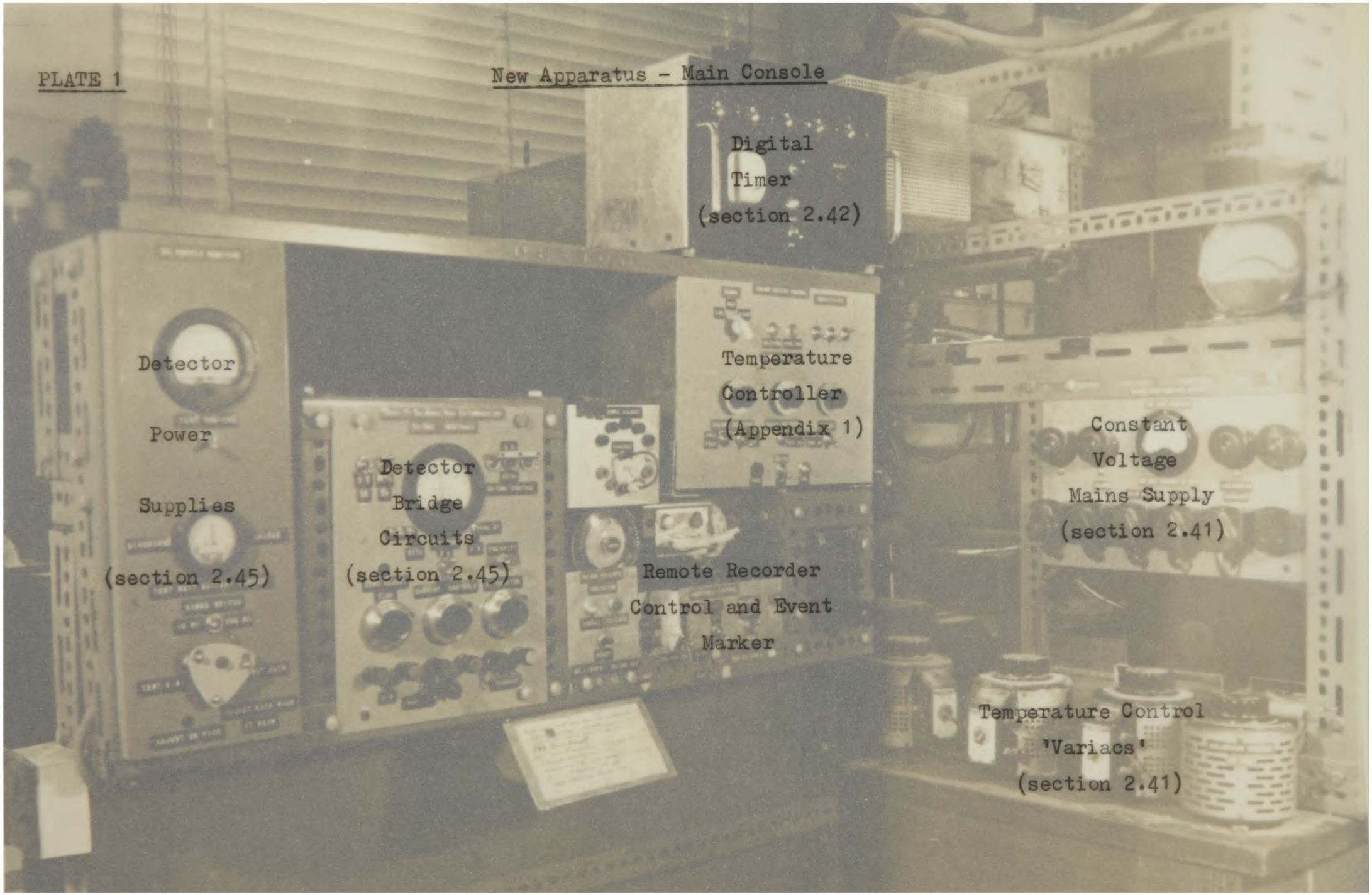


PLATE 1

New Apparatus - Main Console



5/ As much as possible of the heater winding was carried out on the sub-assemblies before erection.

6/ All measuring circuits and precise circuitry e.g. column temperature control, were connected to a remote console (see Plate 1).

7/ All crude heating circuits were connected to a common switchboard. They could be individually or collectively switched in series with an ammeter, via their neutral lines, although they were run off different 'Variac' transformers. (Part of this switchboard is shown on Plate 6).

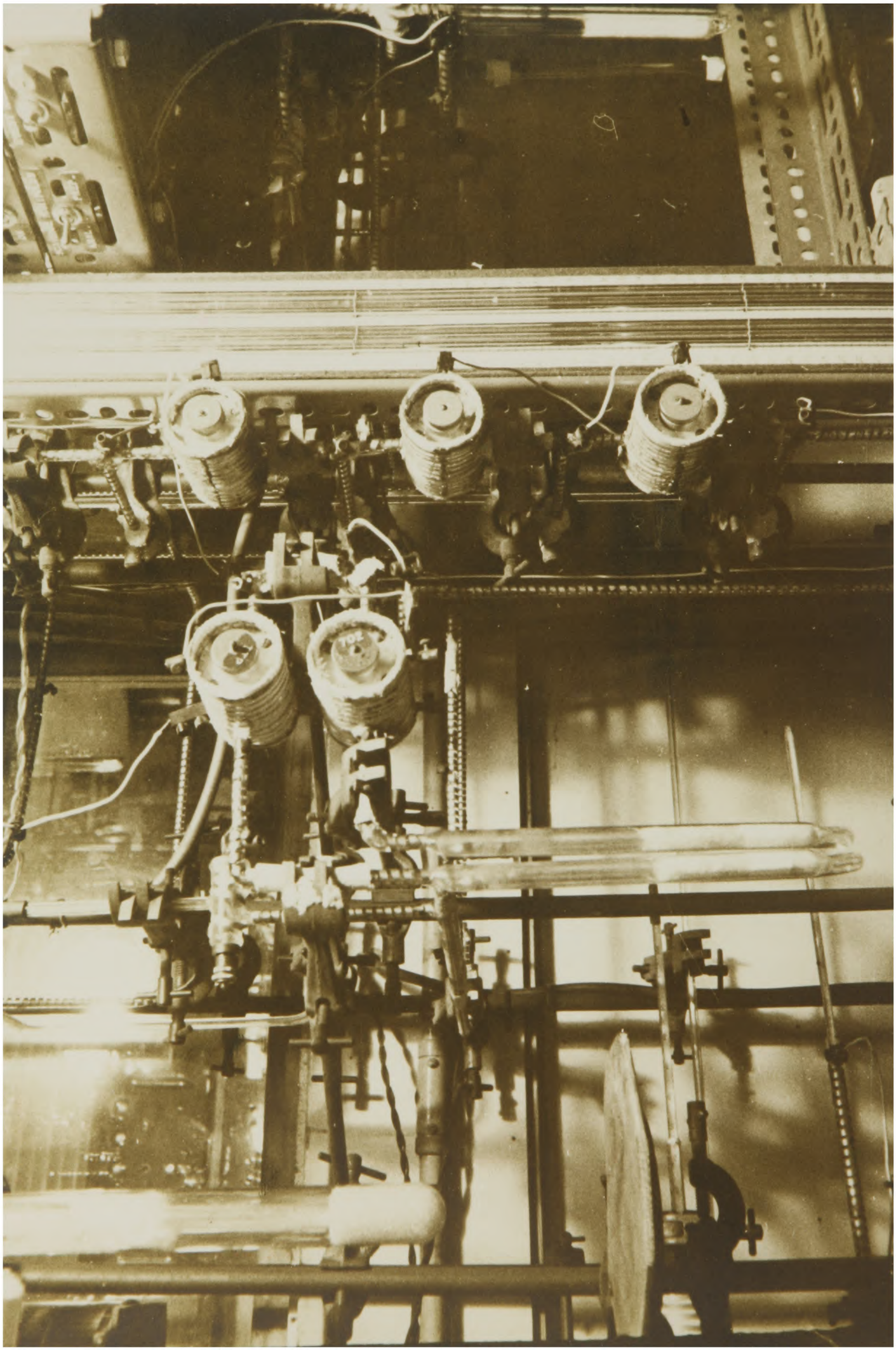
8/ The crude heating circuits were grouped, according to function, as 'Preparative', 'Recycling' and 'Analytical', these groups being separately controlled, so that excessive heating need only be applied when absolutely necessary, and then only to the parts in use.

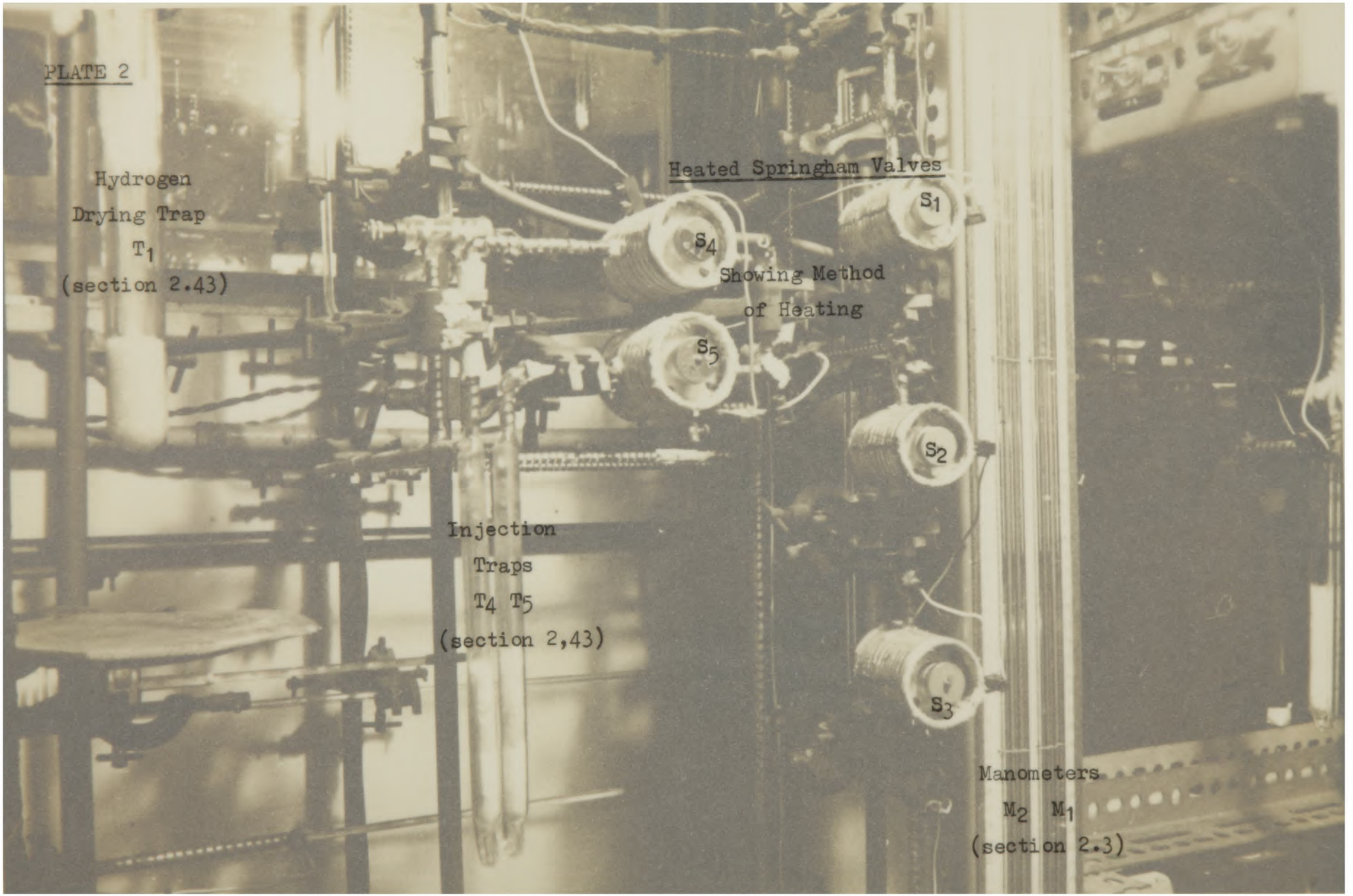
9/ All uninsulated electrical components, e.g. tape heating, were kept below 110V above Earth, and when they were located in the vicinity of taps, traps, etc., or near the operator, they were kept below 55V.

A diagram, of somewhat simplified topology, of the New Apparatus is shown in Fig.7. Owing to cartographic difficulties, the working sections are shown to be relatively larger than they in fact were.

2.4 Components, Systems and Techniques of Operation

This section is concerned with the development, construction and operation of various components and systems fitted to the New Apparatus. Reference is made to the previous apparatuses where




PLATE 2
Hydrogen
Drying Trap
T_1
(section 2.43)
Heated Springham Valves
S_1
S_4
Showing Method
of Heating
S_5
S_2
Injection
Traps
T_4 T_5
(section 2,43)
S_3
Manometers
M_2 M_1
(section 2.3)

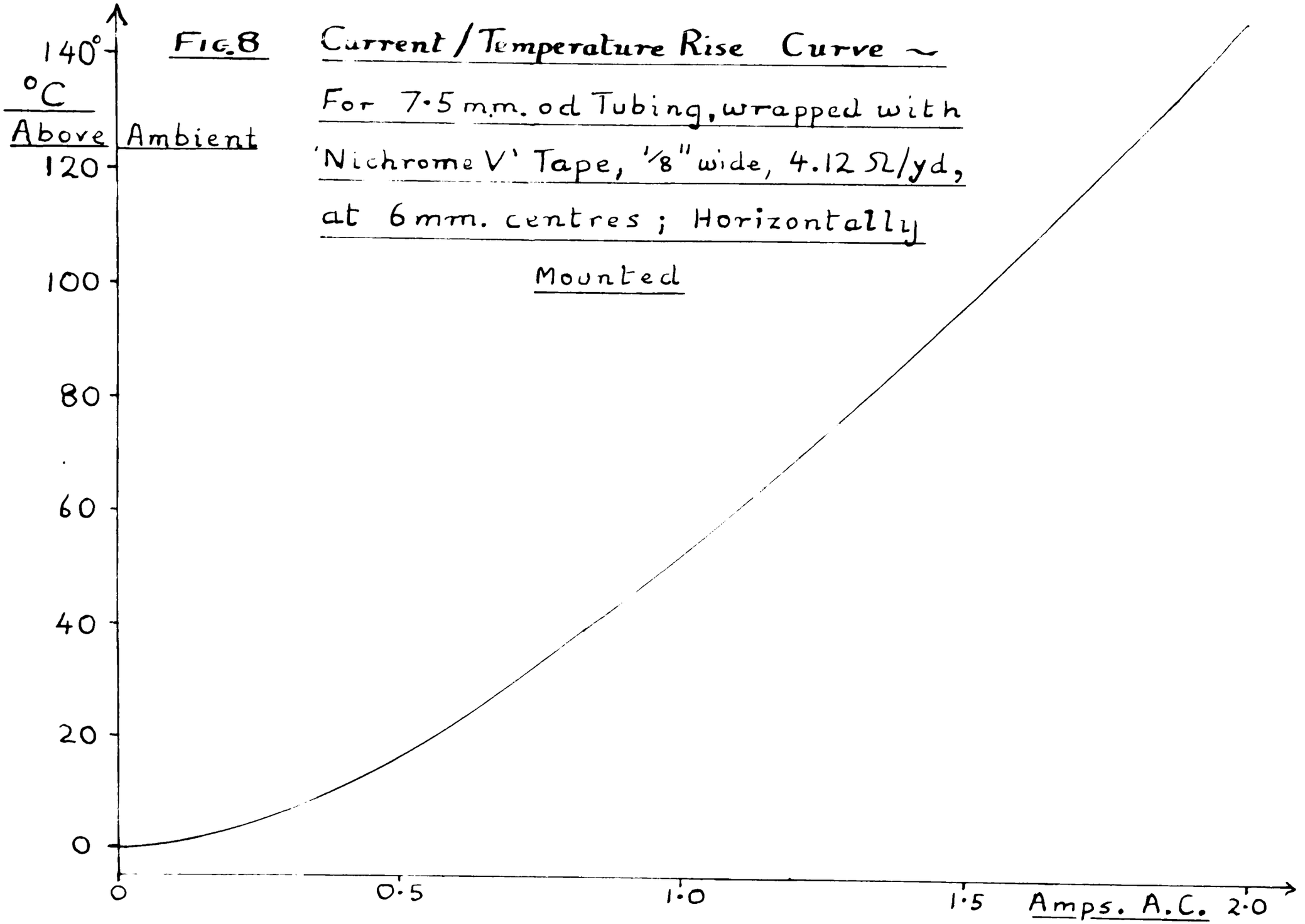
applicable. Letters in brackets refer to the diagram on Fig.7 and these letters are also used on the Plates.

2.41 Electrical Heating

In the First Apparatus and the New Apparatus, heating of tubes, taps, detectors, reactors and furnaces was achieved by wrapping the components, or casings around the components, with heating tape, with approximately evenly spaced turns. The tape used was Nichrome V (British Driver Harris), usually of 1/8" width with resistance 4.1 ohm/yd., although other sizes were used as well. In the case of taps and valves even spacing was not possible, so turns had to be insulated by sleeving or asbestos paper. Subsequently, the Springham valves were mounted in aluminium cans which were wrapped with asbestos paper and then were wrapped with heating tape in the normal way (see Plate 2 which shows S1 - S5 in the New Apparatus). Tape was chosen in preference to a method which had become traditional in the laboratory, but which the Author considered to be generally ill-advised, namely, the method of wrapping with wire, followed by lagging with asbestos string. Tape enabled better thermal contact between heater and glass to be obtained; local hot spots were avoided as about half the glass surface was covered with tape. The assembly was less bulky, breakages and leaks were easier to detect, and the system could be designed to operate at a predictable temperature (see Fig.3). 'Araldite' adhesive proved suitable for sticking down occasional turns, particularly near corners, as it survived 160°C for short periods and 100°C indefinitely. Junction between sections

FIG.8 Current / Temperature Rise Curve ~

For 7·5 m.m. od Tubing, wrapped with 'Nichrome V' Tape, 1/8" wide, 4.12 Ω/yd, at 6 mm. centres ; Horizontally Mounted



of tape was easily and neatly effected by 'crimping' short lengths of copper tube around the overlapping ends. Where the tubes were clamped, the turns were spread slightly and two layers of asbestos paper were provided as electrical and thermal insulation.

This method of tube heating was also used in the early work on the gold chloride reaction described in Sections 4.12 and 4.13, to heat the column in that system. As the column in the First Apparatus was vertical it was not expected that very accurate control would be possible, as the top of the column would be heated by convection from the bottom and this would be susceptible to draughts. It was estimated that control, at column temperatures around 120°C., was only possible to within $\pm 2^{\circ}C$.

When the New Apparatus was designed it was decided to attempt to modify this basic method for heating all the chromatographic columns since it was potentially the easiest and cheapest way of obtaining a controlled variable temperature. In view of the convection effects experienced with the vertical column in the First Apparatus, the possibility of using horizontal straight columns, protected from draughts, was suggested so that natural convection would be the only form of heat loss. Accordingly, glass tubes, selected so that the column tubes would just fit inside, were wrapped with nichrome tape (1/8" wide and 4.18 ohm/yd.) at 6mm. $\pm$ 0.2mm. spacing, and an average spacing of 6mm., each turn being stuck down with 'Araldite', and all surplus adhesive being carefully removed. The tubes were about 4'6" long and were mounted in a topless box, the ends being of asbestos board for electrical and thermal insulation, the sides

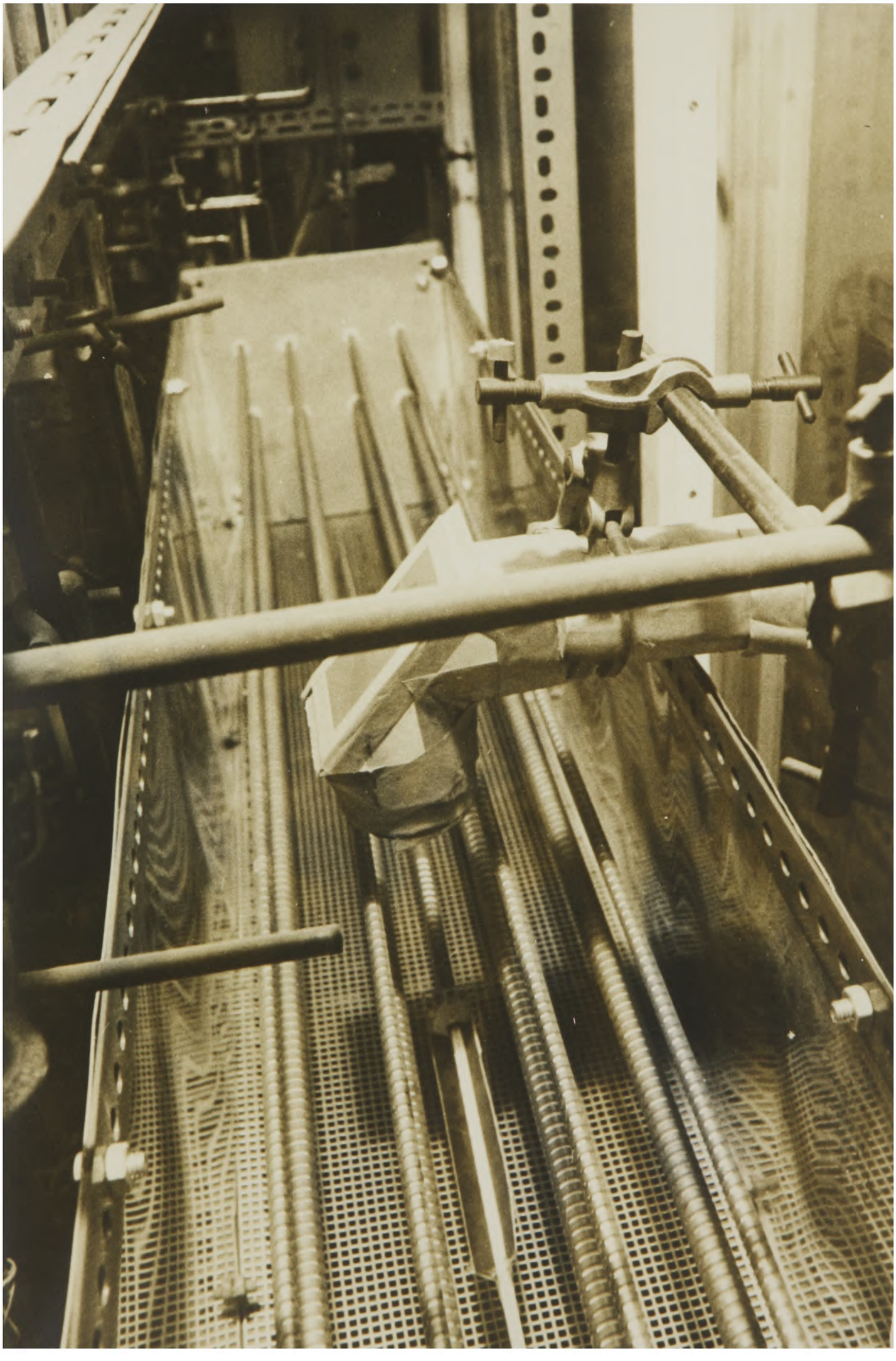
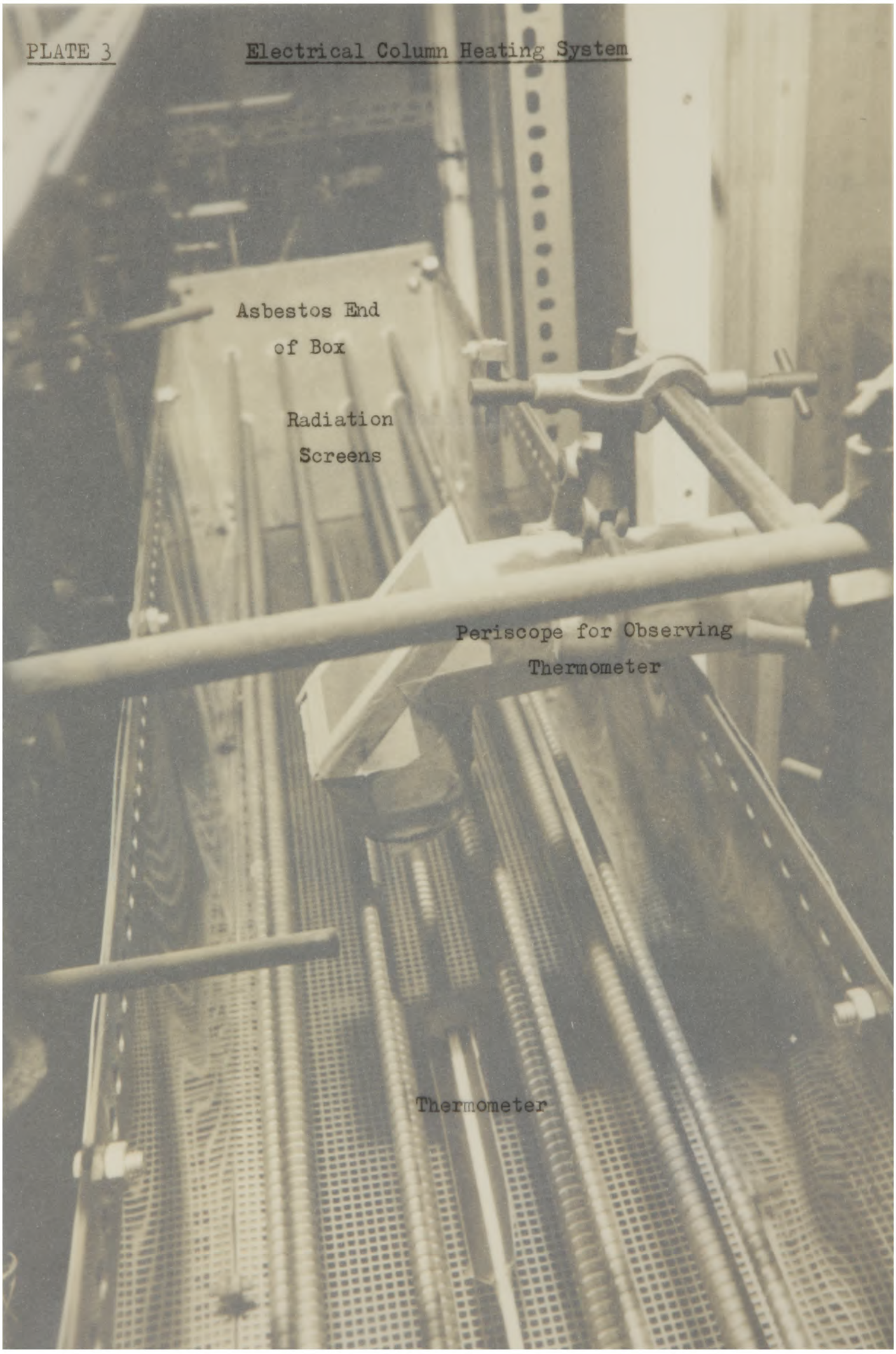


PLATE 3 Electrical Column Heating System



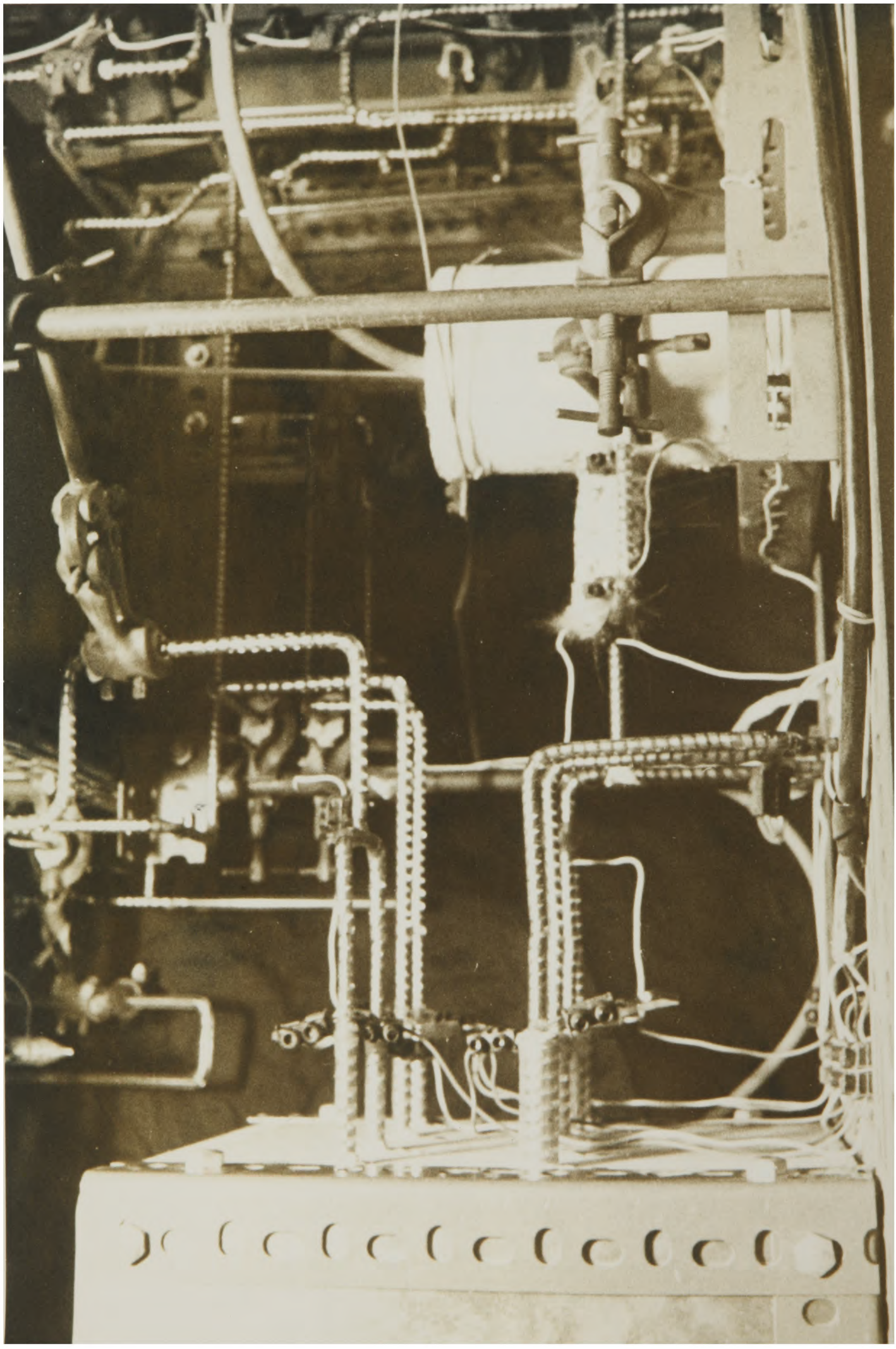
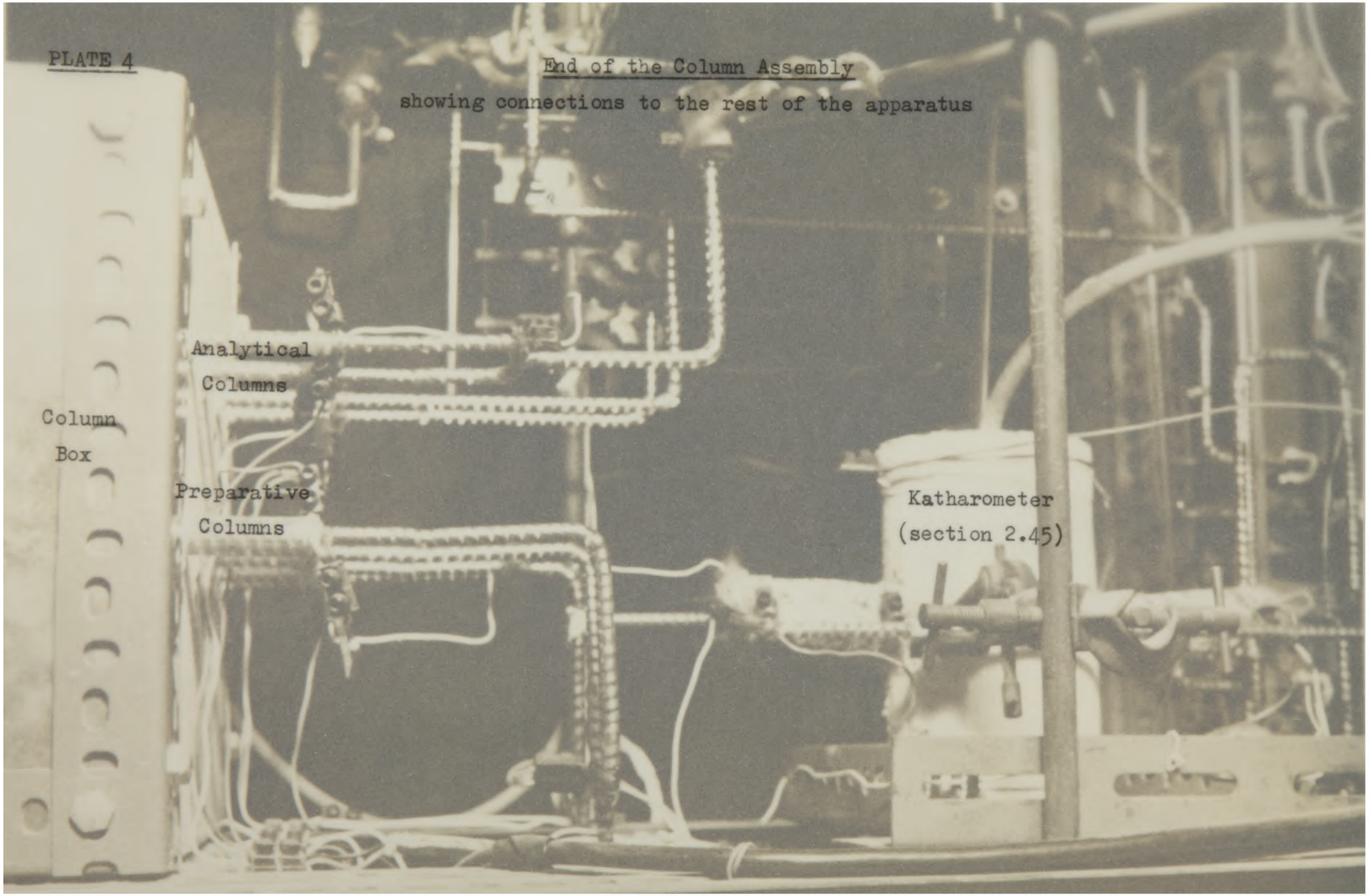


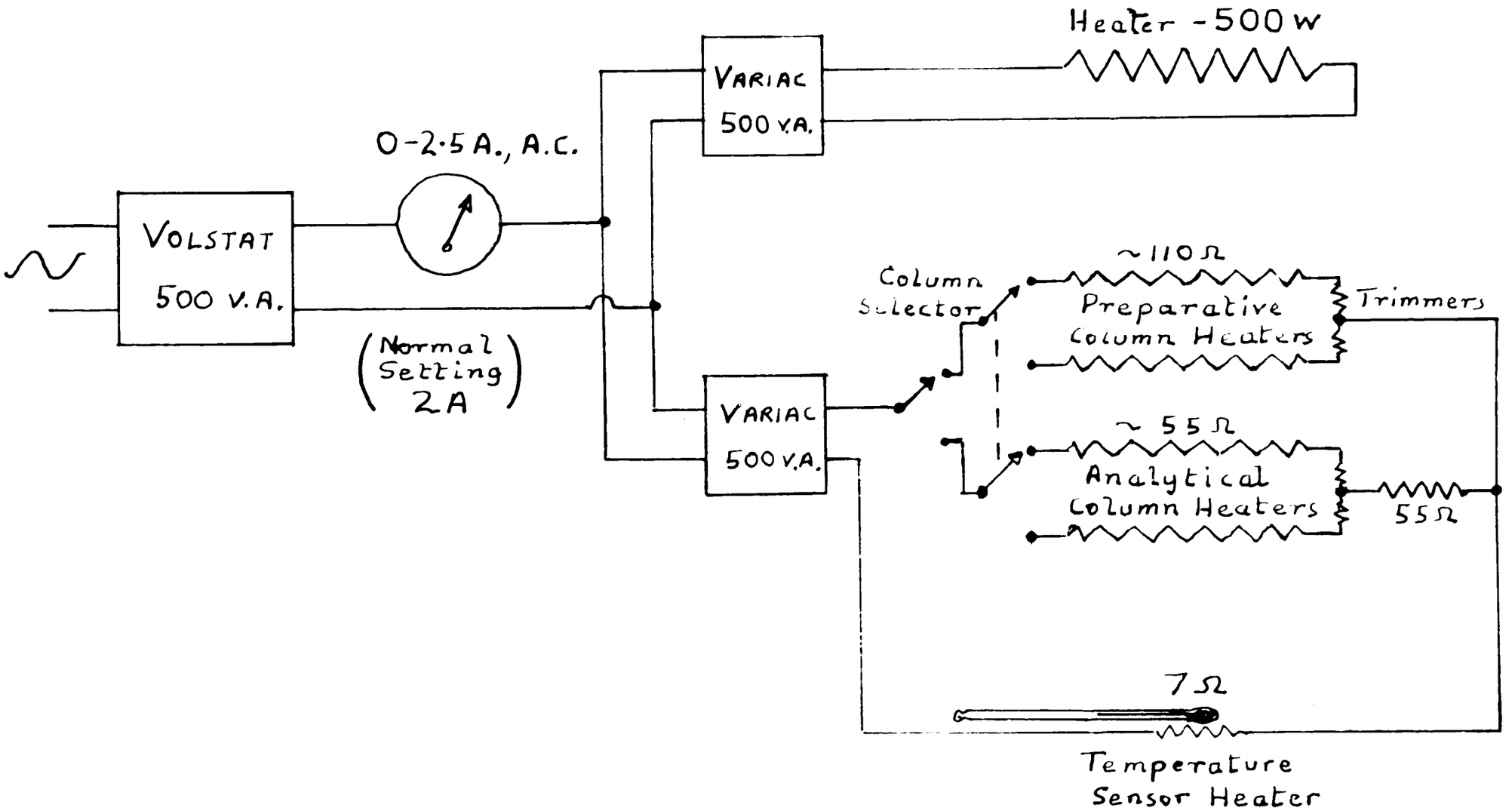
PLATE 4


End of the Column Assembly
showing connections to the rest of the apparatus
Analytical Columns
Column Box
Preparative Columns
Katharometer (section 2.45)

being of bright aluminium sheet as a radiant heat shield and draught excluder, and the bottom being of perforated aluminium sheet to act as a heat spreader and to eliminate sideways draughts while allowing controlled vertical convection (see Plate 3). Each column was packed in two sections, each approximately 4'3" long, which were installed in the heater tubes and connected by a narrow bore U tube at one end of the column box, and connected by easily accessible joints to the rest of the apparatus at the other end (see Plate 4). These joints could be easily cut for column replacement. Only one column at a time was heated and it can be seen from Plate 3 that the columns were sufficiently well separated to be thermally independent. The heater tubes also acted as heat spreaders and greatly simplified calibration, as thermometers could be inserted and observed through the gaps between windings. For calibration the thermometer bulbs were whitened and were buried in column packing material to duplicate, as far as possible, actual column conditions. In series with the heater in use was a similarly wrapped tube, of the same diameter as the analytical column heaters (7.5 mm. o.d.; the preparative column heaters being 15mm. o.d.), containing a thermometer with whitened bulb immersed in column material, and a thermistor similarly immersed. This was installed in the column box, and the thermometer was observed with a no-parallax periscope (see Plate 3).

Two methods of column temperature control were tried, the first employing an electronic temperature controller in conjunction with the thermistor mentioned above. This was relatively unsuccessful (see Appendix 1). The second, and much more simple, method used an

FIG. 9 Schematic Diagram of Column Heater Circuit

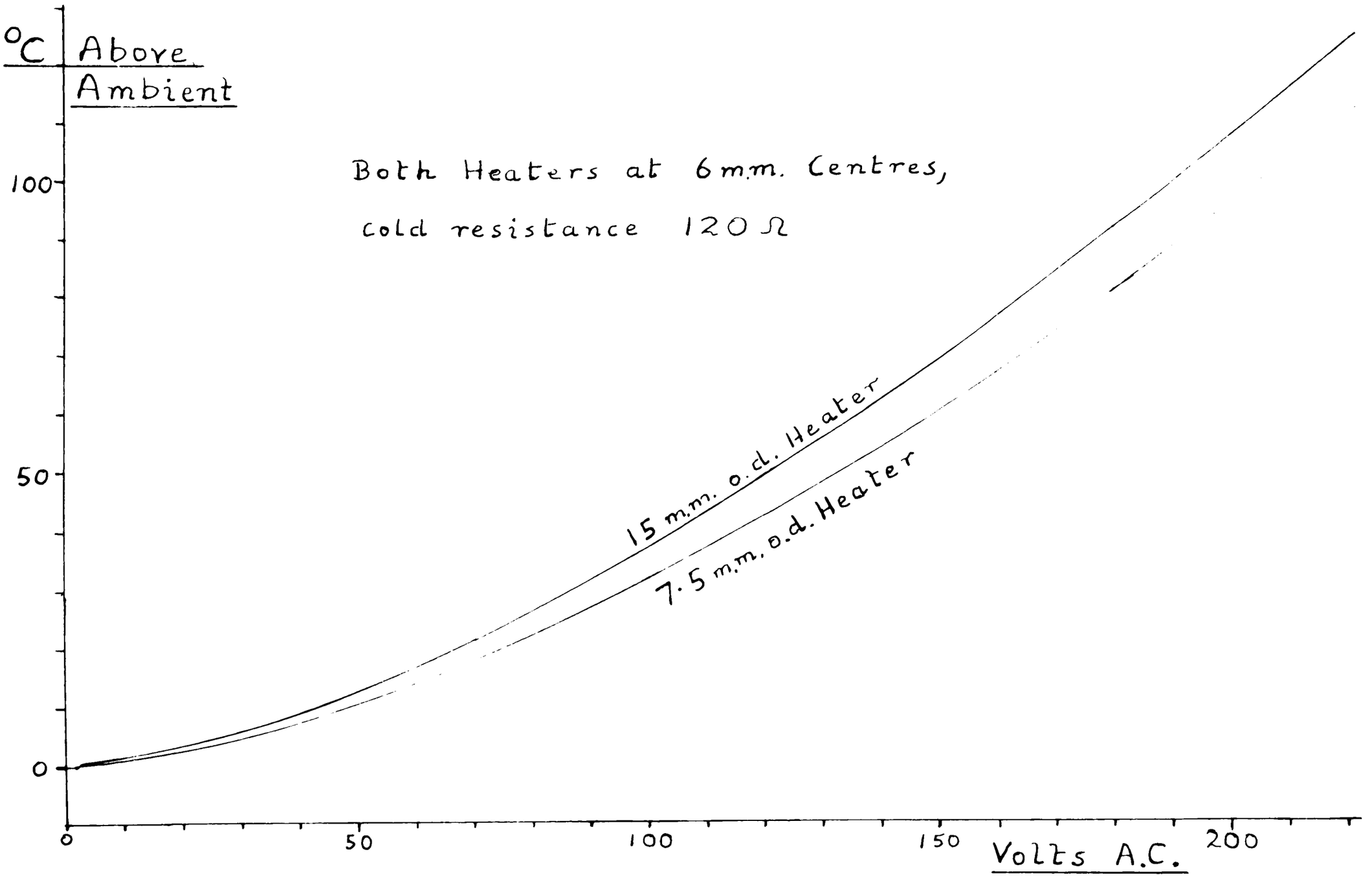


accurately controlled voltage source, and relied on manual adjustment to compensate for ambient temperature variations. The controlled voltage was provided by a 500VA. Variac rotary autotransformer which was supplied from a 500VA. Volstat constant voltage transformer (Advance) run off the mains. A second Variac transformer in parallel with the first, powering a heater, enabled the Volstat to be run under its optimum conditions. The column heaters were adjusted to the same resistance by series resistors, those on the analytical system powering some other tube heating. The complete circuit is shown in Fig. 9. The dial of the column heater Variac was calibrated directly in degrees above ambient which generally enabled a temperature within 1°C of the desired value to be attained, fine adjustment being subsequently made if required. Since the apparatus was constructed in a fume cupboard within a room, the ambient changes were rarely greater than $\pm$0.5°/Hr., particularly at night. Thus, except for precision runs, (which were carried out at night in any case) hourly temperature adjustment was adequate.

During calibration of the column heaters, it was found that the temperature differences from point to point within the heaters varied within a range of less than $\pm\frac{1}{2}$°C with the heater 100°C above ambient, and it was appreciated that the glass tubes containing the columns would act as extra heat spreaders reducing the variation.

It was found that at a given heater current, and hence the same wattage per unit surface area, the preparative column heaters attained a higher temperature than the narrower analytical column heaters (See Fig.10). At low currents the wider tube attained a temperature

FIG. 10 Column Heaters ~ Voltage / Temperature Curves



above ambient 18% in excess of that of the narrower tube, but at higher currents this fell to about 11%.

The thermal time constants of the columns were approximately evaluated: The value for the analytical columns was 4½ minutes, and for the preparative columns, 5 minutes. This meant that temperatures within 0.1° of the equilibrium values would be reached, with the most extreme control changes possible, within 33 minutes and 39 minutes respectively.

2.42 Gas Supplies - Control and Purification

It was found that the pressure control stability of cylinder head controls (B.O.C.) was absolute rather than proportional to pressure, and thus for flow stability in the chromatographs, high pressure settings, consistent with safety in glass apparatus, were desirable. As these pressures were higher than those required for obtaining the desired flow rates through columns, some form of flow impedance was required. Orifices or fine capillary tubes were rejected as being rather unstable and prone to blockage by particulate matter. However, a long porous plug is less prone to these disadvantages and, accordingly, flow restrictors (C1 - C5) were made by packing narrow glass tubes with small glass beads (Ballotini, grades 13 or 17). The packing was held in place, at the downstream end by a plug of glass wool retained by a restriction, and at the upstream end by another glass wool plug.

It proved possible to construct an impedance within 10% of any desired value for a particular gas. Ideally, unless these restrictors

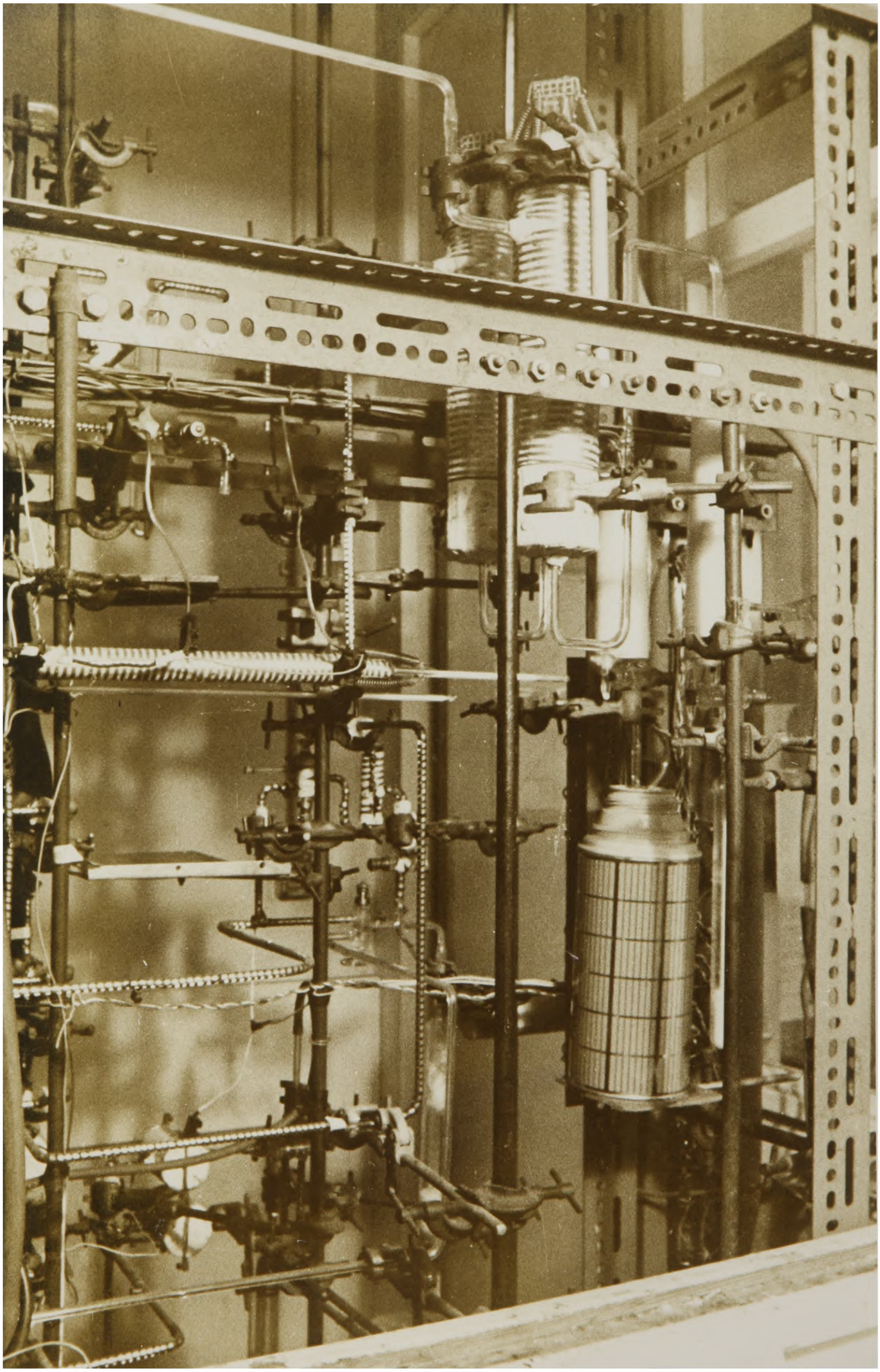
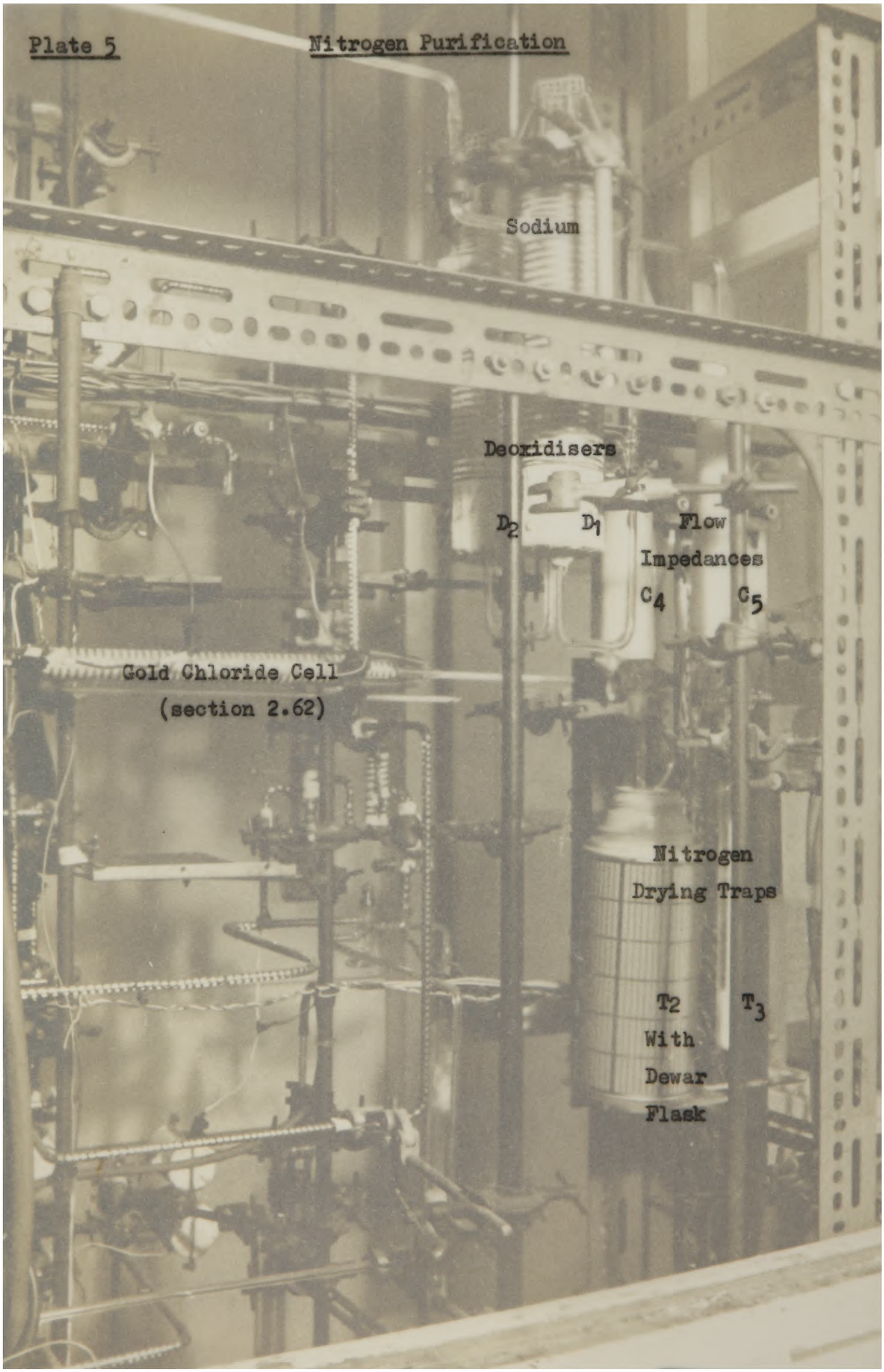


Plate 5

Nitrogen Purification



are very firmly packed, they should be mounted downstream end down to prevent 'Fluidising' of the bed of ballotini, which leads to instability. Recently, attempting to overcome this difficulty, it was realised that Ballotini are made of soft glass and therefore could be sintered inside a Pyrex glass tube. This was successful if the tube was heated until, in subdued daylight, the ballotini appeared faintly red.

The value of any impedance will change with temperature and thus the restrictors were usually lagged with a layer of cotton or glass wool surrounded by a cylinder of either white cardboard, aluminium foil, or asbestos paper (depending on operational requirements), to confer short term stability at least.

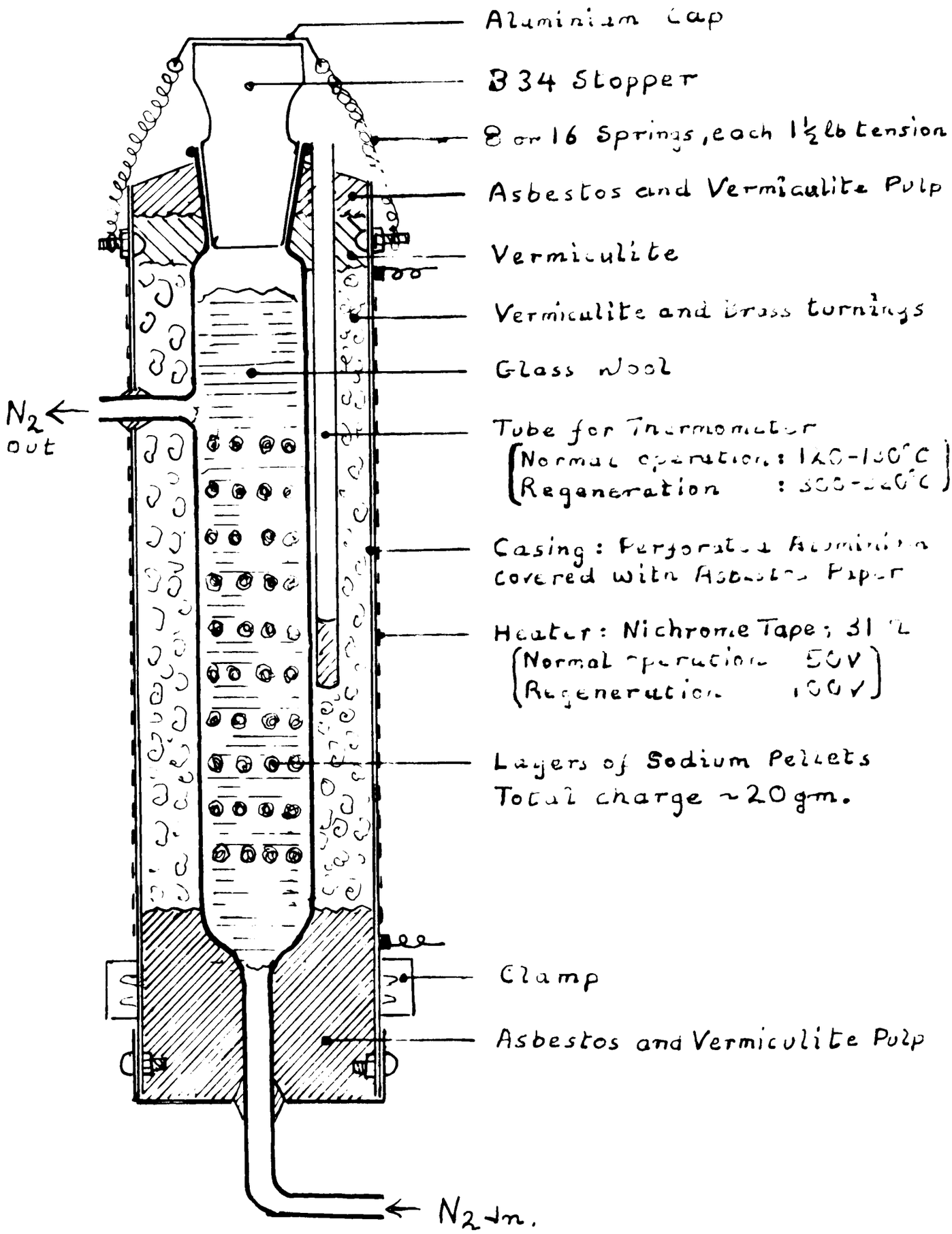
The stability of flow rates using a restrictor and a good cylinder head with an operating pressure around 25 p.s.i.g. appeared to be better than the precision with which the flow rates could be measured ($\pm\frac{1}{2}\%$).

Flow rates were measured using bubble flowmeters[1b] constructed from glass tubing and calibrated with wetted walls. Flowmeters of 100ml. and 25ml. capacity were used respectively for the preparative and analytical chromatographs. The bubble mixture was dilute 'Teepol' (about 5%) and was assumed to be pure water when making water vapour pressure corrections (see Section 2.72). For this purpose, thermometers were attached to the flowmeter walls.

Timing was originally carried out using a stopwatch but it was suspected that operator error was less than stopwatch error ($\pm$0.2 seconds). For precision measurement and digital readout, an electronic decade counter was constructed by the Electronics Staff.

FIG. 11 **Sodium Deoxidiser**

Modified Design ~ Half Scale



The Author ascertained[111] that mains frequency was accurate within $\pm$0.1% for 93% of the time, and thus full wave rectified pulses derived from the mains were counted. This timer was fitted with remote stop/go and reset switches which were installed at convenient places near the main apparatus. It was found that the Author's anticipatory reflex was 0.02 sec. and thus timing to 0.05 sec. was possible.

Whereas adequate purity of the hydrogen supplies for the First and New Apparatuses was achieved by the use of catalytic cartridges (Deoxo) followed by removal of water by traps cooled in liquid nitrogen, the purity of the nitrogen supplies was critical, particularly for the gold chloride technique. Sodium deoxidisers[112] were selected for the purification of the nitrogen supplies. As fitted to the First Apparatus, these consisted of electrically heated vertical glass tubes each fitted with a B29 socket at the top through which alternate layers of glass wool and small sodium pellets were packed, a gas inlet being provided at the bottom, and an outlet at the side near the top. For initial activation and periodic reactivation, each deoxidiser was connected to a flexible vacuum line, via the ground glass socket, and heated to 300 - 320°C at which temperatures the sodium 'sputtered'. Normally each deoxidiser was equipped with a sprung stopper and was run at 100 - 120°C. However major problems were experienced with the springing, as pressures up to 15 p.s.i.g. were employed, and catastrophic failure of the glassware occurred on one occasion.

Accordingly, when the New Apparatus was built, the deoxidisers were completely redesigned, with the aim of making them safer and more easily maintained. A sectional diagram of the modified deoxidisers

is shown in Fig.11: The dimensions were increased to those of B.34 components to facilitate packing and the device was constructed inside a metal case, with the glassware rigidly cemented in place, so that springs could be attached to the case, instead of to glass 'hooks'. The number and size of the springs were adjusted so that the device would act as a smooth safety valve if overloaded. The greater thermal mass of the modified deoxidisers, coupled with internal lagging, conferred a greater thermal stability on the deoxidiser tubes, resulting in greater flow stability of the nitrogen. The heaters on the two deoxidisers in the New Apparatus (D1, D2) were run in series for normal operation off a supply of 100V as it was found that short-circuiting each in turn enabled the other to reach the desired activation temperatures. Activation was still carried out with a flexible vacuum line attached to the top, allowing the deoxidisers to cool down to near room temperature and providing a positive pressure of nitrogen before removal and replacement of the stoppers. Reactivation in both apparatuses was carried out at three-weekly intervals, and the deoxidisers only required fresh charges of sodium annually.

The nitrogen supplies and purification apparatus is shown on the right of Plate 5.

2.43 Sample Introduction, Injection and Trapping

Sample introduction into a closed circuit system can be effected in two principal ways: The first is by attaching a preparative apparatus to the system, as in the silane preparation described in Section 2.52 and in the distillation from the stainless steel bombs (Section 2.51).

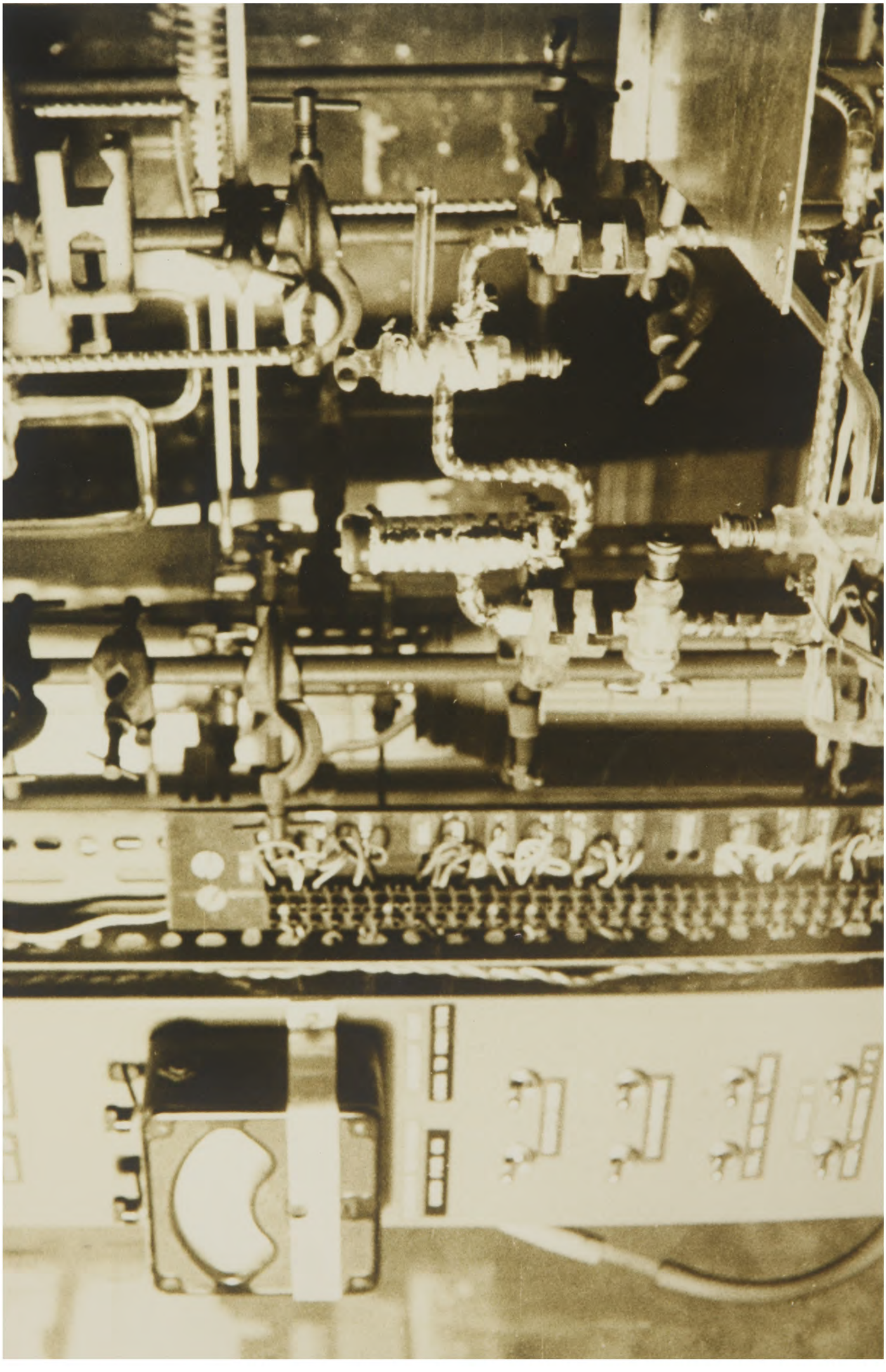


PLATE 6

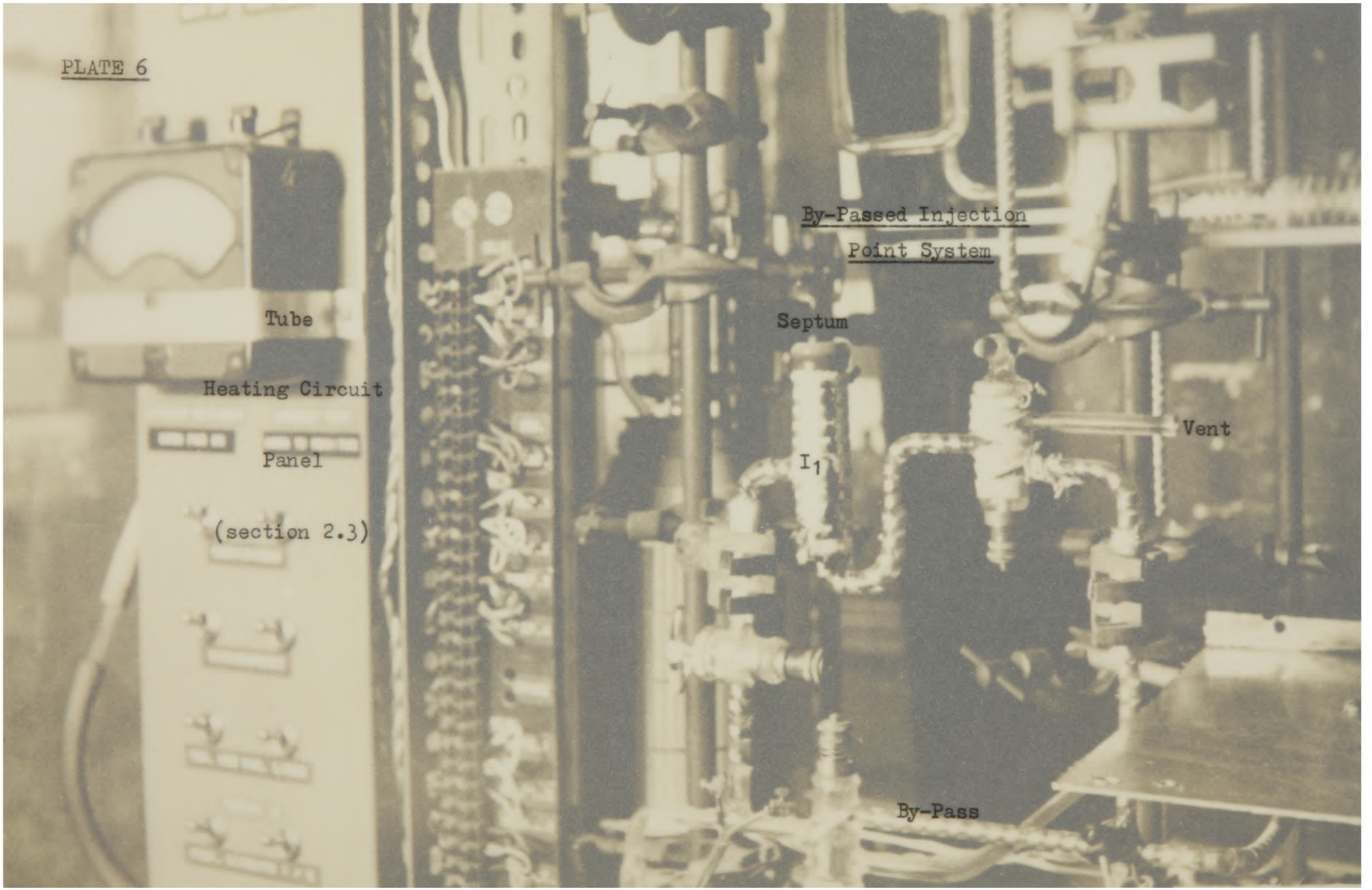
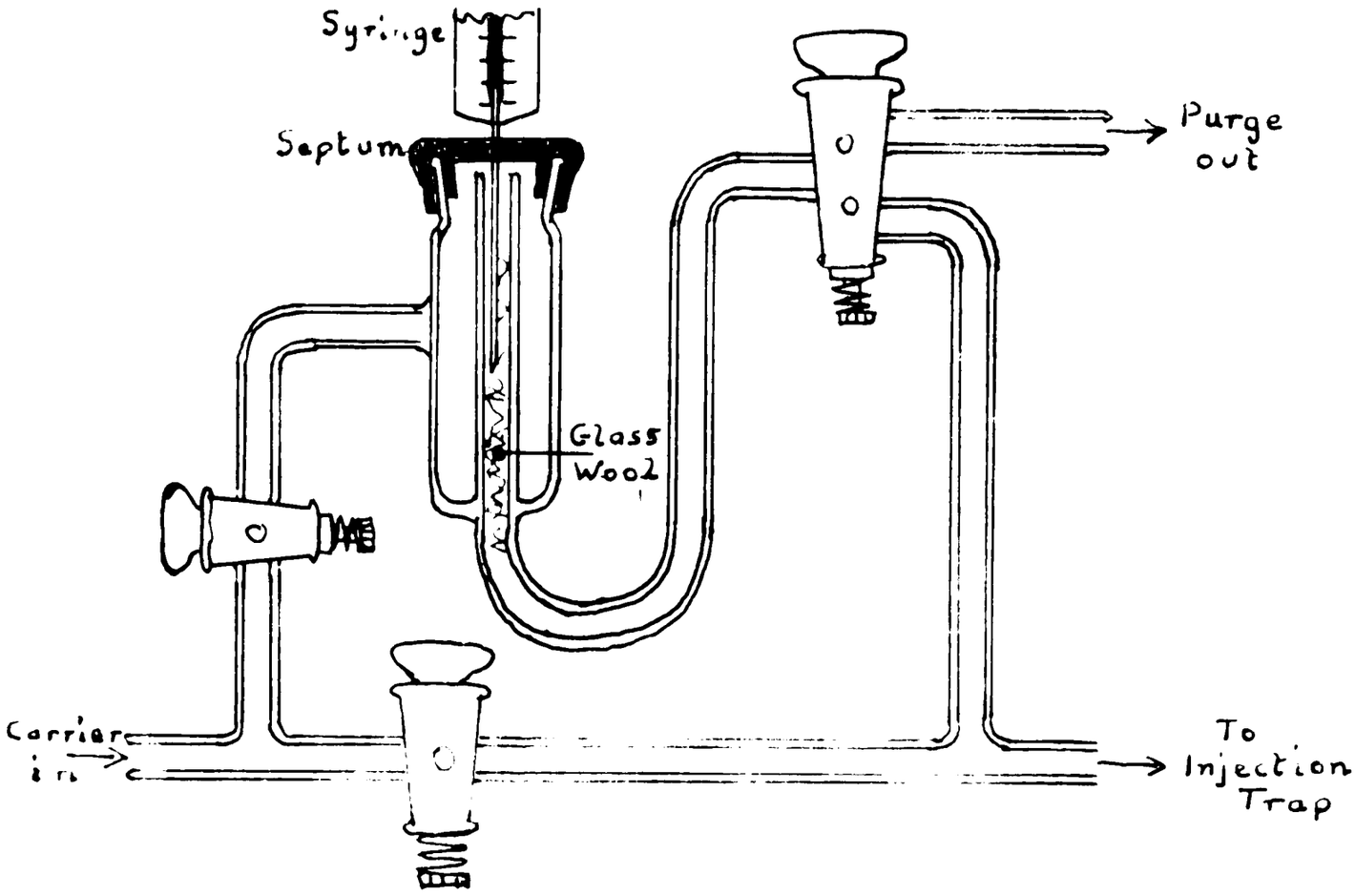
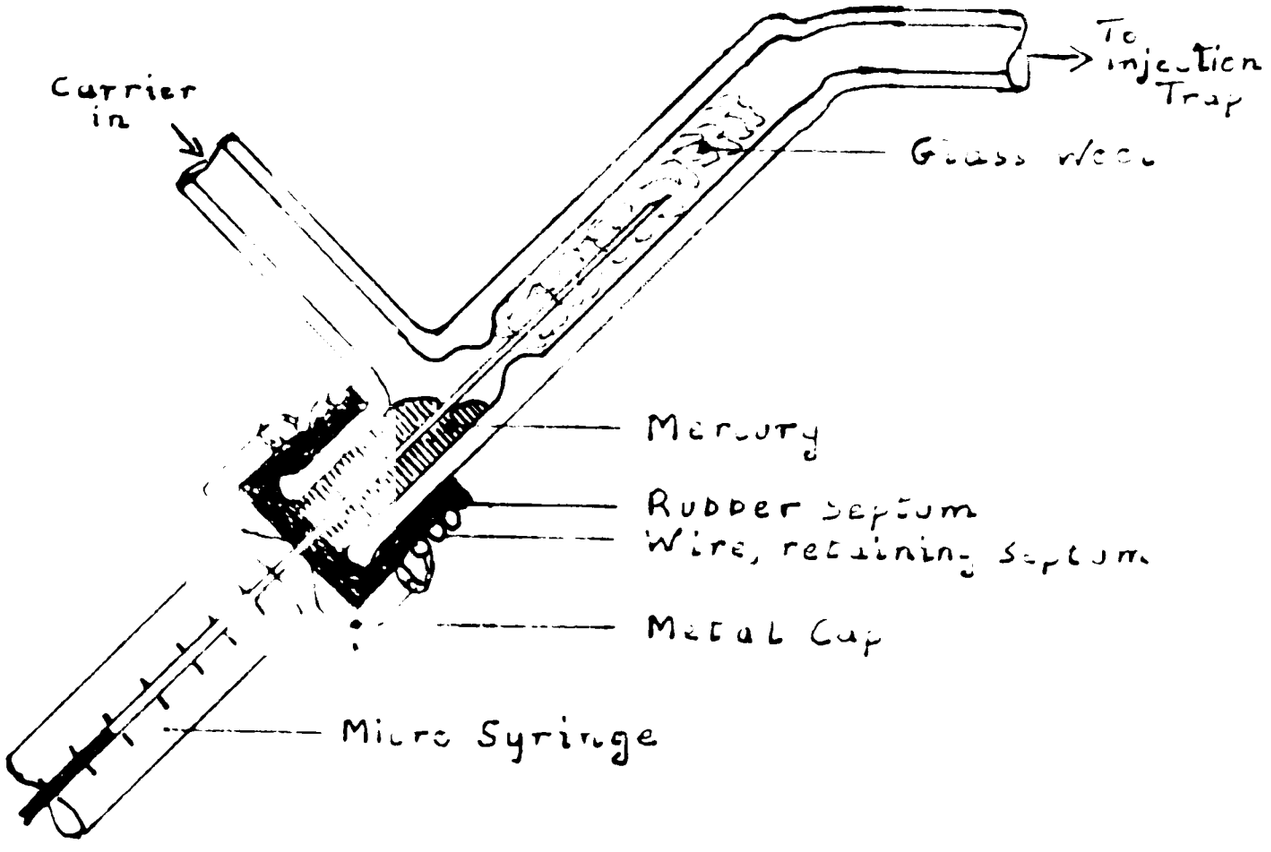

Tube
Heating Circuit
Panel
(section 2.3)
By-Passed Injection
Point System
Septum
Vent
I_1
By-Pass

FIG. 12 A/ By-Passed Injection Point

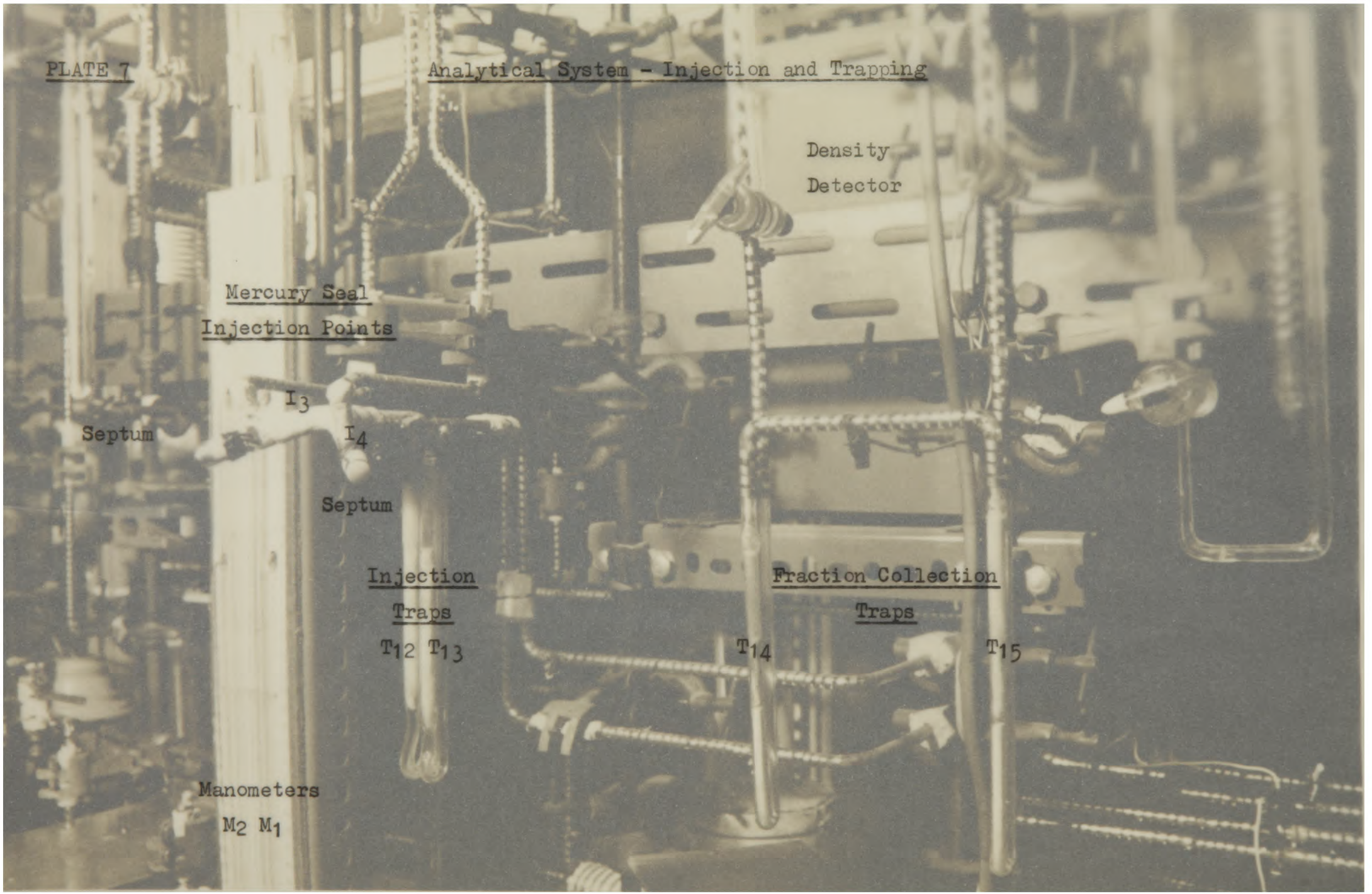


B/ Mercury Seal Injection Point



The second method is by direct injection, by syringe, of a sample, usually through a rubber septum. The use of rubber septa has a serious drawback: Even under moderate pressures (7 - 10 p.s.i.g.) septa tend to leak after a few injections, resulting firstly in unstable carrier flowrates and consequent detector 'noise', and secondly in the ingress of air and moisture. The injection point in the First Apparatus (I_1 in Fig.5) was of this type and was normally replaced by a stopper for these reasons. Two systems have been devised to overcome this and they are shown in Fig.12. The by-passed injection point permitted low pressure injection without contamination, as the system could be purged. The use of greased taps, however, prevented the use of this type of device for quantitative work, but one was fitted to the Preparative system in the new apparatus (I1) and this is shown in Plate 6. A similar injection port, but without the by-pass and taps was fitted to the sub-ambient gas chromatograph (see Section 7.51). The difficulties of quantitative injection were solved by use of an inverted septum with an internal mercury seal (Fig.12B) devised by the Author[30]. This did have minor operational difficulties, as when an injection into a high pressure was made, a drop of mercury accompanied the withdrawal of the needle. Failure of the septum resulted in a stream of mercury, and thus a catchment tray had to be provided. However, a positive seal was formed as long as there was some mercury above the septum, and injection could be made directly into the system. Three of these injection points were fitted to the analytical system of the New Apparatus (I_2 - I_4, see Plate 7).

The actual injection of samples onto the chromatographic columns was


PLATE 7
Analytical System - Injection and Trapping
Density
Detector
Mercury Seal
Injection Points
I_3
Septum
I_4
Septum
Injection
Traps
T_{12} T_{13}
Fraction Collection
Traps
T_{14}
T_{15}
Manometers
M_2 M_1

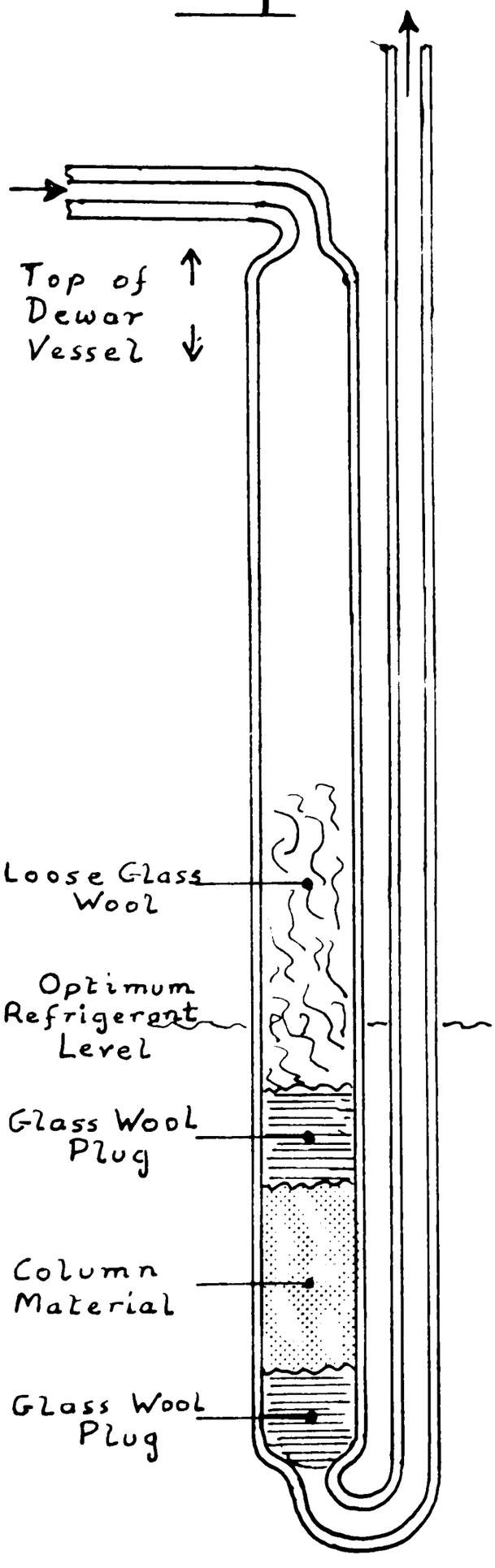
accomplished, in both apparatuses, by the use of injection traps. For collection of sample, these were cooled by immersion in liquid oxygen or liquid nitrogen. Injection was then achieved by rapidly exchanging the Dewar flasks of refrigerant for beakers containing hot water or hot oil. As this procedure frequently resulted in 'bumping' due to rapid evaporation of residual refrigerant, special beakers were lagged and equipped with handles to protect the hands. One of these beakers was fitted with an electrical heater and was usually used as an oil bath for high temperature injections.

The collection traps in the fraction trapping sequences were similar to the injection traps except that they did not have to survive rapid changes of temperature and were therefore constructed of somewhat thicker glass.

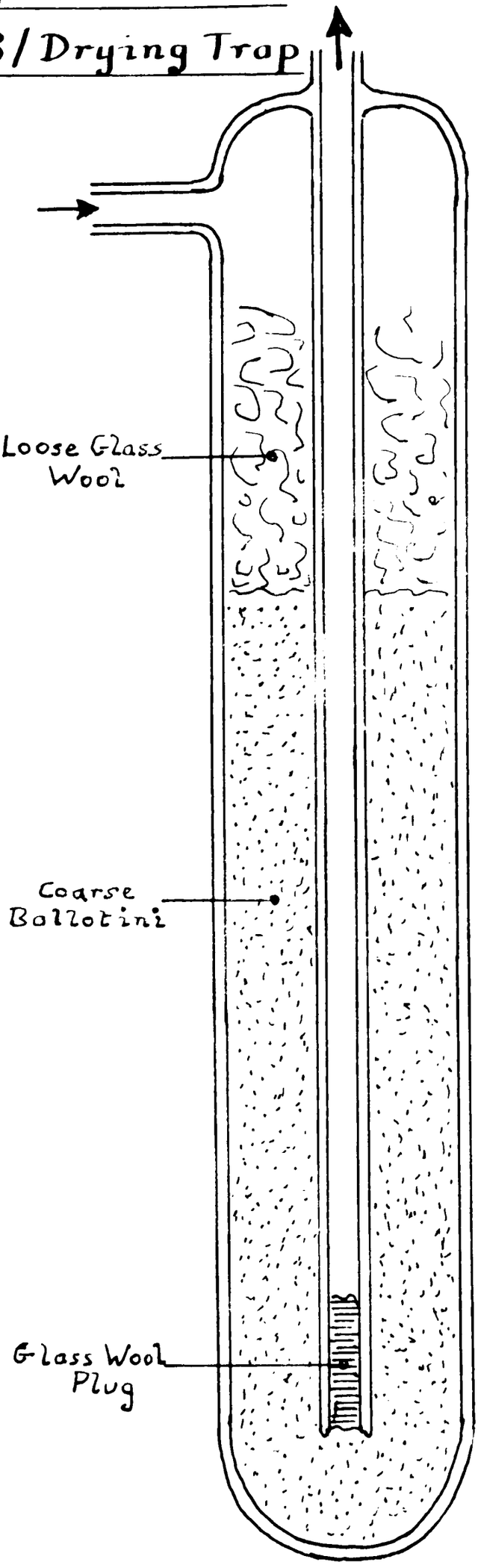
Both injection traps and fraction collection traps had to have high trapping efficiencies, but, since they were components of chromatographs, low volumes were desirable, and thus high gas velocities through them were inevitable. Cases have been cited in the literature[113a] where high boiling compounds, due to the formation of fogs or solid aerosols, had passed through traps of the U tube type. Traps had therefore to be designed so that rapid cooling, (with the formation if possible of large droplets) could happen, and they had to contain some sort of filter to remove any fogs. Timms[29], for his original apparatus, designed traps containing column material as a filter. This idea was developed for the subsequent apparatuses. Two rather surprising facts emerged: A fully packed trap did not behave as efficiently as a partially filled trap, and traps surrounded by completely filled Dewar flasks were not as

FIG. 13 Section of Traps (To Scale)

A/ Injection/Fraction Trap



B/ Drying Trap



efficient as partly filled flasks, provided that the flasks went up to the top of the traps. A difficulty arose with the small injection trap in the gold chloride system of the First Apparatus, which contained rather a large plug of column material. When high temperature injections were attempted, the trap divided the sample into two distinct injections a few seconds apart, giving rise to multiple peaks, which caused considerable confusion until the trouble was pinpointed. The final design of the injection (T_4, T_5) and the fraction collecting (T_6 - T_{11}) traps fitted to the analytical system in the New Apparatus is shown in Fig.13A, those of the analytical system (T_{12}, T_{13} and T_{14}, T_{15}) being somewhat shorter and thinner. When trapping under normal operating conditions in the preparative system, a six-stage operation (i.e. six evaporation and trapping operations) resulted in the recovery of 97% of a sample. This indicated that such traps had an efficiency of about 99.5%. Work by Timms on the traps of earlier design[29] had indicated that their efficiency was 95 - 97% from hydrogen streams but only 70 - 75% from nitrogen. In the New Apparatus the efficiency of the traps in nitrogen was not directly measured, but as no 'ghost' chromatograms were observed after transfer of large samples to the injection traps, it was deduced that the efficiency of the traps in the analytical system was probably in excess of 98% when properly employed. The analytical system traps are shown in Plate 7, and the preparative trapping sequence (T_6 - T_{11}) is shown in Plate 8.

For the drying of the carrier gases, traps of a much larger volume, with consequent longer gas contact times, could be employed. The traps used (T_1 - T_3) were of the internally-sealed type and were packed with

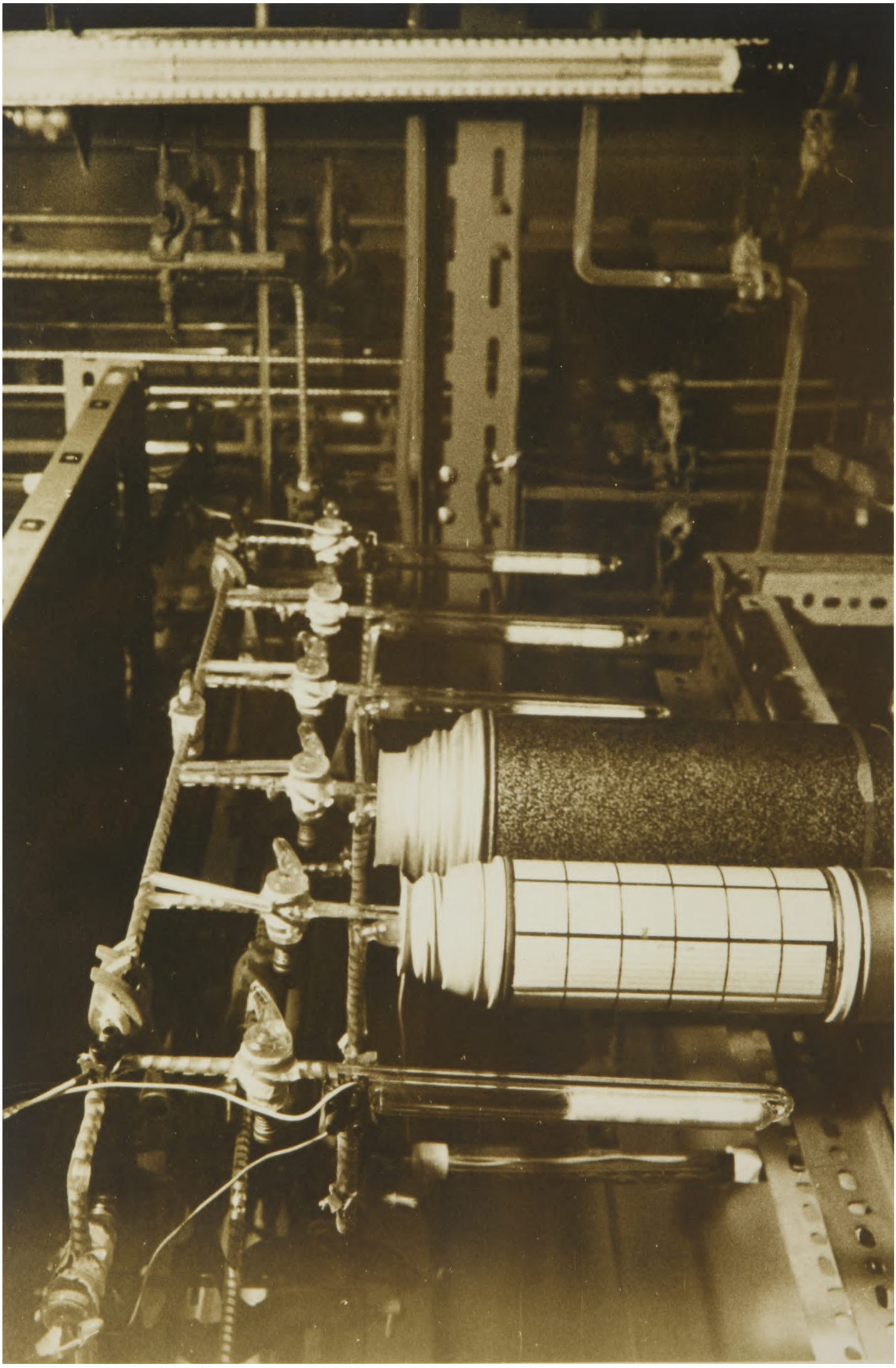
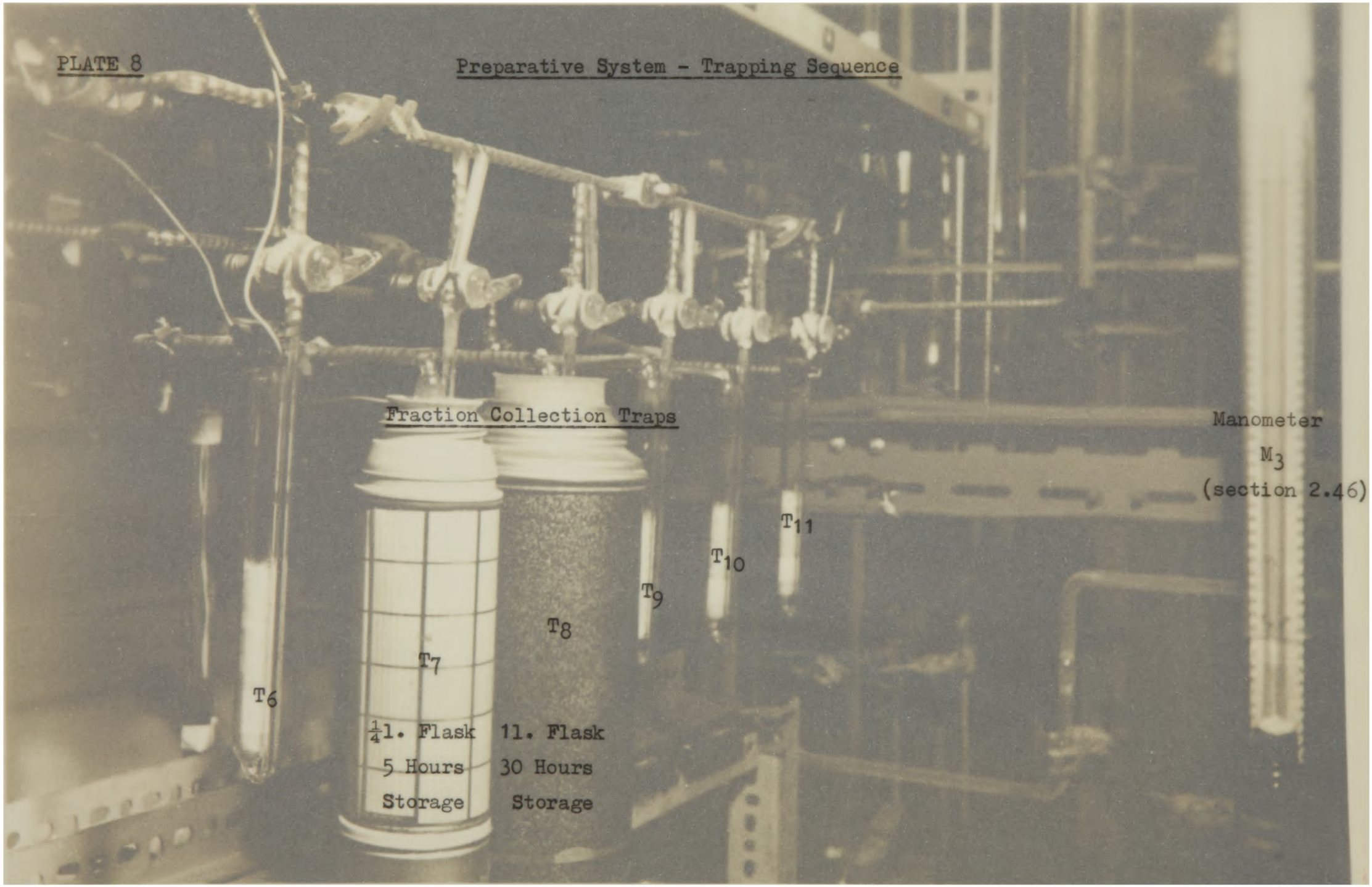


PLATE 8

Preparative System - Trapping Sequence



Ballotini of a coarse grade. Their design is shown in Fig.13B. These were periodically dried by passage of carrier gas while heated, the taps immediately after them being used as outlets to prevent contamination of the rest of the system. The vacuum line drying trap (T_{17}) was similar in construction to these but was unpacked and had a cone and socket joint at the top for cleaning purposes. The vacuum distillation trap (T_{18}) was similar to T_{17} but was narrower.

The vacuum line trap (T_{20}) was a simple U tube for collection of samples transferred in gas streams from the main apparatus, and the finger trap (T_{19}) was used for sample storage and also acted as a collection trap for any mercury blown over from the manometer valves.

The sample evaporation trap (T_{16}) was a thin-walled U tube packed with coarse Ballotini. Its function was to allow controlled evaporation of samples when immersed in baths of appropriate temperatures. Its trapping efficiency was probably under 90%, but this was not critical.

All traps were very well annealed during construction in view of the very large and sudden changes in temperature to which most of them were subjected. No trap failures were experienced with the New Apparatus.

2.44 Chromatographic Columns

The prime requisites for the stationary phase in a chromatographic column are that it must be effectively involatile at the desired operating temperatures, and that it must be inert to the compounds passed through the column. The substantially non-polar stationary phases Squalane and Silicone 702 (Midland Silicones) had been shown

to be inert to the silicon hydrides[22], and the latter was shown to be inert to $SiCl_4$, and $GeCl_4$ and fairly inert to chlorine[29], thus being employed for the early gold chloride work. However, choice of a polar phase was more difficult as such esters as dinonyl phthalate were found to be reduced by the hydrides, but ultimately it was found that tritolyl phosphate (tri p-cresyl phosphate) was satisfactory for these compounds[22].

Silicone 702 and tritolyl phosphate were both employed in the First Apparatus and, in the interests of continuity, were selected for the New Apparatus. However, it was unknown whether tritolyl phosphate would be sufficiently inert to the products of the gold chloride reaction. In principle this phase offered selectivity to chlorinated hydrocarbons[1c], and thus was of great potential use in the separation of the multiple peaks obtained from the chlorination products of the silicon and germanium alkyls when chromatographed on a silicone 702 column. In practice it was found that $SiCl_4$, and to a certain extent the methyl silicon chlorides, did react to a small extent with tritolyl phosphate (see Section 5.42), resulting in rather low silicon analyses. In addition, a slight change in relative retention times on this stationary phase was probably due to reaction with chlorine, as this was the only compound passed through the column in sufficient quantities to have caused an observable effect[113b].

In the First Apparatus the columns were made of 10% of the stationary phases on Embacel (May and Baker). The preparative columns were each packed in four sections arranged as a flat 'W', of overall length 360cm.,

and a diameter of 10mm. The analytical columns were packed in the form of a flat 'U' of overall length 200 cm., and a diameter of about 3mm. In the design of the New Apparatus, it was decided that these stationary phase loadings were too high for use on the higher-boiling compounds and accordingly the stationary phase loadings were reduced to 5%. The preparative columns were reduced in size to an overall length of 240cm. and an internal diameter of 9.5 mm., each then containing about 52gm. of column material. The analytical columns were made to the same length and had inside diameters of approximately 4mm. They contained about 7.5 gm. of material apiece. The column temperatures most commonly employed in the New Apparatus were 30°, 60°, 90° and 120° although temperatures up to 160°C could be achieved.

The column materials were made up by evaporation of etherial solutions of weighed amounts of the stationary phases, gently stirred with weighed quantities of previously sieved (60 - 100 mesh) Embacel. The materials were then dried at 120°C in an oven and were subsequently sieved again. The columns were packed in glass tubes suspended vertically, by horizontal tapping with suction applied to the bottom to assist settling. As the columns were to be used horizontally in the New Apparatus, rather firmer packing than normal[113c] was necessary to prevent channelling. As tight packing had been shown to have a deleterious effect on column efficiency[113c], the analytical Silicone 702 column was deliberately packed tightly to obtain the reduced efficiency desired (see Section 2.3). The columns were retained at both ends by glass wool plugs, held in place by restrictions. In time, a loss of column efficiency, probably mainly due to channelling, was experienced, but approximately 100 one

hour runs could be carried out before this became serious. As column replacement was comparatively simple and the advantages of the use of horizontal columns were so great, this was not considered to be a disadvantage.

The columns were treated with hexamethyl disilazane[114], but contrary to normal practice[113d], only after installation in the apparatus. This treatment was carried out by introduction of a large amount by syringe and allowing it to evaporate into a very slow flow of carrier gas passing through the columns, which were heated to about 150°C. This had the advantage of removing traces of water as well as hydroxyl groups from the entire apparatus and was usually carried out for about 3 hours on each column. This procedure was repeated whenever the apparatus was recommissioned after a shut down or repair. In the analytical system, when it was uncertain whether the apparent loss of silicon in the gold chloride analyses, when chromatographed on tritolyl phosphate, was due to reaction with the stationary phase or moisture in the column, $SiCl_4$ was employed in a similar fashion as the hexamethyl disilazane. However, the loss of silicon persisted so it was concluded that reaction with the stationary phase was occurring.

In certain diagrams and tables the columns are identified by the following abbreviations:

TTP = tritolyl phosphate

702 = Silicone 702

2.45 Detectors and Detector Circuitry

The nature of the silicon and germanium volatiles places some

restriction on the methods that can satisfactorily be employed for their detection[22, 32]:

Flame ionisation techniques have been employed with some success and, using stream splitting, have even been used for preparative purposes[28]. This method does however suffer from the technical disadvantages caused by deposition of SiO_2 and GeO_2[115,116]. A commercial gas chromatograph (Perkin-Elmer, Model F11) was used in this work for investigations into the formation of the higher permethyl silanes (see Section 5.3). However, deposition of silicaceous material in the detector caused a progressive loss of signal and ultimately caused permanent damage. Accordingly these particular investigations were terminated.

Closed circuit chromatography imposes further limitations on the type of detector that can be used, as the samples must not be destroyed, and it has to be possible to collect all the detector effluent. The hot wire detectors; the katharometer[117] and the gas density detector[20] have both been satisfactorily used on silicon and germanium compounds[22,110], and the former had been used in a closed circuit configuration[29, 30]. The density detector, although it satisfied the basic requirements for closed circuit work, required two separate gas supplies that were combined within the instrument, and it was found to be flow sensitive to both[30]. Therefore the detector would be expected to be very susceptible to changing flow impedance on the outlet side. This was found to be the case, but the detector could be operated satisfactorily with a single trap after the outlet.

The katharometer (gas thermal conductivity meter) has particular

advantages in closed circuit chromatography in that it operates best with hydrogen as carrier gas, which is the carrier gas that gives optimum column performance[113e], enables the highest trapping efficiencies (see Section 2.43), and is most readily freed of oxygen. In addition, the type of katharometer used for this work (Gow-Mac Pretzl Cell) was found to operate quite satisfactorily with flowrates of up to 750 ml/minute[29,30]. This made it suitable for the preparative system.

The gas density detector has been overlooked by many workers, largely because, in the early stages of its development, it suffered from low sensitivity and a rather high volume, and hence slow response time. In its more modern forms (e.g. the Gow-Mac detector used for this work) its general performance has been found to compare with that of the katharometer, particularly as no noise was detectable, with the improved circuitry described below, even on a 1 mV. recorder. This type of detector has one significant advantage over all other types of detectors, in that it directly measures a parameter calculable for all volatile compounds; vapour density. Thus this detector can be used for quantitative work if molecular weights are known and even for molecular weight determinations if pressure/volume measurements are also made[110]. The response is effectively linear up to concentrations of the order of 2% v/v (see also [34]). Thus the relative amounts (in molar quantities) of two components X and Y having molecular weights x and y and peak areas on a chromatogram A^x, A^y, with a carrier gas of molecular weight m, is given by:-

$$X : Y = \frac{A^x}{x - m} : \frac{A^y}{y - m}$$

As the particular type of density detector employed operated best

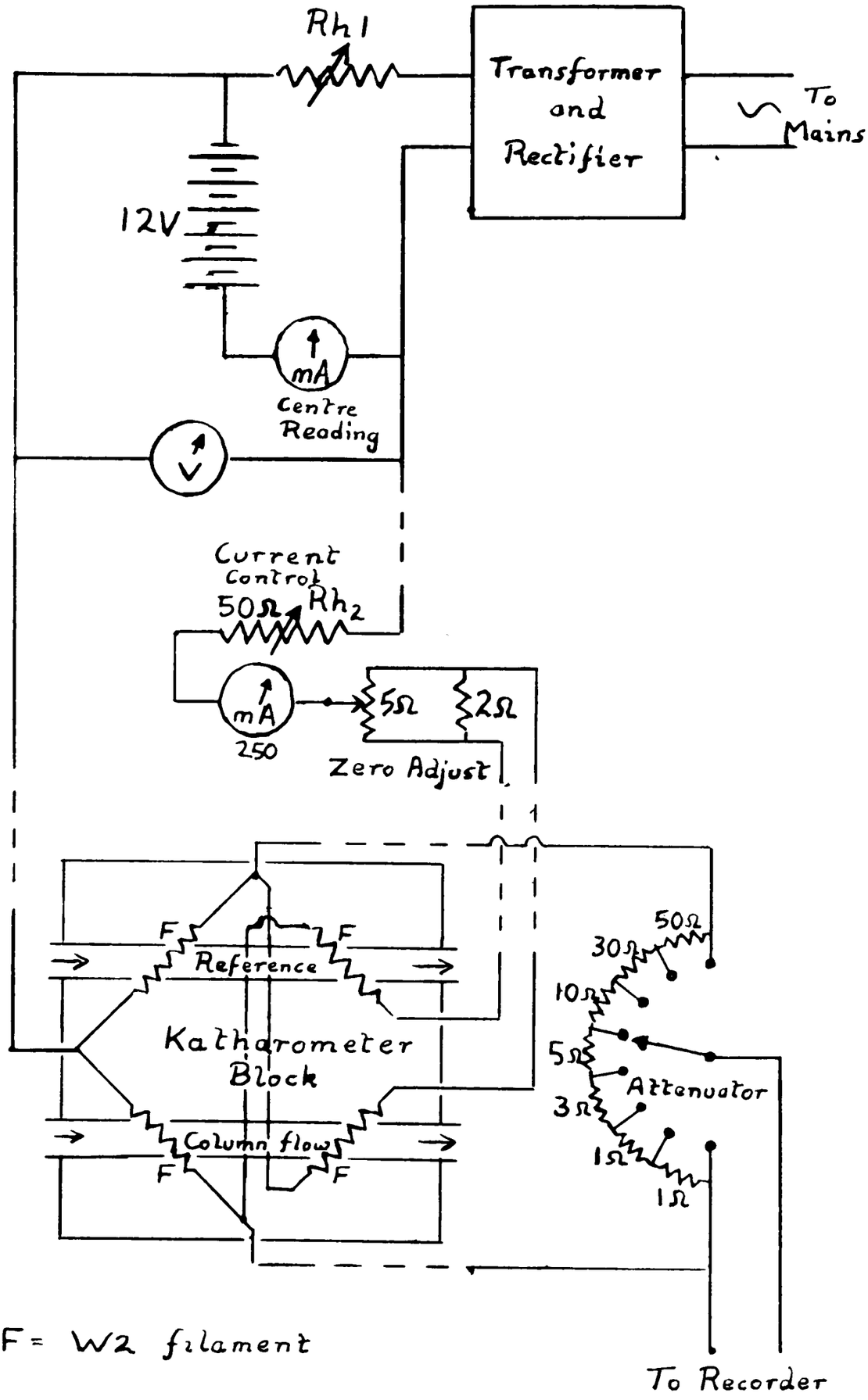
in nitrogen (see Gow-Mac operation manual) it was particularly suitable for the gold chloride reaction where a chemically inert carrier gas was required.

Both the katharometer and density detector had the following additional advantages over other detectors for this work: They would rapidly recover from gross overload and their basic circuitry was simple, in particular not requiring an amplifier.

As the katharometer is a two-stream device, it proved possible to connect the reference and detection streams effectively in series, with the injection traps and the columns in between them. Thus under normal operating conditions, the flow rates were proportional to each other and the flow sensitivities of the two halves tended to cancel out each other. In order to reduce the effect, due to flow sensitivity, of changing traps in the fraction collection sequence, a flow restrictor was placed between the trapping sequence and the katharometer. The katharometer was installed in a brass tube with an electric heater, insulated by asbestos paper, wound on it (see Section 2.41). The intervening space between tube and detector was packed with a mixture of brass filings and Vermiculite and this was retained at top and bottom by a cement made of asbestos pulp and Vermiculite. This conferred reasonable short-term temperature stability.

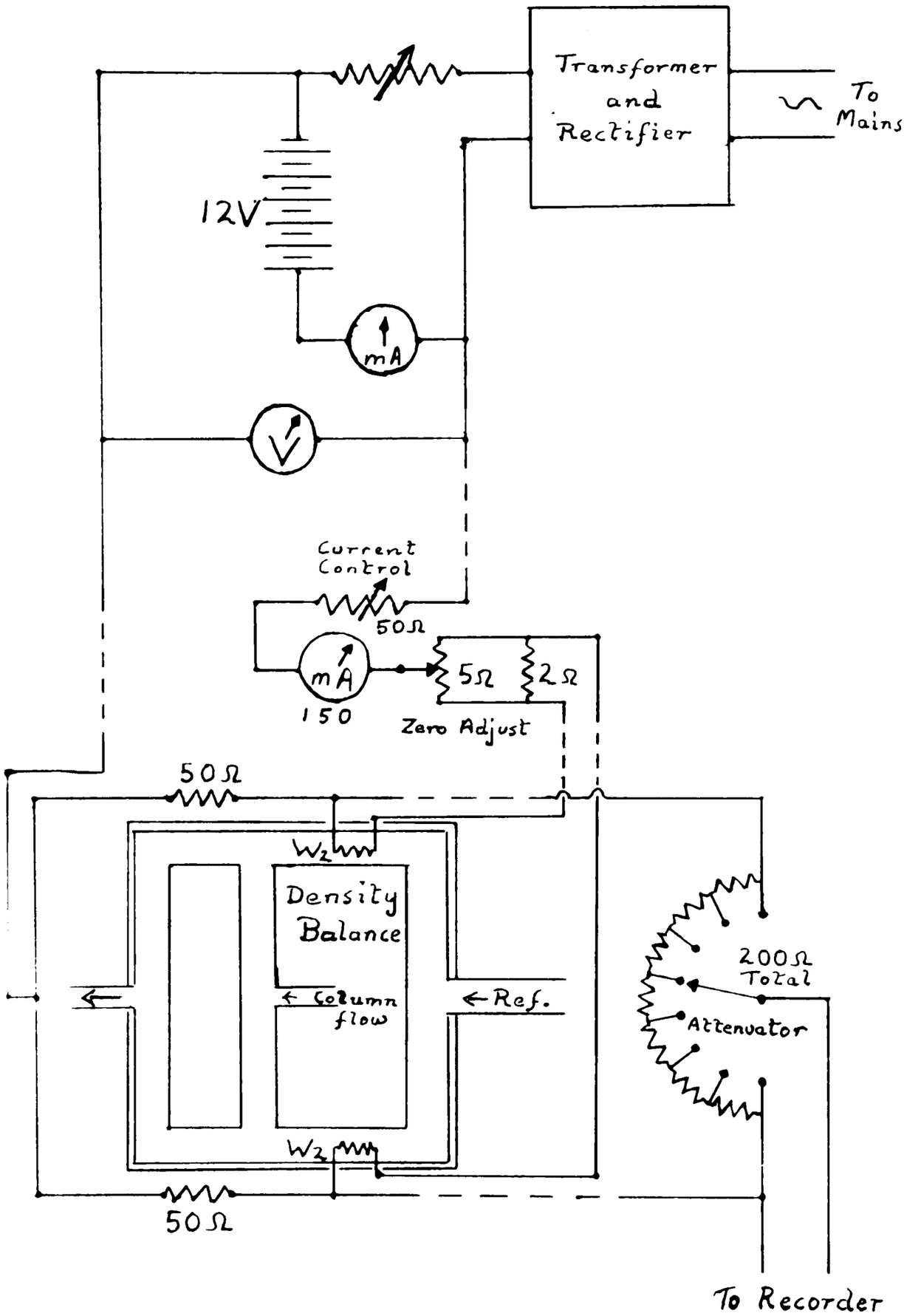
The density detector was already mounted in a lagged box with a heater as supplied by the manufacturer. This was maintained at a reasonably constant temperature using a similar circuit to the column heater (see Section 2.41), as the sample sensitivity was found to be temperature dependent[30].

FIG. 14 Simple Katharometer Circuit



F = W2 filament

FIG. 15 Simple Density Detector Circuit



In the first Apparatus the detector circuits were constructed as suggested in the manufacturer's technical manuals. Reasonably stable supplies of D.C. for these circuits were provided by accumulators continually 'topped up' by simple battery chargers so that a nett charge of 2 - 5 mA was maintained (see Figs. 14 and 15). It soon became obvious that for the more precise quantitative work neither the bridge circuits nor the D.C. supplies were adequate.

The original bridge circuitry was unsuitable for three main reasons:

1/ Both the current setting and zero setting potentiometers, being wire-wound and single turn, were too coarse in nature. Vibration caused jumping of the wipers and, as a consequence, considerable baseline noise on the recorder trace.

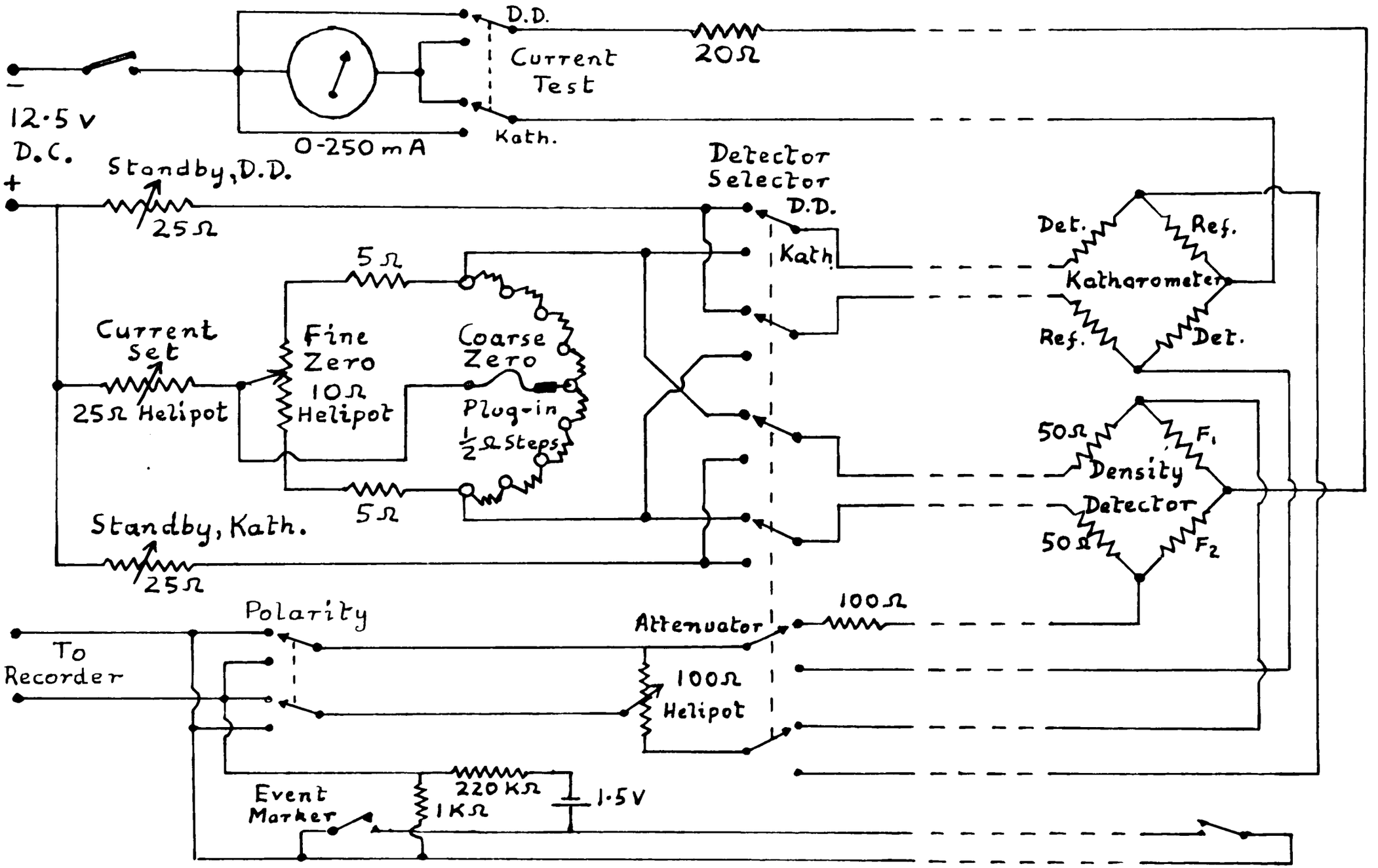
2/ The wipers of the attenuator switches and potentiometers seemed to get corroded very easily, intermittent contact frequently occurring.

3/ The degree of zero adjustment was sometimes insufficient to keep the bridges balanced.

An attempt was therefore made to try and improve the circuitry and in view of the expense involved, to see if the two detectors could be made to operate off the same circuit, one detector being controlled and the other on standby at any one time. In addition, all the precision circuitry was moved out of the fume cupboard occupied by the apparatus, and grouped on a console (see Section 2.3, Plate 1). in an attempt to cut down on corrosion.

The 'Current control' potentiometer was replaced by a 10-turn helical potentiometer (Beckman) to increase its sensitivity. Since the zero

FIG. 16 **Modified Bridge Circuit for Two Detectors**



adjustment potentiometer was part of the Wheatstone bridge itself, it was considered that too much current was being passed from wiper to windings in addition to the defect mentioned above. It was therefore decided to make a 'fine zero' control using a de-rated helical potentiometer and to pass most of the bridge current through a 'coarse zero' control, initially constructed of switched resistors, but subsequently using a plug board as selector since, by this time, the Author had little faith in rotary wiper switches. The attenuator system was replaced by another helical potentiometer which had the additional advantage that any attenuation could be provided. Additional resistors were provided since the operational requirements of the two detectors were somewhat different. The circuit was completed with ganged changeover switches for detector selection, and an electrical event marker (see Fig.16).

Operationally, it was found that, when the power supply modifications described below had been carried out, neither detector interfered with the other. A rather peculiar effect occurred in the attenuator circuit under conditions where a 'noisy' signal was obtained (before all the supply modifications had been carried out). The absolute 'noise' level (i.e. noise level multiplied by attenuation factor) was dependent on the attenuator setting, maxima occurring at harmonic intervals along the helical track (see Fig.17).

The use of accumulators on a trickle charge as power supplies for the bridge circuits was not satisfactory; There was considerable 'drift', possibly because of temperature variations altering the accumulator voltage, and in addition there was noise of both long and short term, presumably due to mains variations altering the charge rate. Separate

FIG. 17 Maximum and Minimum Absolute 'Noise' levels at Various Attenuator Tappings

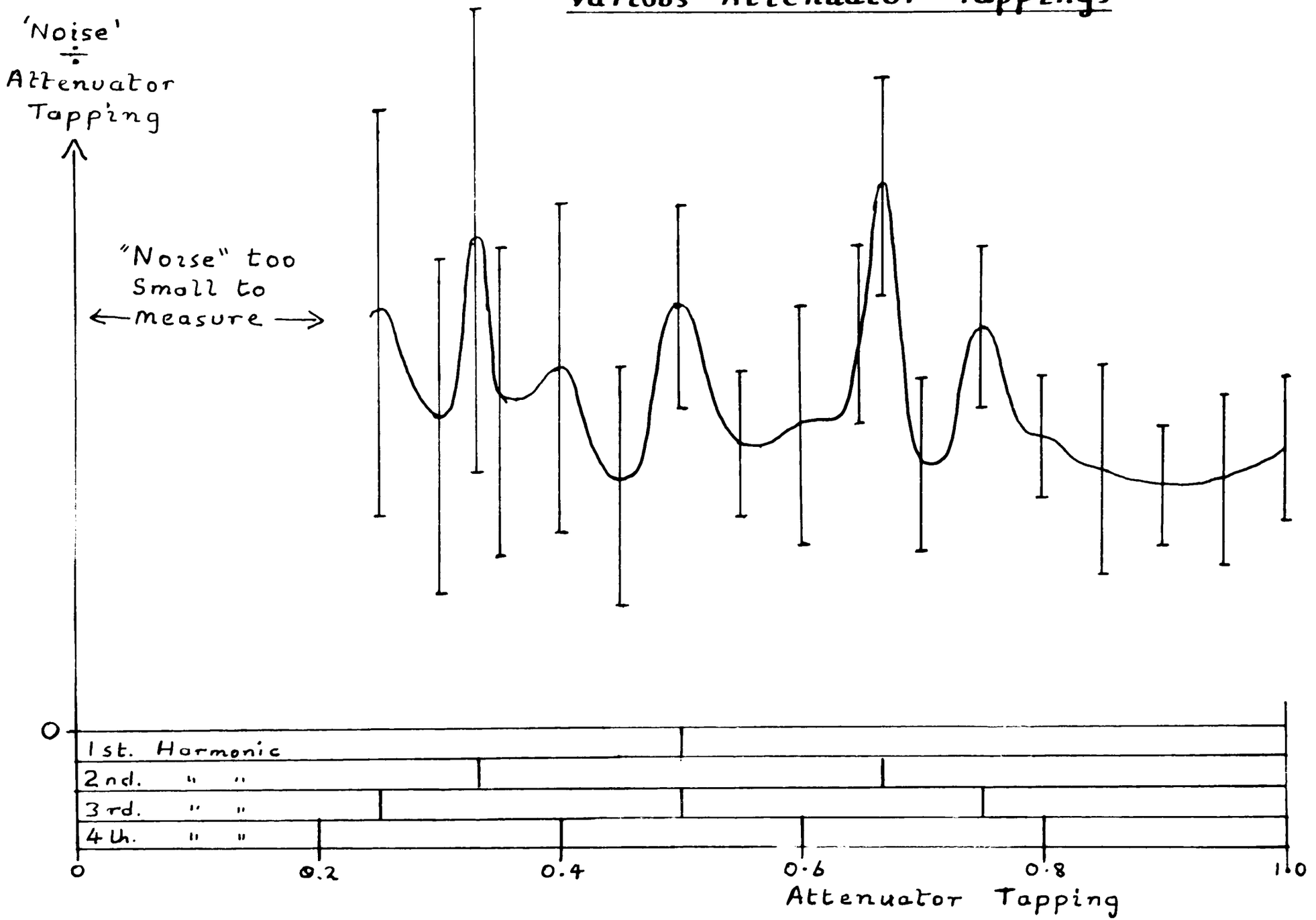
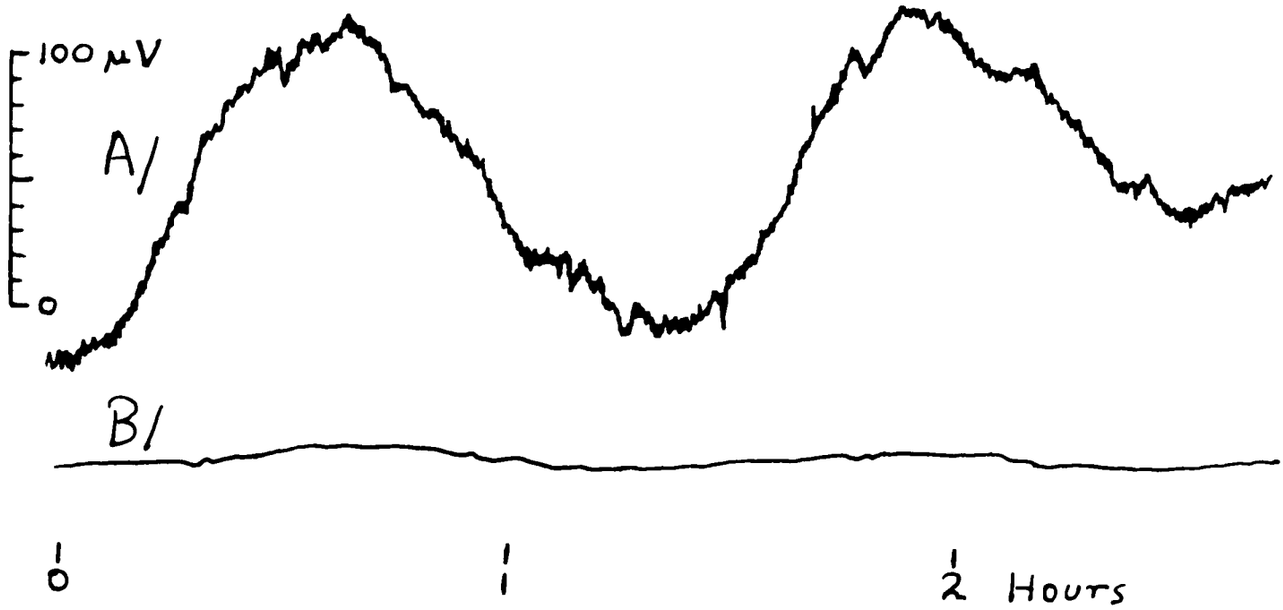
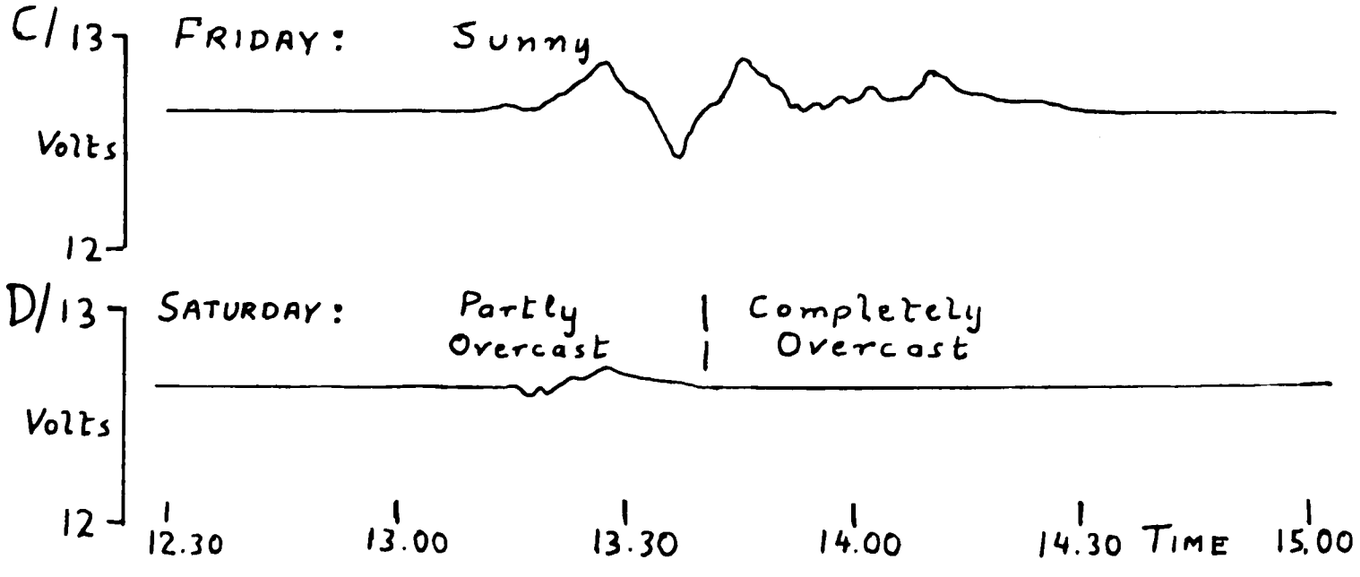


FIG 18 **Detector Power Supplies**

Baseline of Density Detector, with no Gas Flows,
A/. Run off Pye Power Pack, supplied from Mains
B/. Run off A.E.I. Pack, supplied from 'Volstat'
(All other conditions identical)



Voltage of A.E.I. Power Pack, Supplied from a "Volstat" – Showing the Effect of Sunlight



systems were required for each detector as there were considerable interactions if it was attempted to run two detectors off the same accumulator. For the more precise work it was advisable to turn off the charger and to allow the accumulator to discharge through the detector for two hours prior to the experiment, accepting a considerable, but relatively constant,'drift'. The katharometer was more sensitive to these variations of supply than the density detector.

When the bridge circuit modifications, mentioned above, were carried out it was decided to try alternative power supplies. The first chosen was a constant current unit (Pye) originally employed for solution chemistry, with an adjustable D.C. output of up to 110 mA in the 12 - 18 V range. This was employed in the density detector circuit, initially with an accumulator in parallel. At the same time a transistorised constant voltage unit (A.F.I.) with adjustable output 12 - 17 V was installed, set to accumulator plateau voltage (12.7V), in parallel with an accumulator, and used in the katharometer circuit. Both power packs were supplied from a Volstat constant voltage transformer. The baseline stabilities of both detectors with these supplies were approximately the same as those obtained with accumulators on plateau voltage, but there were slight variations similar to those attributed to mains variations with the original supplies, but much smaller. Further experiment showed a twofold improvement in baseline stability in the density detector circuit if the accumulator was removed and the Pye power pack run directly off mains (Fig.18A). If the A.F.I. powerpack, supplied from the Volstat transformer, without an accumulator in parallel, was used with the density detector, a twenty-fold improvement

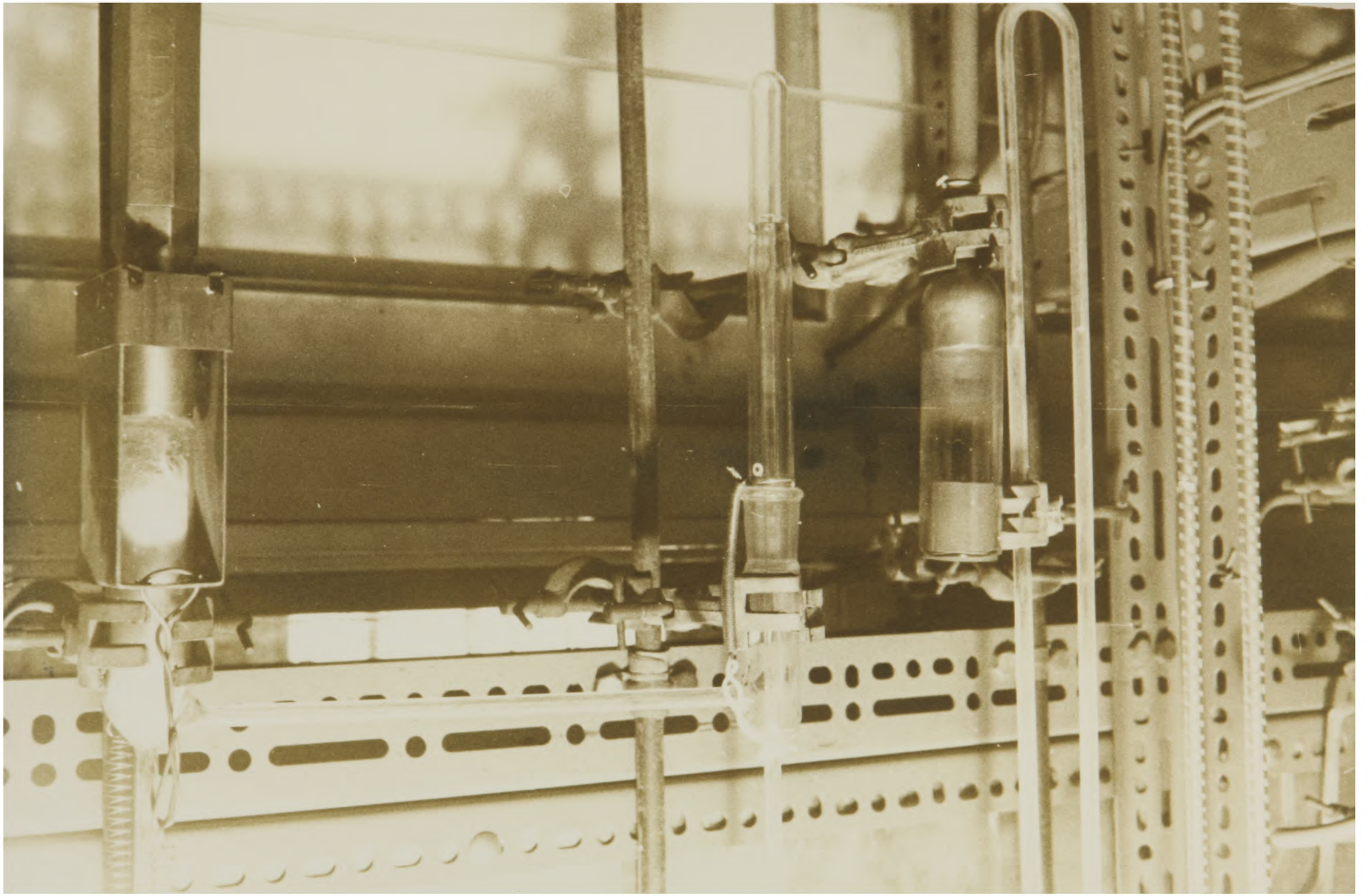
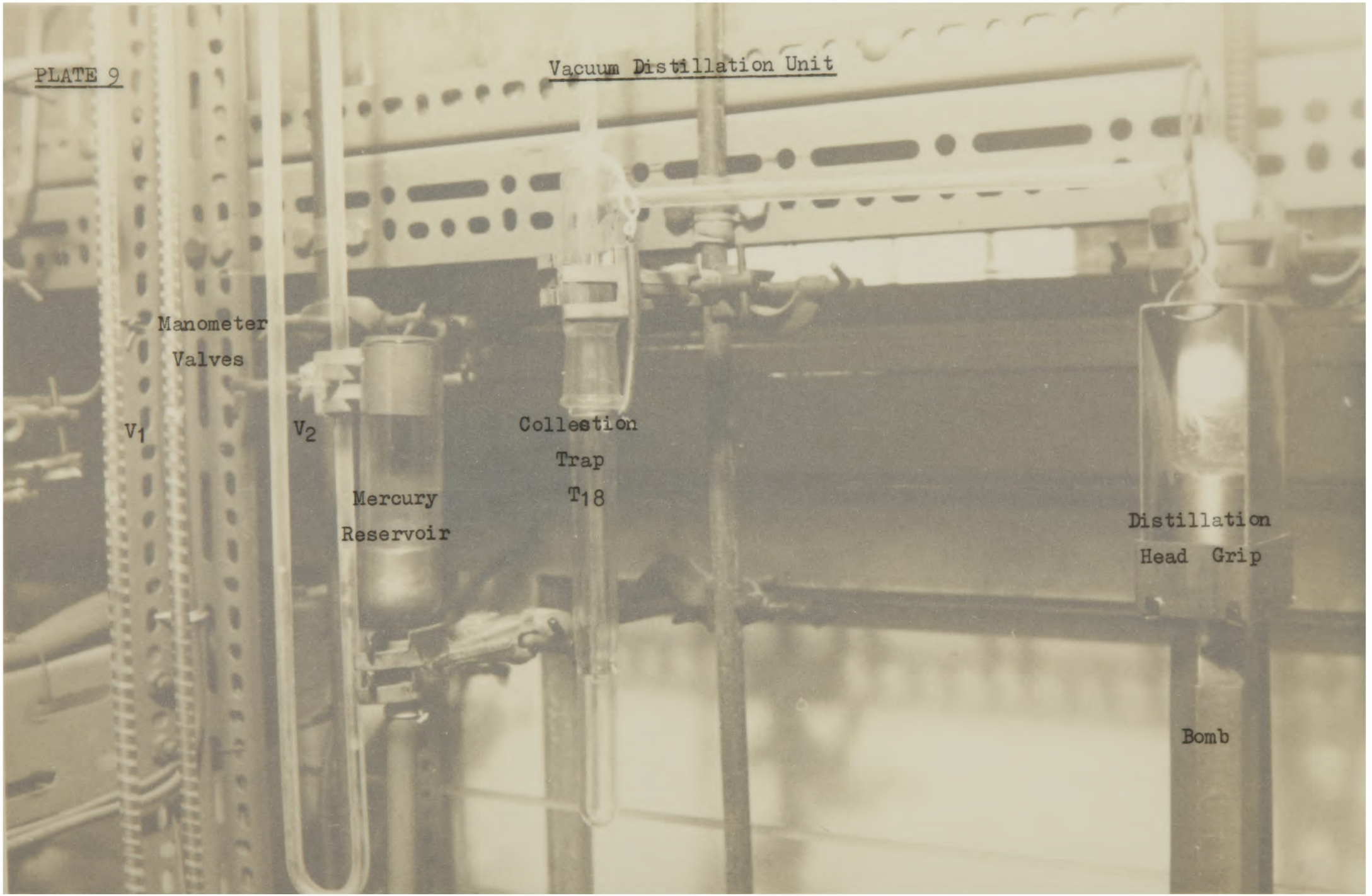


PLATE 9

Vacuum Distillation Unit



resulted (Fig.18B). At this stage it was realised that with this stability it might be possible to run the two detectors off this last supply and the bridge circuit was consequently modified to its final form as shown on Fig.16.

The power supply was tested by feeding a potentiometrically reduced signal directly to a recorder and it was found that normal ambient temperature variations had no detectable effects. However, in the early afternoon variations did occasionally occur (Fig.18 C,D). This was attributed to sunlight, presumably causing temperature gradients within the power pack, as the peaks were found to correspond to the shadows of scaffold poles situated immediately outside the laboratory window. A layer of polished aluminium sheet was accordingly placed between the power pack and the window, to act as a radiation screen, and no further trouble was encountered.

2.46 The Vacuum System

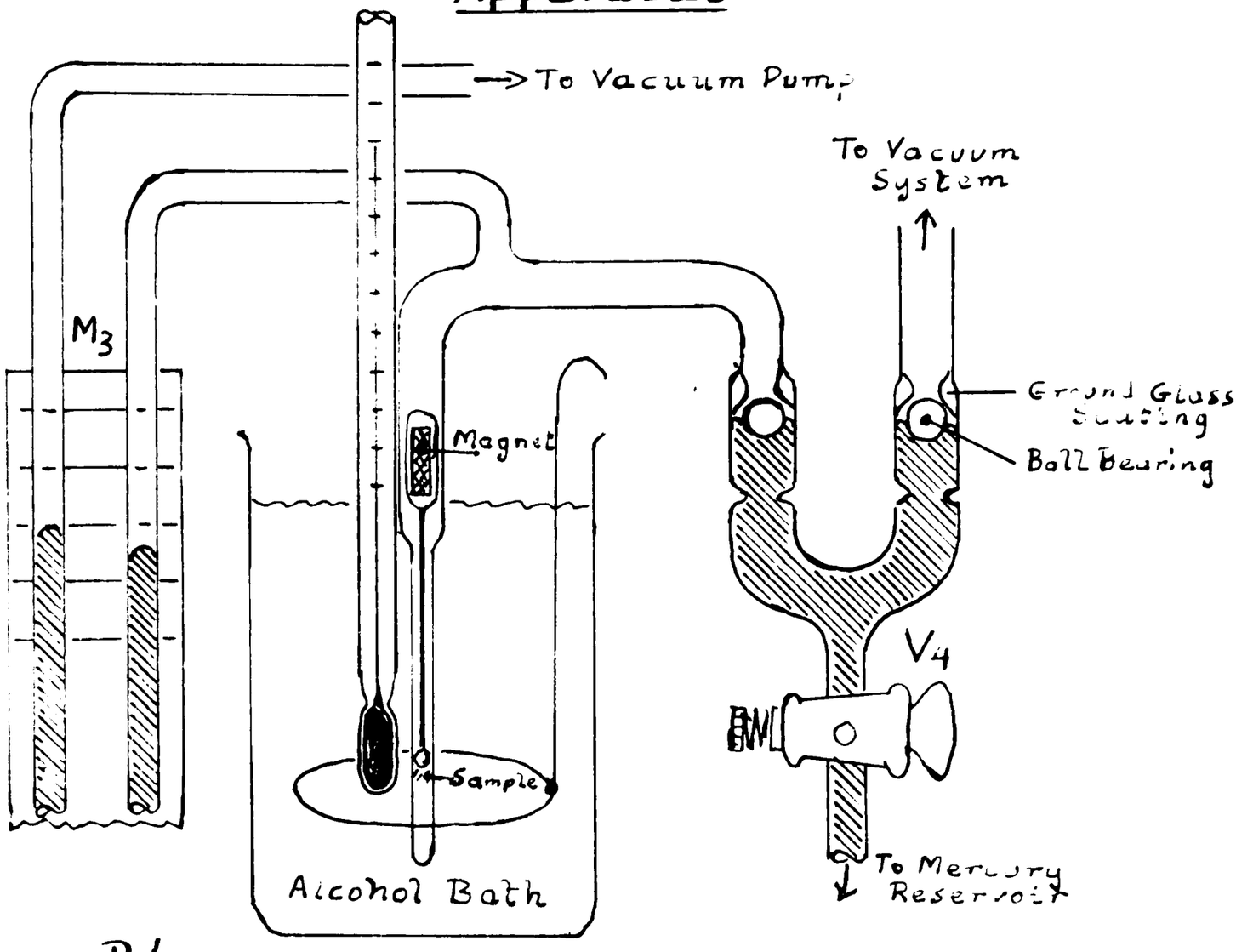
As has already been described (Section 2.2) the molecular weight system used in the First Apparatus was not suitable for this work and was not fitted to the New Apparatus. Otherwise, the vacuum system in the New Apparatus was based on that of the First Apparatus, but with the addition of a vacuum distillation unit (Plate 9) for recovery of products from the stainless steel bombs (see Section 2.51). In addition the connection of the system to the chromatographic apparatus and the arrangement of the peripheral gas supplies were made more logical, providing greater ease of sample handling.

Serious trouble had been experienced with the mercury/steel ball

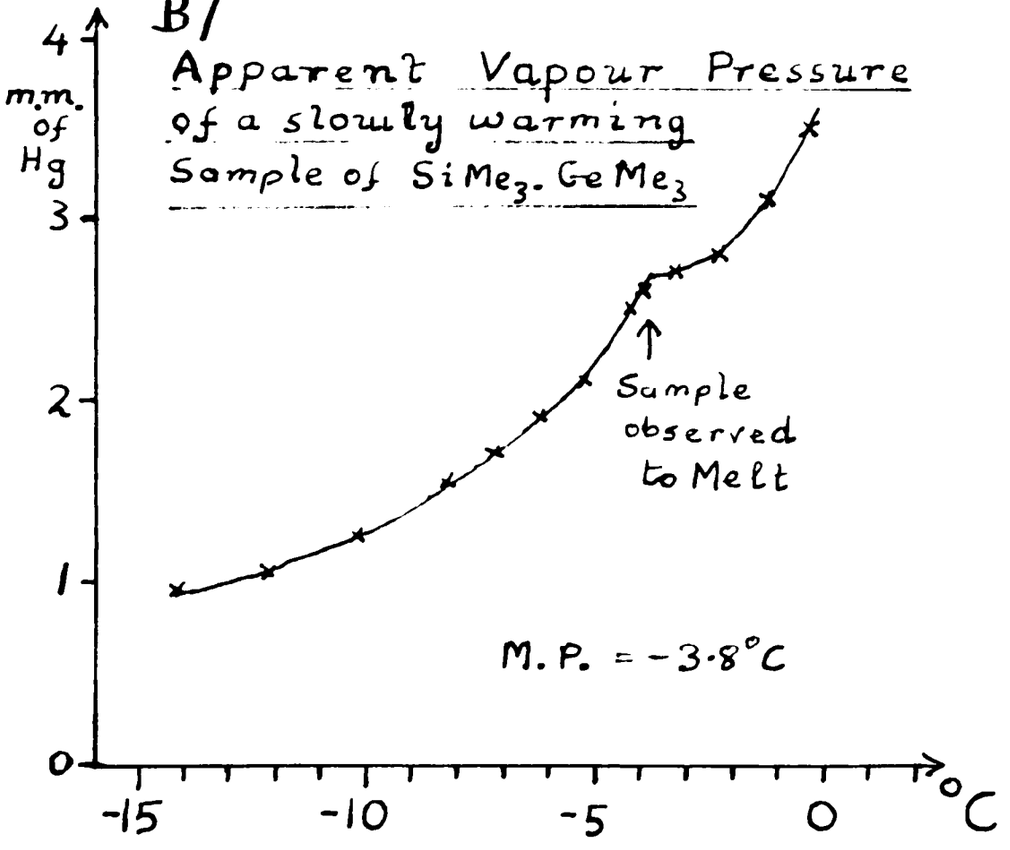
valves (see Fig.19A) in the first apparatus, as the ground glass seatings tended to distort during glass blowing, and the balls tended to collect particulate matter. Both of these effects resulted in seepage of mercury past the seals, whenever a reasonably high differential pressure existed across the valves, with consequent seal breakdown and flooding of the system with mercury. In addition, these valves could only be opened if the differential pressures were low. Thus, in the New Apparatus only two valves of this type were fitted, and these only where differential pressures of a few millimeters of mercury were expected (V_3, V_4). For vacuum seals, where pressure differences of the order of one atmosphere were expected, manometer type valves, (V_1, V_2) were employed. They were designed to withstand up to 100 cm. pressure in one direction and up to 40 cm. in the other. These valves, which had an inside diameter of about 5mm., could be opened and closed, by removal and addition of mercury via a tap at the bottom which was connected by a flexible tube to a reservoir, when quite large pressure differentials could exist. Moreover, excess pressures could be released by bubbling. In addition they could be used for pressure measurement and leak detection. Their main disadvantage was that they took up a lot of space and the mercury reservoir had to be capable of movement from 80 cm. below the bottom bend to near the top of the shorter arm.

The melting point/vapour pressure apparatus (Fig.19A) was based on a design of Stock[38] and consisted of a fine glass finger in which a thin glass rod, flattened at the bottom, and having a magnet sealed in glass at the top, was free to slide. This apparatus was attached

FIG. 19 A/ Melting Point / Vapour Pressure Apparatus



B/



to the main vacuum line via a mercury valve and was completed by one half of a differential manometer (M_3), the other half of which was connected directly to the vacuum pumping system.

A previously purified sample was transferred to the vacuum line U trap, T_{20}. The system was then evacuated and sealed by the mercury valves (V_1, V_2, V_3). The glass rod was raised by an external magnet and the sample was condensed, as far as possible, around the flattened end of the rod. The solidified material was then capable of supporting the rod and the external magnet could be withdrawn. Valve V_4 was then closed and the finger was surrounded by a bath, usually of alcohol, cooled to at least 20°C below the anticipated melting point of the compound. A previously calibrated thermometer was put alongside the finger and the bath was allowed to warm up, with stirring, at about 1°/minute. The following points were watched; the level of the probe, the condition of the sample and the apparent vapour pressure (as sufficient time for vapour equilibrium did not elapse). If a large enough sample was available, the first of these observations was sufficient but, if less than about 5 mg. of sample was available, the rod could slip before the sample had melted and the other observations had to be used as a cross check (see Fig.19B).

For vapour pressure measurements it was merely sufficient to surround the finger with a bath of the appropriate temperature for about 20 minutes with agitation of the sample by raising and lowering the rod with a magnet. The differential manometer was read using a lens and a no-parallax technique (see Plate 10).

Unfortunately, in the work on the silicon-germanium methyls, only

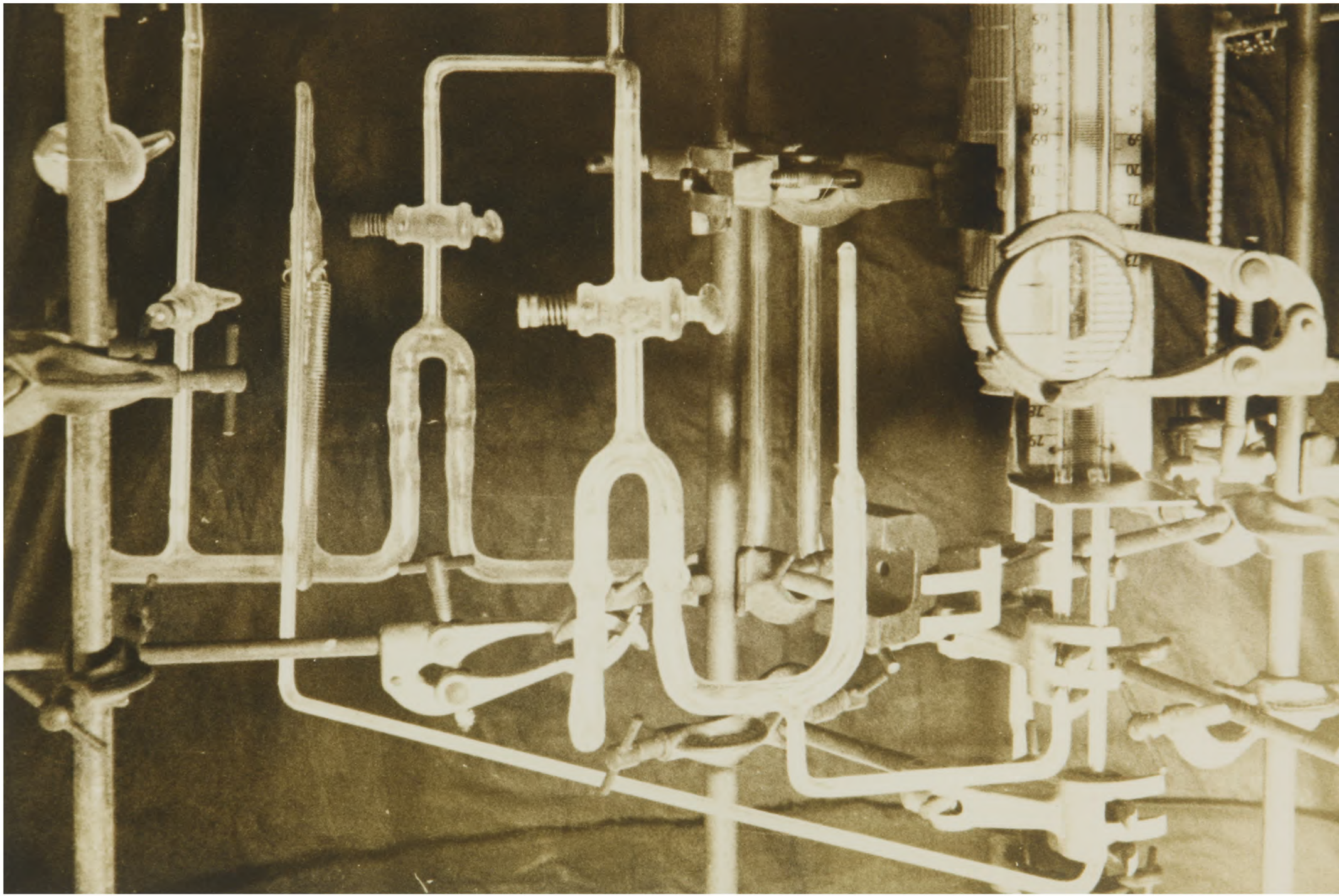
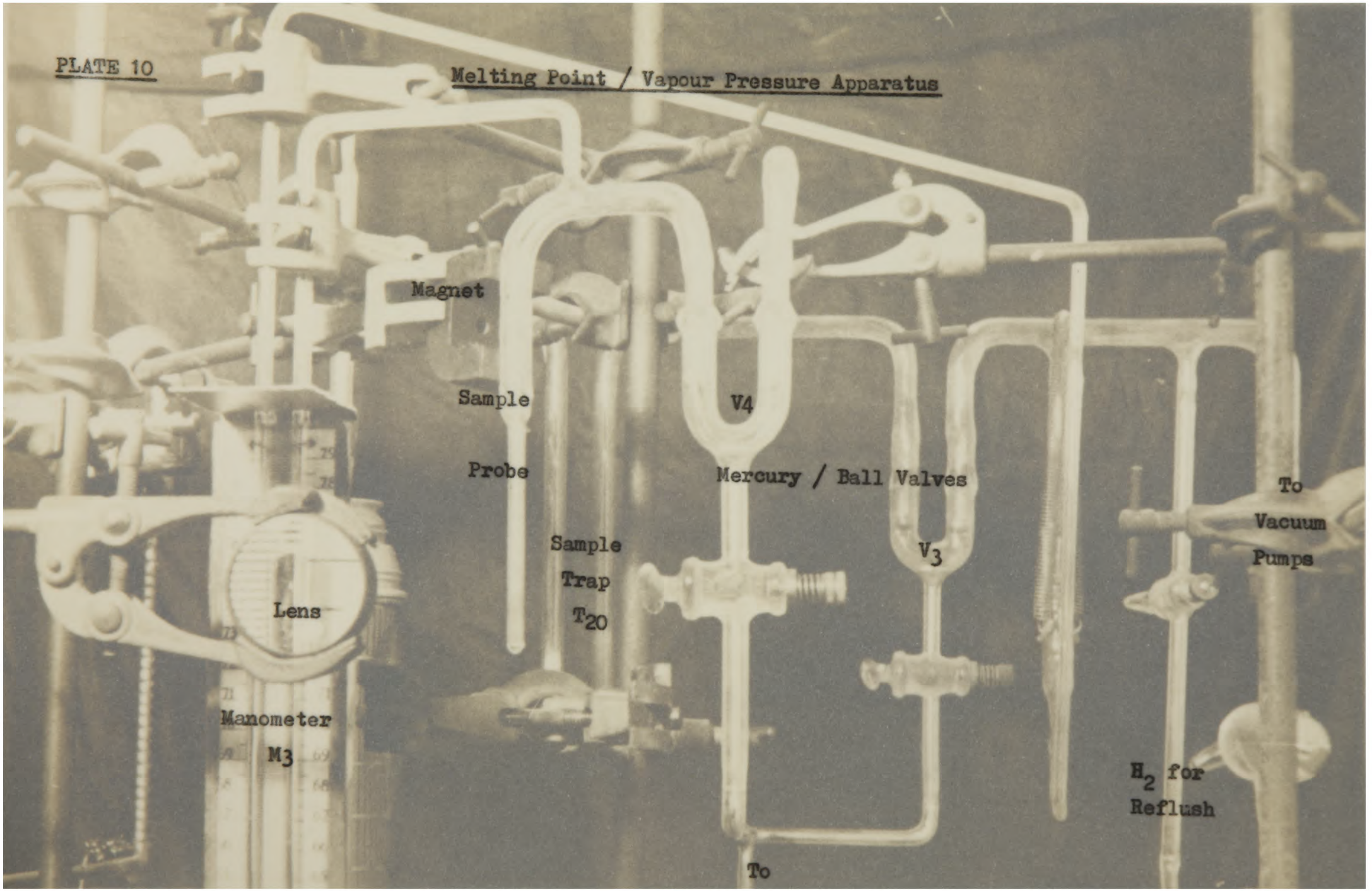


PLATE 10

Melting Point / Vapour Pressure Apparatus



the first member $SiMe_3GeMe_3$ was available in sufficient quantity and purity for this method to be applied. Moreover, since the apparatus was effectively limited to substances melting below room temperature, it was not certain whether the higher silicon-germanium methyls could have been handled by this method.

The results obtained with $SiMe_3GeMe_3$ were as follows:-

TABLE 1

Melting point :	By observation	-3.9°	-3.7°	-3.8°
	By vapour pressure curve	-3.6°	-3.9°	-4.0°
Vapour pressure :	$0^\circ C$	5.1mm	5.3mm	5.0mm
	$22.5^\circ C$		16.1mm	16.3mm

From these figures may be deduced:

$SiMe_3.GeMe_3$ M.P. $-3.8^\circ C$ V.P ($0^\circ C$) 5.1mm. V.P.($22.5^\circ C$) 16.2mm.

(B.P $169^\circ C$ extrapolated).

which may be compared with[72]:-

$SiMe_3.SiMe_3$ M.P. $+12^\circ C$ B.P. 113/760mm.

$GeMe_3.GeMe_3$ M.P. $-40^\circ C$ B.P. 138/750mm.

indicating that there might be a slight Si-Ge polarity.

2.5 Preparative Techniques

This section is concerned with the salient points in the preparative techniques used in this work.

2.51 Preparations in Stainless Steel Bombs and Miniature Carius Tubes

In view of the fact that most of the preparative reactions used in

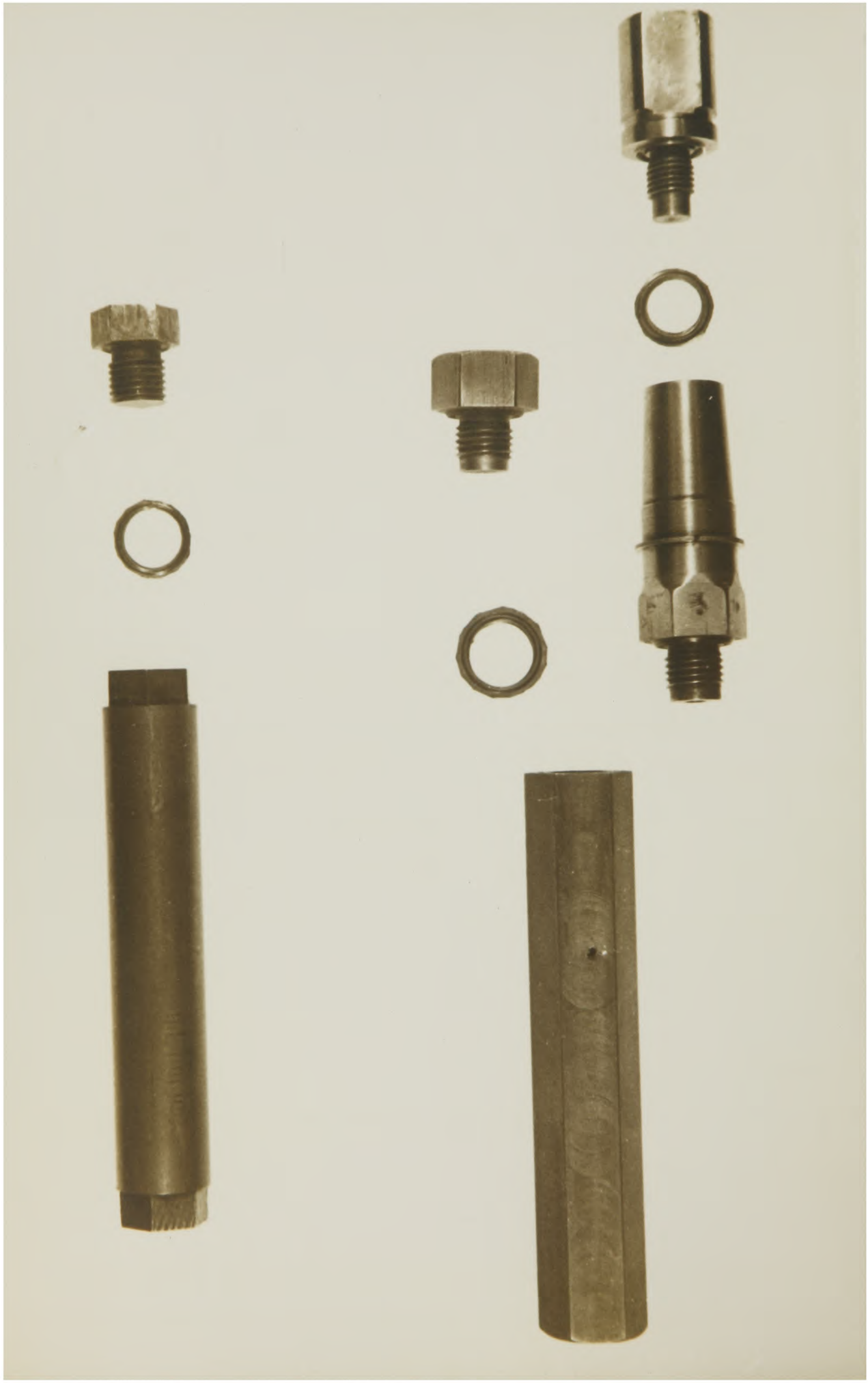


PLATE 11

The Stainless Steel Bombs

Bomb 'A'



Body
length; 6", o.d.; 1"
i.d.; ½", capacity; 19 ml.



Compression Ring
0.008" copper

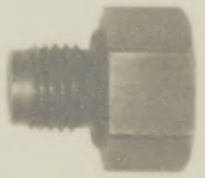


Top Bolt

Bomb 'B'



Compression Ring



Top Bolt



Body
length; 6", max. width; 1.18"
i.d.; ½", capacity; 19.5 ml.



Distillation Head
B24 cone



Compression Ring



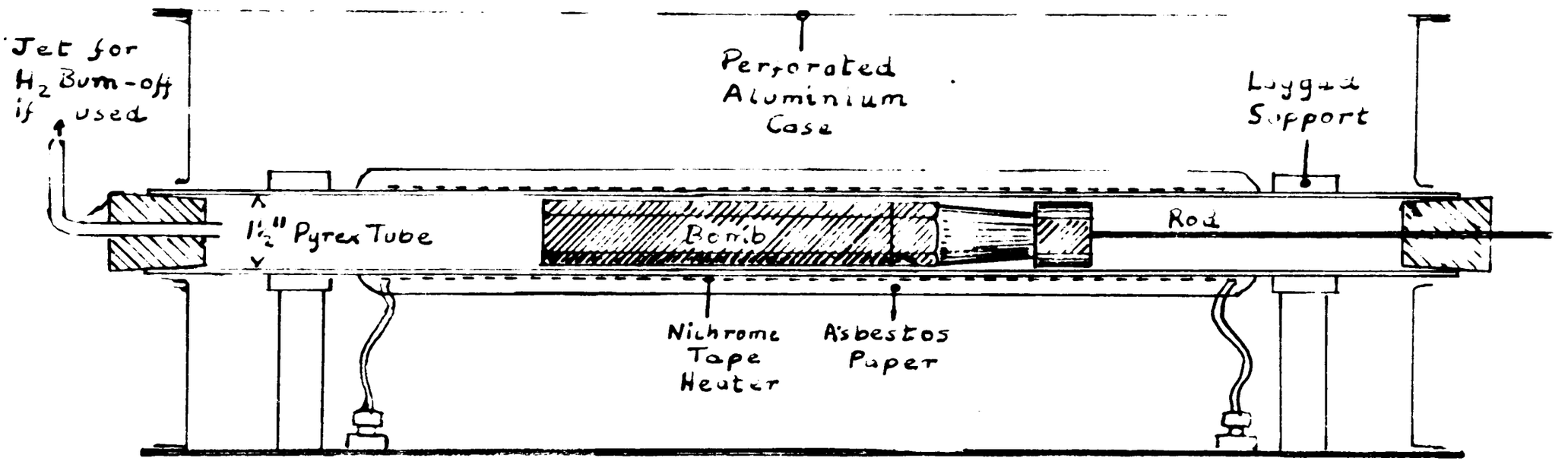
Top Bolt

this work were expected to yield mixtures of compounds, it was decided at an early stage to try to carry out the reactions in the absence of solvents and, since some of the compounds were moisture sensitive, in sealed systems. These techniques would yield products free from any solvent interactions and this would simplify their purification.

As the pressures expected in some of the reactions were high, and since it was desirable to use distillation as a means of extraction, special stainless steel bombs were designed by the Author with provision for attachment to a vacuum distillation system. These bombs were used for all of the reactions but eight, and are shown on Plate 11.

Initially a simple bomb (Plate 11,A) was employed. It was sealed by an annealed copper ring, made from 0.008" sheet, compressed into a circular recess on the bomb body, of 'V' section, by an elevated ring of 'V' section on the top nut. For vacuum distillation the top nut was exchanged for a stainless steel adaptor fitted with a B_{14} cone (not shown) similar to that on bomb B. Subsequently a bomb of modified design was constructed (Plate 11,B) where the bomb could either be used in the same way as the original bomb with a single top nut, or it could be assembled complete with its distillation adapter (B_{24} cone), in turn having a similarly sealed top nut. This assembly was only completely dismantled for cleaning or, in certain cases,for filling. The original form of bomb (A) was fitted with a hexagon at top and bottom of the body only, but the second bomb was machined with a hexagon over the entire length, making manipulation easier when it was very hot or cold. All nuts were lubricated with colloidal graphite. Both bombs had an internal diameter of $\frac{1}{2}$" and

FIG. 20 The Bomb Furnace ~ Section



a volume when closed of about 20ml.

The bombs were heated in a horizontal tubular furnace made of pyrex glass, wound with nichrome tape (see Section 2.41) which was overlaid with two layers of asbestos paper. This furnace was mounted inside a box made of perforated aluminium sheet, for safety reasons (see Fig.20), and could be fitted with a gas supply, e.g. when used for annealing copper sheet or preparing the reduced copper required for the 'Direct Method' (see Section 3.3). The original bomb (A) was inserted into the furnace in a cradle made of wire, but the modified bomb had a hole in its top nut tapped to take a piece of threaded welding rod (see Fig.20).

The furnace was powered using a combination of Volstat transformer and Variac similar to the column heating (see Section 2.41). It had a design maximum temperature of 400°C at 2 Amps and the dial of the Variac was calibrated in degrees, assuming ambient to be 20°C. Accordingly, it is estimated that the reaction temperatures quoted in this work are correct $\pm$ 5°C. When inserted, the bombs achieved a temperature within 5° of their final value within $\frac{1}{2}$ hour. Reaction times are quoted from this time.

The basic technique for carrying out reactions in these bombs was as follows: Solid reactants were usually introduced first, liquid reactants being subsequently introduced by hypodermic syringe through a septum made of adhesive tape. This prevented, as far as possible, ingress of moisture. The septum was then removed and the nut rapidly screwed down. A spanner with about a foot of leverage was used to tighten the bomb, the body of the bomb being held in a vice. The bomb

was then weighed so that a check could be carried out after reaction for any loss in weight due to leakage. On only one occasion was a measurable loss of weight (more than 0.1 gm) observed. After reaction, which was usually continued for 20 to 24 hours for convenience, the bomb was removed from the furnace and cooled in a vertical position to room temperature. Generally, to assist in the initial pumping out in the vacuum distillation, the bomb was further cooled in liquid nitrogen prior to removal of the top nut and attachment to the distillation system. This prevented loss of the products. The system was rapidly pumped out via the top stopcock, prior to pumping via the trap, as a restriction was placed after this trap to prevent rapid pumping, with consequent loss of sample, if sample was coming over too rapidly to be condensed.

For recovery of all the compounds that would be detectable on the chromatographic systems, the temperature of the bomb was slowly raised to about 150°C in an oil bath and pumping was continued for about half an hour. If only the lower boiling compounds were required, the bomb was heated to about 100°C. After distillation, the bomb was usually cooled and the apparatus was filled with nitrogen (this was particularly important in the case of the Wurtz reactions) prior to removal of the distillation trap.

The following types of reactions were carried out using this basic technique:

1/ Rearrangement reactions at germanium of methyl and chlorine groups[94-97] (see Section 3.2):

These reactions were attempted using various catalysts, some of

which were presumed to be formed in situ. Typical reaction conditions employed were 250°C for 20 - 24 hours. In addition to the reactions carried out in bombs, a set of reactions was carried out, to discover if the stainless steel of the bombs or the copper of the sealing rings were acting as catalysts, using miniature Carius tubes made from pyrex glass tubing with 5mm. walls and an internal diameter of about 3mm. These were sealed under vacuum with the reactants frozen out in liquid nitrogen and the seals were annealed as well as possible. The finished tubes were about half full of the reaction mixture and had an overall length of about 15 cm. These were, with one exception, successfully employed at 350°C and it could be seen that, at that temperature, a mixture of $GeCl_4$ and $GeMe_4$ was below its critical point. In most cases the tubes were broken and the products simply injected by syringe into the chromatograph, otherwise the products were vacuum distilled.

2/ Direct reaction of germanium with methyl chloride (see Section 3.3)

Although this reaction was originally carried out as a continuous stream method[99-101], it was decided to see if it could be carried out in a bomb. Powdered germanium and reduced copper were put in a bomb and the distillation head was fitted. The bomb was cooled to about -30°C and methyl chloride was passed in from a cylinder. A dip tube connected to an outlet indicated when the bomb was full enough. The supply was turned off and the bomb cooled somewhat more prior to fitting the top nut.

3/ Wurtz-Fittig type reactions with methyl silicon and germanium

chlorides (see Chapters 5 and 6)[24, 27, 32, 72, 76].

In these reactions several metals were used in attempted couplings but only sodium and potassium gave any appreciable yields, potassium being most effective, (see also[72]). When either of these metals was used, the metal was cut, under dried petroleum ether, into small clean pellets which were dried on filter paper immediately prior to placing in the bomb. No particular advantage was observed whether the metal was put in the bomb before or after the liquid. As the potassium tended to get hot before the top nut was put on, speed was imperative: Thus, if a single liquid was used, it was put in after the metal, but if a mixture of liquids was used, they were usually introduced separately before addition of the metal. Thence the rest of the normal procedure was followed. The most satisfactory method of getting rid of the surplus metal after extraction of products was found to be to drop the opened bomb into a bucket of water outside the building.

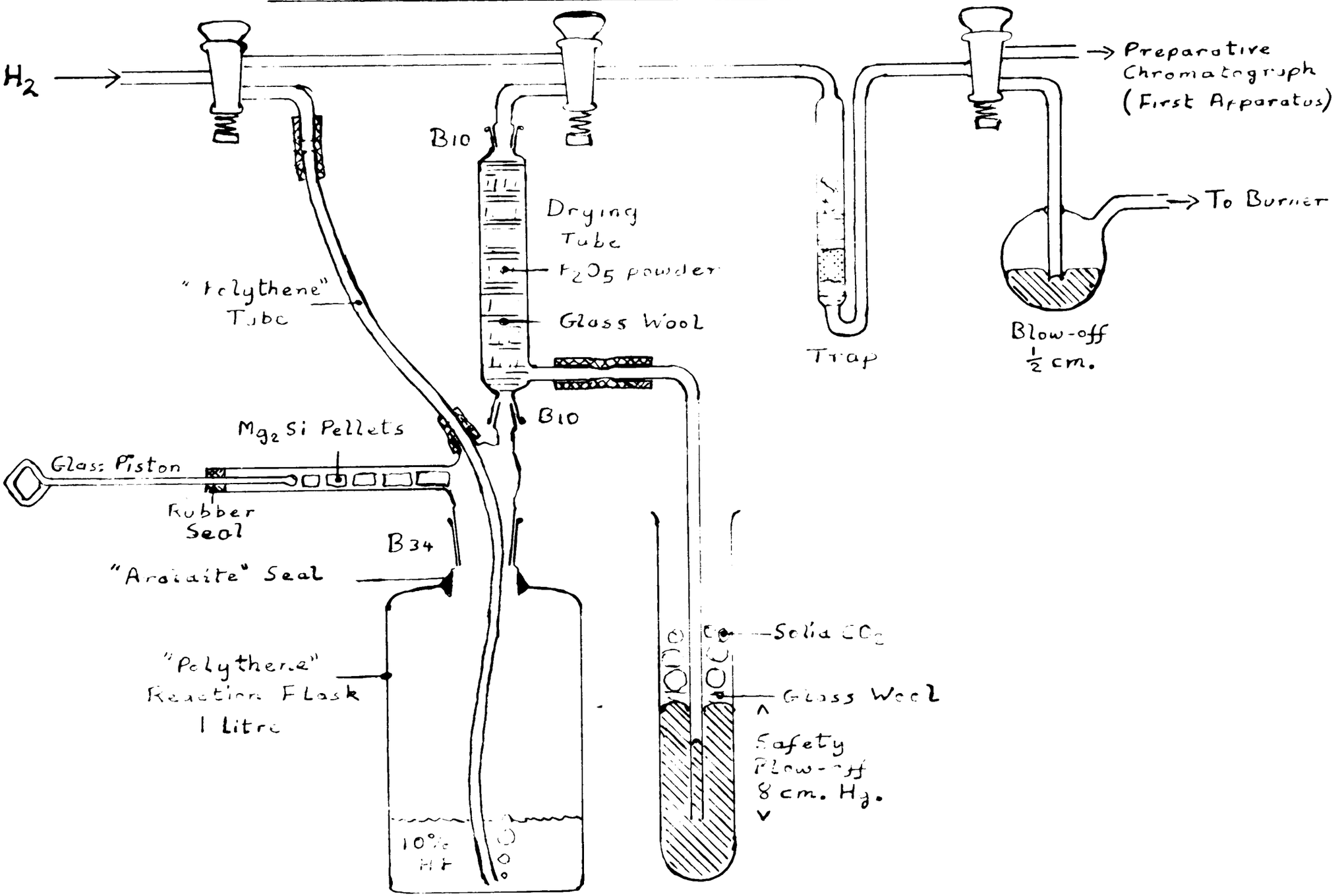
2.52 Silicon Hydride Preparation (see Appendix 2)

On one occasion a sample of the silicon hydrides was prepared. The method employed was developed by Timms[29] from the original method of Stock[38]. The hydride preparation unit on the preparative system of the First Apparatus was used, and this is shown in detail in Fig.21.

200 ml. of 10% hydrofluoric acid was put in the polythene reaction flask, and seven pellets consisting of decreasing amounts of magnesium silicide (Plessey), with a total charge of 2 gm., wrapped in aluminium foil (Cadbury's), were put in the side arm. The apparatus was then purged with a stream of 400 ml./min. hydrogen for half an hour.

FIG. 21

Silicon Hydride Preparative Apparatus



Some pellets of solid CO_2 were then placed on top of the mercury in the glask blow-off to prevent ignition of any escaping gases. The pellets of magnesium silicide were then added one at a time, the purging hydrogen being turned off as soon as each pellet started to react, and on again as soon as the pellet had stopped reacting to prevent suck-back by the rapidly cooling gases. Approximately five minutes were allowed to elapse between each addition to prevent the flask from getting too hot and melting.

After addition of the last pellet the flask was purged with hydrogen for a further half hour. The products were dried by passage through a column of alternate layers of phosphorus pentoxide (about 40 gm) and glass wool. The products were collected in a trap initially cooled by liquid nitrogen. For part of the final purging stage this refrigerant was replaced by an acetone/CO_2 bath to permit the large excess of SiH_4; and some of the Si_2H_6 to escape. Finally, this bath was replaced by a flask of liquid nitrogen.

The total yield of hydrides produced in this way is usually less than 20% of the theoretical, most of which is SiH_4 and Si_2H_6 but also contains the following compounds[21, 22, 29-32]:

1/ Straight chain; up to Si_8H_{18} at least.

2/ Single branch chain; at least one set of isomers from iso-Si_4H_{10} to iso-Si_8H_{18}.

3/ Double branched isomers, precise structures unknown; Si_5H_{12}(doubtful), Si_6H_{14}, Si_7H_{16}.

The sample collected was then transferred to the preparative system and separated into the desired components (see Appendix 2). The reaction

flask was isolated from the rest of the system and solid CO_2 pellets were introduced via the side arm so that most of the hydrogen in the flask was displaced. This avoided the explosion, that had almost invariably occurred in the past when this precaution was not taken, shortly after removal of the reaction flask, caused by the spontaneous ignition of the ensuing hydrogen/air mixture by residual traces of silanes.

2.6 The Gold Chloride Analytical Reaction - Technical

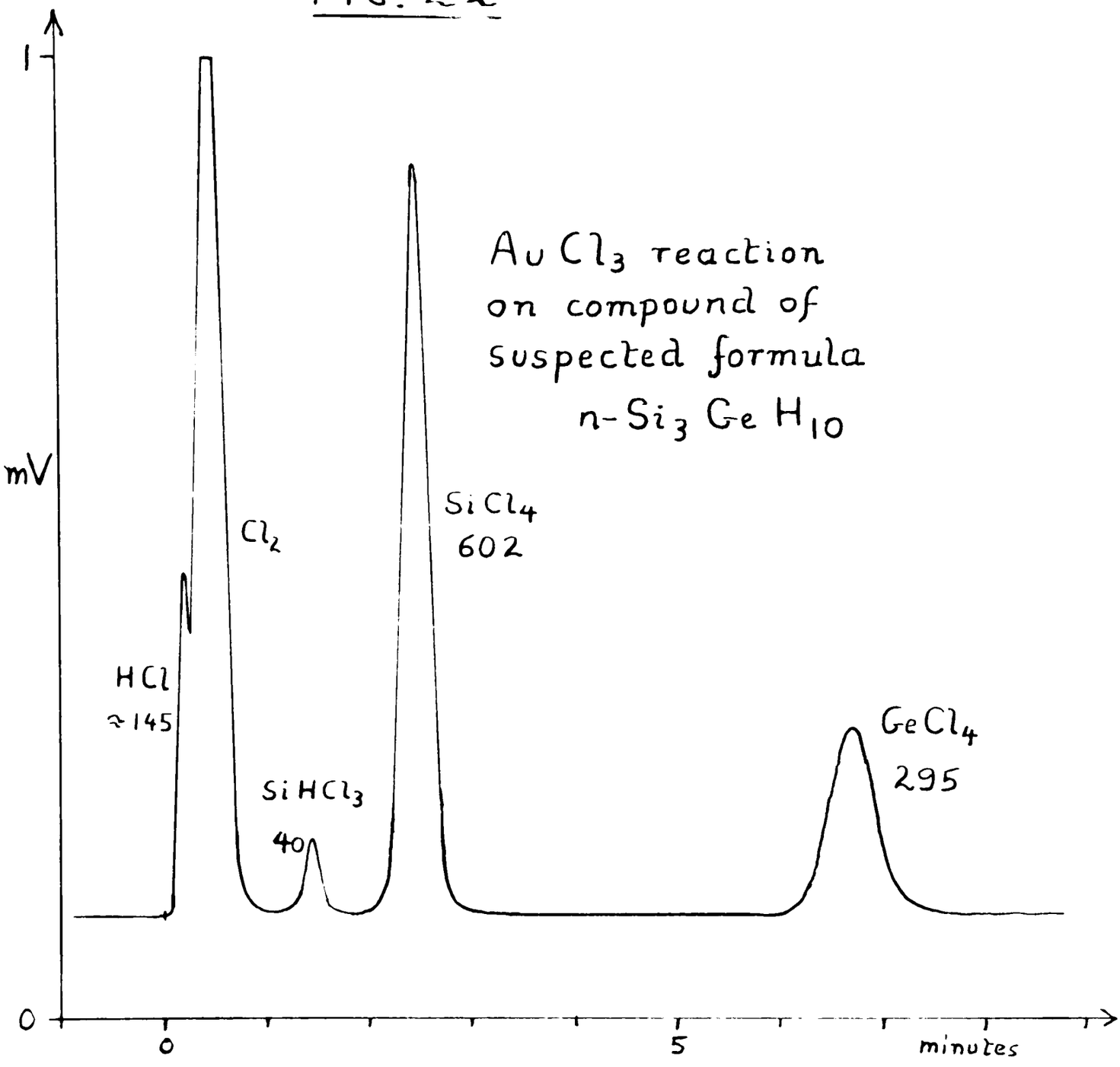
2.61 Introduction

In the early work by Timms[29] on the silicon-germanium hydrides, a method was devised for obtaining the silicon: germanium: hydrogen ratios of microgram to milligram samples of these compounds. This was used in conjunction with chromatographic and other data to ascertain their molecular formulae and, to a certain extent, their structures.

Chlorination under controlled conditions was selected as the basic method, and $AuCl_3$ (chlorine partial pressure at 170°C, 1.8 mm. Hg.)[118] was chosen as the source of chlorine. Samples of the hydrides, at partial pressures controlled by evaporation from a trap immersed in baths of appropriate temperatures, were passed in a stream of nitrogen through a reactor with a boat containing $AuCl_3$ followed by a zone heated to about 300-400°C. The products were collected in a high efficiency trap cooled in liquid oxygen and then injected into a chromatograph equipped with a density detector.

The reactions were originally supposed to take place as follows:

FIG. 22



Si : Ge : H Ratio :—

$$= \frac{\text{Area}(SiHCl_3)}{M.W._{SiHCl_3}-28} + \frac{\text{Area}(SiCl_4)}{M.W._{SiCl_4}-28} : \frac{\text{Area}(GeCl_4)}{M.W._{GeCl_4}-28} : \frac{\text{Area}(HCl)}{MW_{HCl}-28}$$

$$= \frac{40}{106.3} + \frac{602}{141.8} : \frac{295}{186.4} : \frac{\approx 145}{8.45} = 4.62 : 1.59 : 17.2$$

$$\therefore \quad Si : Ge : H = 2.91 : 1 : \approx 10.8$$

(error in Si : Ge = 3% Ge : H = 8%)

$$2\ AuCl_3 \xrightarrow{170^\circ C} 2\ Au + 3\ Cl_2 \text{ (removed in gas stream)}$$

$$n\text{-}Si_3GeH_{10} \xrightarrow{Cl_2\ \text{excess}\ 300^\circ C} 3\ SiCl_4 + GeCl_4 + 10\ HCl.$$

although in practice, particularly if large samples were used, some $SiHCl_3$ was also formed.

Since, under a given set of conditions, the signal of the density detector divided by the difference in molecular weights of sample and carrier gas is proportional to the molar concentration of the sample (see Section 2.45), it was merely necessary to measure the areas of the product 'peaks' (see Section 2.74) on the chromatogram and divide these by the molecular weight differences of the products and carrier to obtain the Si:Ge:H ratios (the last only with a limited accuracy) of the parent compound (see Fig.22).

When it was realised that this method might be applicable to the alkyls of silicon and germanium (Section 1.32) the initial problems were to see if all the products could be identified, and to see if there was any tendency to form involatile products. Thus the preliminary work had to be carried out on known compounds (see Chapter 4). It was realised fairly early in this programme that the reaction did not take place exactly as originally assumed, as reaction was shown to take place under conditions where no detectable amounts of chlorine were evolved (see Section 4.13). Thus some modification of the basic equipment was necessary.

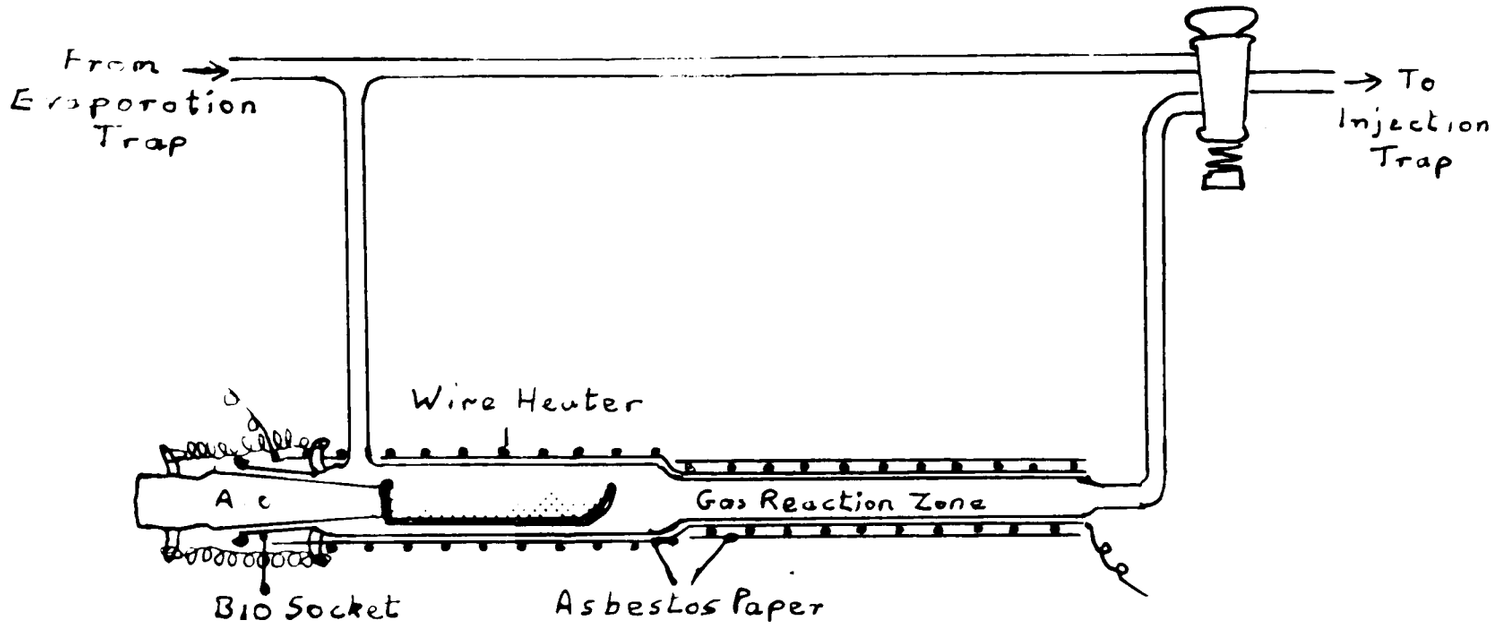
2.62 Design of the Reaction Cell

The original reaction cell of Timms[29] (see Fig.23A) had a removable porcelain boat containing about 1 gm. of precipitated gold which was

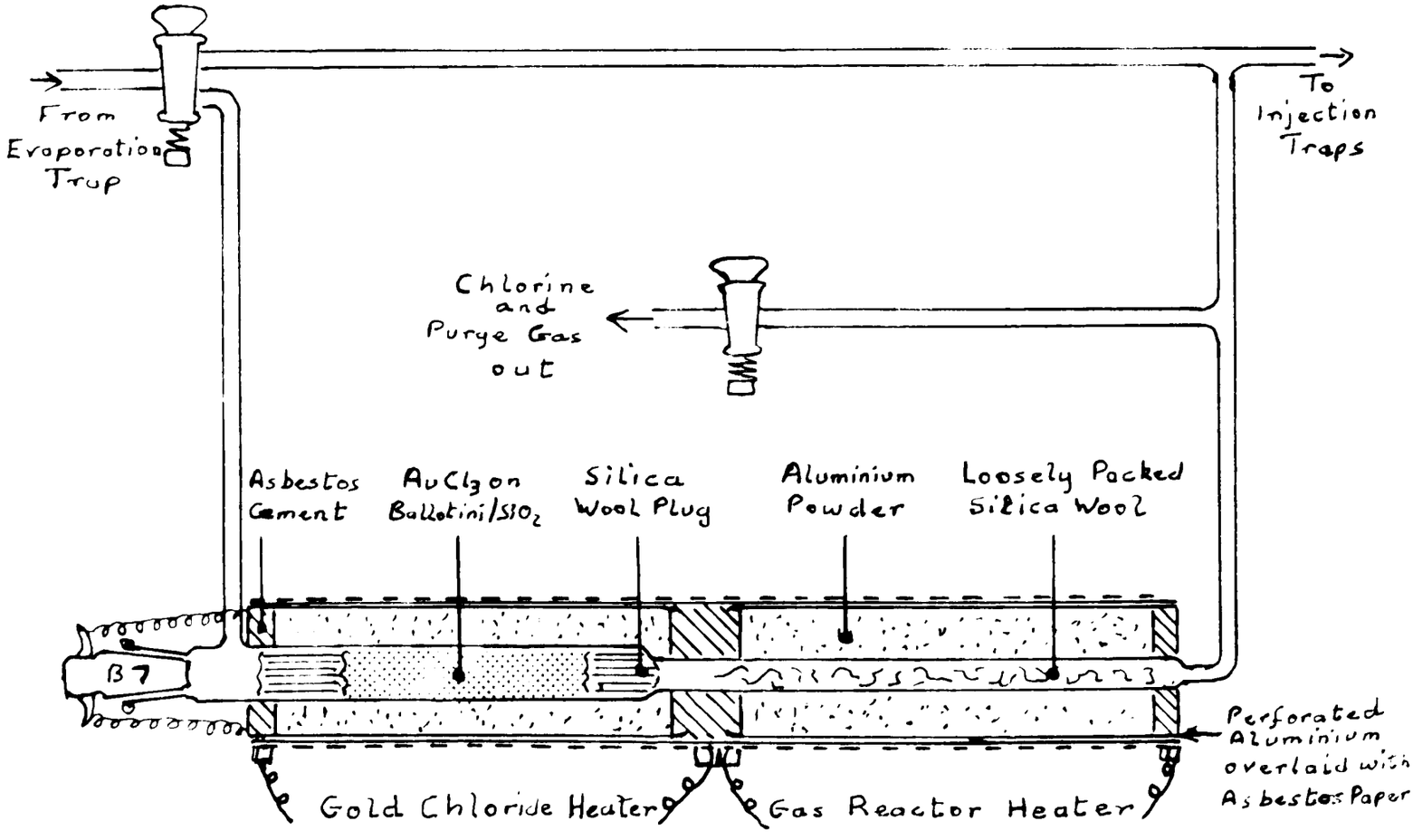
FIG. 23

Gold Chloride Cells

A/ First Cell *



B/ New Cell *



* In both systems, All taps and tubes were heated by Nichrome tape heaters and thermometers could be mounted in tubes alongside both parts of the reactors.

removed for conversion to $AuCl_3$. The heater for the zone containing the boat was wired in series with that of the gas reaction zone, so that when the former was at equilibrium at 170°C, the latter was at around 300°C. Transfer of the deliquescent, freshly prepared, $AuCl_3$ to the cell was effected while the boat was hot and this led to no serious inconvenience, after an initial purge of about 15 minutes under reaction conditions. Total removal of water was assumed to have taken place when no detectable amounts of HCl were evolved in a 'blank run'.

This reactor was used for the initial investigations on the silicon and germanium tetraalkyls (see Section 4.1) but when it was realised that some reaction must be taking place in the immediate vicinity of the gold chloride, if not with the chloride itself, it was seen that the original cell must be inefficient and that more satisfactory results would be obtained by passing the sample through a plug of gold chloride.

Accordingly a new cell was devised (Fig.23B) for the New Apparatus. In view of the difficulties of packing the reactor material in plug form, chlorination of the gold in situ was necessary. Thus the surrounding apparatus had to be redesigned to prevent contamination of the analytical system by chlorine and moisture: Facility for purging the cell from both ends, and a special outlet for the chlorine had to be provided.

Some difficulty was experienced in making a suitable plug of gold chloride, as a plug of precipitated gold, retained between two plugs of silica wool, became almost impervious on chlorination. Attempts to make a plug of a mixture of 'Ballotini' and gold resulted in

stratification, and a mixture of crushed silica wool and gold again resulted in a high impedance to flow. These problems were solved by making a mixture of silica wool, Ballotini and gold which was found to have neither of these defects; the silica wool retaining the gold and the mixture with Ballotini providing the desired permeability. This plug contained about 1 gm. of gold, and was retained between two plugs of silica wool. The diameter of the cell was reduced for the gas reactor, and this restriction assisted in the retention of the plug. The gas reactor was lightly packed with silica wool. Each end of the cell was mounted in a can of perforated aluminium, covered with asbestos paper with the heating tape wound on this. As it was desired to operate under a variety of conditions, the gold chloride and gas reactor heaters were separately wound so that they could be individually controlled. The space between the two parts of the reactor assembly was filled with asbestos pulp to minimise lateral heat transfer and tubes for thermometers or thermocouples were placed alongside the two parts of the reactor. The space between each part of the reactor and its heater was packed with aluminium powder for good thermal contact, and the ends were sealed with asbestos cement.

2.63 Chlorination of Gold

In the case of the original gold chloride cell, chlorination of the gold was carried out in a special reactor heated to 200 - 210°C. Chlorination in situ in the modified cell was carried out at the same temperature with the chlorine supply connected in place of the B7 stopper. All manipulations such as removal of the stopper were carried out under

a positive pressure of nitrogen to prevent ingress of air and moisture. During chlorination a slow flow of nitrogen was provided through the rest of the analytical system, leaving via the chlorine outlet, thus preventing contamination. After chlorination, the cell was purged by an additional flow of nitrogen leaving in the same way.

Chlorine was prepared by dropwise addition (about 2 drops/min.) of concentrated hydrochloric acid to potassium permanganate. The chlorine had most of the accompanying water vapour, and some of the HCl, removed by passage through 3Å molecular sieve prior to introduction to the cell via a 'teflon' tube and a pyrex B7 cone.

Chlorine was passed for about half an hour with the cell at around 200°C and this flow was continued while the cell was allowed to cool to around 170°C. The supply of chlorine was then removed and the cell resealed. Purging of the cell was carried out at about 180°C, with a nitrogen stream of about 40 ml./min.

2.64 Gold Chloride Experimental Technique

(This section describes the operation with the new cell and apparatus. The technique with the First Apparatus was substantially the same).

A sample of the compound to be analysed, either purified in the preparative system or injected directly via injection point I_2 (see Fig.7), was transferred to the evaporation trap (T_{16}) which was cooled by liquid oxygen. A suitable temperature for evaporation was selected so that the total sample was in the range of 5 micrograms to 1 milligram (25 - 250μg.being most commonly employed). This was usually determined

by experiment. Typically the temperatures chosen for $GeMe_4$ were -65°C to -80°C, and for Ge_3Me_8, around 25°C. The desired gold chloride and gas reactor temperatures were then set up and a flow of nitrogen established through the analytical apparatus and the appropriate column, as for a chromatographic run. Usually the standard column flowrate (50 ml./min. measured at the outlet) was used, but when longer reaction times were required, slower flowrates were employed. For every new compound introduced to the system, a blank run, following the procedure described below with the exception of replacement of the coolant around the evaporation trap, was carried out to check that the system was not contaminated with the previous sample. A similar blank run was carried out after each regeneration of the gold chloride to check that no HCl was evolved.

The standard analytical procedure was as follows: The injection traps (T_{12}, T_{13}) were cooled with liquid oxygen and the nitrogen supply was then switched from the by-pass, through the gold chloride cell. The liquid oxygen cooling the evaporation trap was then replaced by a bath of the desired evaporation temperature; slush baths, alcohol or water baths were used for this (with suitable precautions if the bath contained an inflammable compound), and the sample was allowed to evaporate for a period, usually between 1½ and 7 minutes. The bath was then replaced (with suitable precautions) by liquid oxygen, and the cell allowed to purge for between 2 and 5 minutes prior to re-establishing the gas flow through the by-pass. The nitrogen stream was then allowed to purge the tap before the injection traps for a further 10 - 15 minutes, during which the column flow and

temperature were adjusted to the precise values desired (50 ml/min. and 30°C), prior to injection, by exchanging the liquid oxygen around the injection traps for boiling water.

The results of the first run on each new sample were either discounted or treated with reservation because of the absorption of the sample and possible desorption of traces of the previous sample held in the grease of the cell selector tap. The preliminary runs did however serve the purpose of indicating whether the cell conditions were satisfactory for the reaction.

2.65 Chromatography of Products

In the original gold chloride reaction on the silicon-germanium hydrides, a single Silicone 702 column operating at room temperature was sufficient to separate the products completely (with the exception of the partial separation of HCl from Cl_2) and assignment of the peaks was extremely simple (see Fig.22).

When the method was applied to the silicon and germanium methyls and ethyls, using the First Apparatus, it was seen that under different reaction conditions a wide range of products was formed: Replacement of the alkyl groups by chlorine gave the entire range of alkyl silicon and germanium chlorides, and only under the most vigorous conditions, were the tetrachlorides formed. The displaced alkyl groups were both converted to the full range of chloromethanes, chloroethylenes and chloroethanes. The identities of the 'peaks' obtained from these parent compounds were established by comparison with pure compounds which were obtained from a variety of sources:

E.g. the chlorinated hydrocarbons mainly from B.D.H. and Eastman Kodak, the methyl silicon chlorides from B.D.H., the ethyl silicon and germanium chlorides from Dr. P. Powell (Inorganic Chemistry Laboratory, Oxford) and the methyl germanium chlorides from the reactions described in Chapter 3. The parent compounds were obtained from the following sources: $SiMe_4$ from Koch Light, $SiEt_4$ from Dr. P. Powell, and $GeMe_4$ and $GeEt_4$ from The Organisch Chemisch Instituut T.N.O., Utrecht.

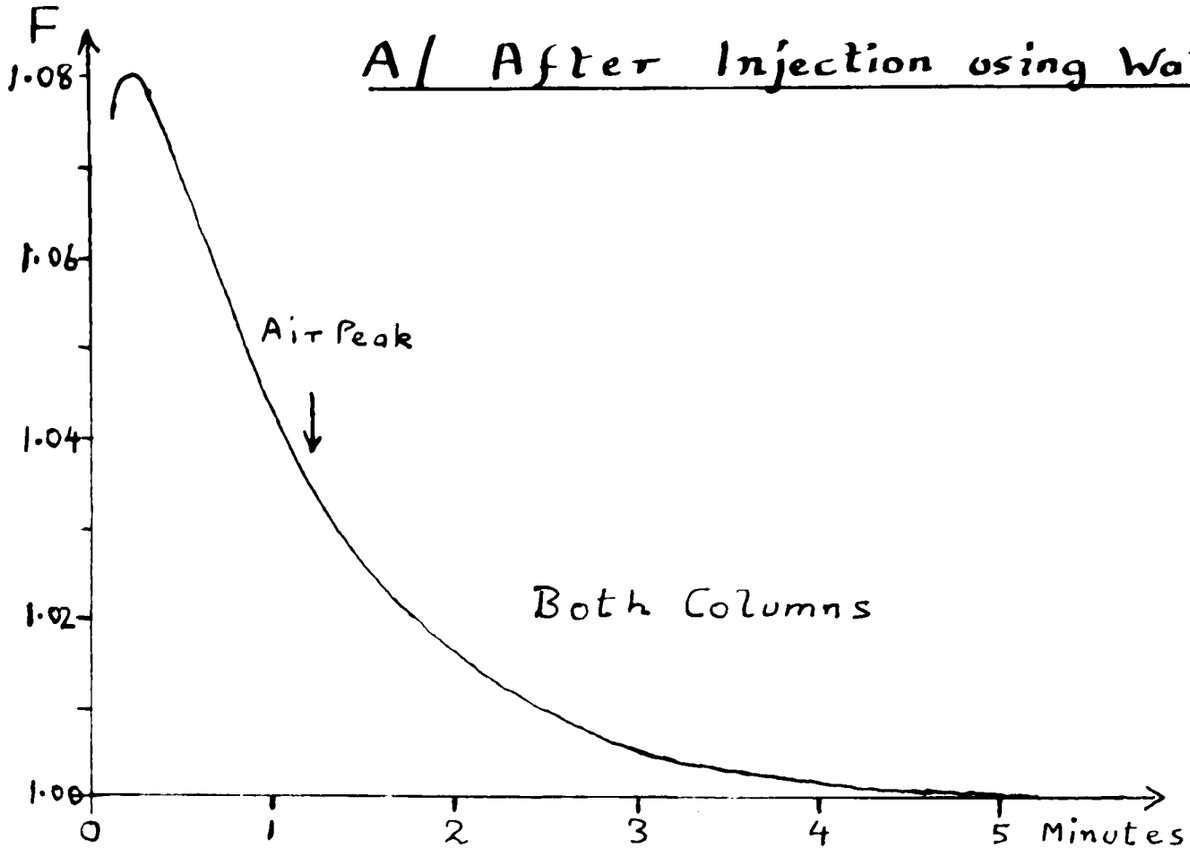
Some of these compounds had high boiling points and some were almost chromatographically coincident with others, and therefore the chromatographic techniques had to be altered. Initially, the chromatographic column was equipped with the crude heating system described in Section 2.41. This was switched on immediately after the peak correspondong to tetrachloroethylene (see Fig.25) and the column reached an equilibrium temperature of approximately 90°C. This was reasonably satisfactory once the correction for the change in flowrate (see below) had been applied.

It was realised that operation at room temperature, with its day to day variations would not be satisfactory when operation with unknown parent compounds was attempted, as even the use of 'Relative Retention Times' could lead to errors in identification, particularly in the case of nearly coincident 'peaks'. In addition, the heating up technique was dependant on mains voltage and was thus not very consistent. Accordingly, in the design of the New Apparatus, in addition to equipping the gold chloride system with two columns to assist in the identification of the components of multiple 'peaks', the column temperatures were controlled more precisely, 30°C being selected as the initial condition.

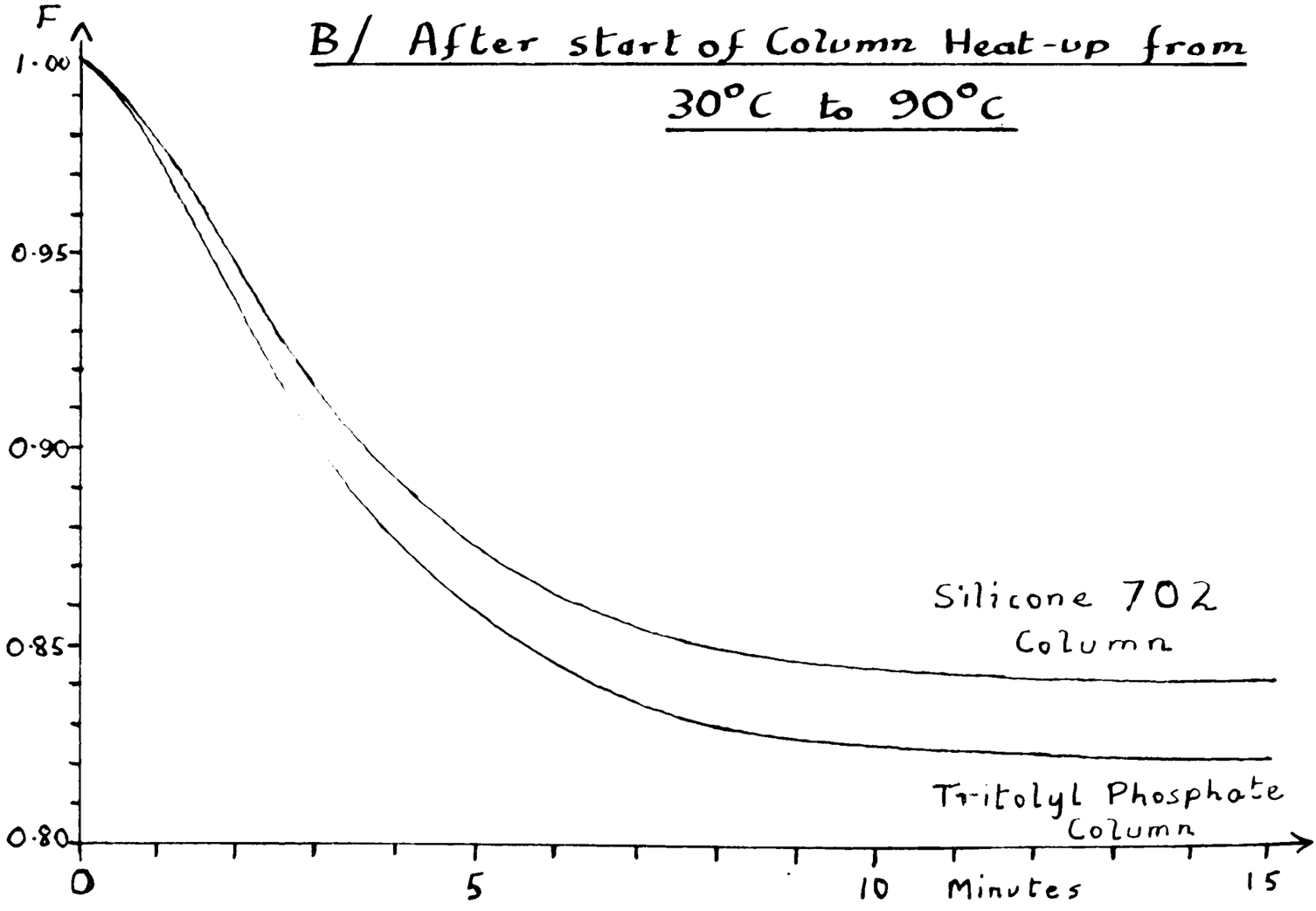
Fig. 24 Flowrate Correction Factors (F);

Gold Chloride Technique, New Apparatus

A/ After Injection using Water at 100°C



B/ After start of Column Heat-up from 30°C to 90°C

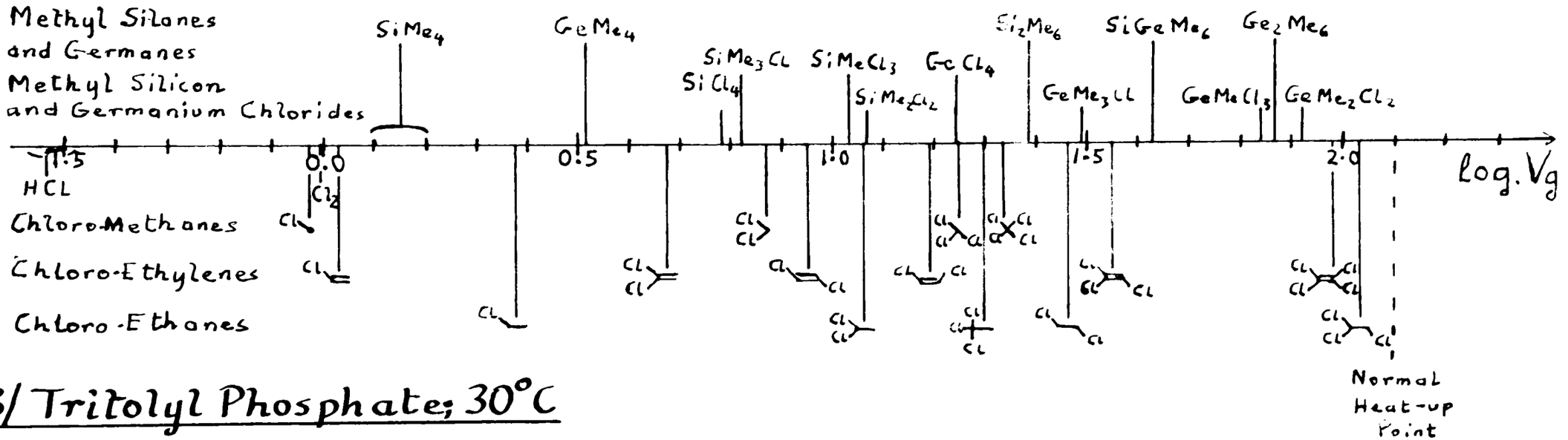


The heating-up procedure was retained, 90°C being selected as the equilibrium temperature. This was started just after 1,1,2, trichloroethane (or its position) on Silicone 702 (32 minutes from injection) and just after $GeMeCl_3$ (or its position) on tritolyl phosphate (25 minutes from injection), as very large gaps in the chromatograms occurred after these compounds if the columns were maintained at 30°C.

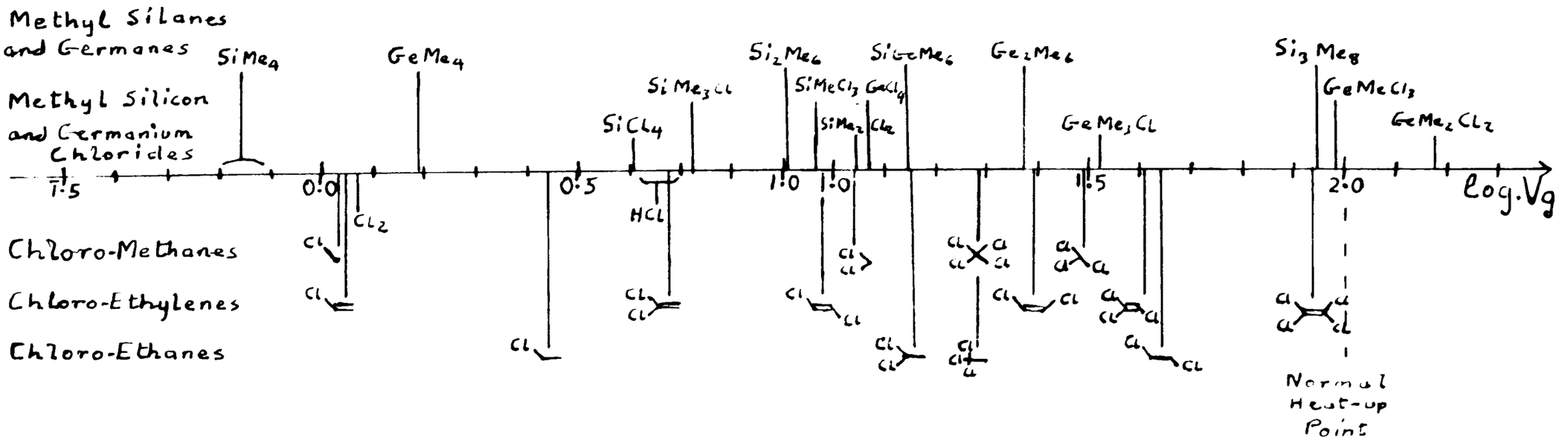
Under given conditions of reference gas flow-rate, temperature and filament current, the signal of the density detector should theoretically be proportional to the density difference between reference and sample gas, irrespective of the sample gas flowrate, provided that there is sufficient sample gas flow to prevent diffusion of reference gas into the sample arm of the pneumatic bridge. This has been shown to be approximately the case with the Gow-Mac detector[30] for small (less than 30%) flowrate variations. This implies that the peak area, at constant chart speed, of a given sample will be inversely proportional to the carrier flow rate. Thus, in quantitative runs where the flowrate varies, all peak areas should be multiplied by the flowrate at the time of their emergence. The change of flowrate after the start of the heat-up was measured on both the gold chloride columns, and the surge flowrate after injection was estimated by manometric measurements in the New Apparatus. These were expressed as their ratio (F) to the standard flowrate of the cold column operation. The values obtained with the New Apparatus are shown in Fig.24. The actual 'peak' areas, (A) were multiplied by the appropriate value of F to give the theoretical area that would be obtained if the column was running under standard conditions (i.e. 50 ml./min., measured at room temperature). Thus

FIG. 25 Retention Values for some of the Starting Materials and Products in the Gold Chloride Reaction (New Apparatus)

A/ Silicone 702; 30°C



B/ Tritolyl Phosphate; 30°C



the molar amount of a component (Q) was given by:

$$Q = K. \frac{A.F.}{M-m}$$

where K is a constant for a given set of detector conditions, M is the molecular weight of the compound and m is the molecular weight of the carrier gas. Since the experiments were concerned with relative amounts of the components of the mixtures there was no need to evaluate K.

In the New Apparatus, since column conditions were more closely defined than those of the First Apparatus, simple retention distances were generally sufficient to identify all components except those causing multiple 'peaks', however, as a check, relative retention times were used as there was always at least one obviously identifiable 'peak'. The values were based on the Specific Retention Volumes (Vg) which were previously determined (see Section 2.72). The retention of the more common low-boiling products of the gold chloride reaction on silicon and germanium alkyls are shown, expressed as log.(Vg), in Fig.25. These values clearly show the relative attraction of the more polar phase, tritolyl phosphate, compared to Silicone 702, for hydrogen of a protonic nature in the descending order HCl, H-CCl_3, H-CCl_2, H-CCl etc., where CCl_4, C_2Cl_4 and CCl_3-CH_3 are practically unaffected. In addition it may be seen that despite the lower attraction of tritolyl phosphate for the silicon and germanium tetra-alkyls and tetrachlorides, it has a high affinity for the more 'salt-like' methyl germanium chlorides.

It can be seen from Fig.25 that certain limitations, owing to the difficulties of separation of potential multiple peaks (i.e. where the log.(Vg) values of two compounds differ by less than 0.06 at the centre

or to the right of Fig.25, increasing to 0.2 at the left), were imposed on the analyses that could be satisfactorily carried out: Methyl chloride and chlorine were practically coincident on both columns. Thus for accurate methyl analysis conditions had to be either sufficiently mild so that no detectable amounts of chlorine were evolved, which could be checked by carrying out a blank run, or alternatively the conditions had to be sufficiently rigorous for the conversion of all detached methyl groups to higher chlorides than MeCL. This was assumed to have occurred if CCl_4 and $CHCl_3$ were present together with only a small amount, if any, of CH_2Cl_2. For ethyl analysis this problem was not nearly so critical, as ethyl chloride was sufficiently well separated from chlorine, that only in the presence of a large amount of chlorine would overlap be likely. As these conditions were sufficiently rigorous to chlorinate ethyl chloride, the problem did not arise.

Analysis of hydrogen as HCl was difficult on Silicone 702 columns except under moderate conditions (under mild conditions no HCl would be formed), when the above difficulties with methyl chloride occurred. Under severe conditions, where a lot of HCl was formed, overlap with the large chlorine peak took place to a certain extent, making it more difficult to estimate the area (see Fig.28 Section 4.13). Fortunately, HCl was greatly retarded on tritolyl phosphate and, despite considerable 'tailing' of the peak, was measurable except in the presence of ethylidene dichloride, $SiCl_4$ and $SiMe_3Cl$ with which it overlapped and which would have to be measured on the other column.

The greatest difficulty in these analyses was the estimation of

$GeCl_4$, as it coincided almost exactly with $CHCl_3$ on Silicone 702, and overlapped to a large extent with CH_2Cl_2 on tritolyl phosphate. As both of these carbon compounds were usually significant products under conditions where $GeCl_4$ was formed, the relative amounts of the three could only be estimated by approximate simultaneous equations based on similar runs on both columns.

All other peaks that were multiple on one column could be resolved on the other.

With the heating up procedure for analysing the higher-boiling compounds, standard retention data could not be used. However, as the compounds were (for the most part) well separated, a system of 'relative chart distances' from the heat-up point was fairly reliable.

In conclusion, from the chromatographic interpretation standpoint, it seemed best, when working with methyls of silicon and germanium, to either use very mild gold chloride cell conditions (30 - 60°C) or very severe conditions (180 - 200°C). As will be seen, these requirements fitted very well with other desirable operational features; amongst them, the fact that fewer products were formed under mild or severe conditions than under moderate conditions.

2.7 Experimental Chromatographic Measurements and Calculations

This section covers all the routine chromatographic measurements made in this work. Unless stated otherwise, all measurements mentioned later in the text were made using these methods.

2.71 Measurement of Retention Distances

All chromatographic measurements, with the exception of efficiencies, are usually made from the point at which the portion of carrier gas that carried the sample onto the column passes through the detector. This point corresponds to the emergence of a sample that had no interaction whatsoever with the column, and is thus a logical starting point. The point, in time or distance on a moving chart is usually referred to as the 'Air Peak'. An approximation to this is the best that can be achieved in practice, as all compounds are absorbed to a certain extent. In this work, all injections were effected by rapid evaporation from a trap, originally cooled by liquid oxygen or nitrogen. Thus the compound selected for indicating the air peak position had to be condensible and yet as inactive with the column as possible. The first peak obtained from the condensible components of coal gas (hydrogen and carbon monoxide passed straight through) was usually employed. The time or distance, measured from injection, of this peak was found to be effectively constant in each system provided the injection technique and flowrate was standardised ($\pm$ 1 second; $\pm$ $\frac{1}{3}$ mm. at 48"/hr.). Once these values were found, only rarely was an air peak marker added to the sample to be injected. The chromatograms usually were measured from the expected air peak position, the injection point being marked electrically.

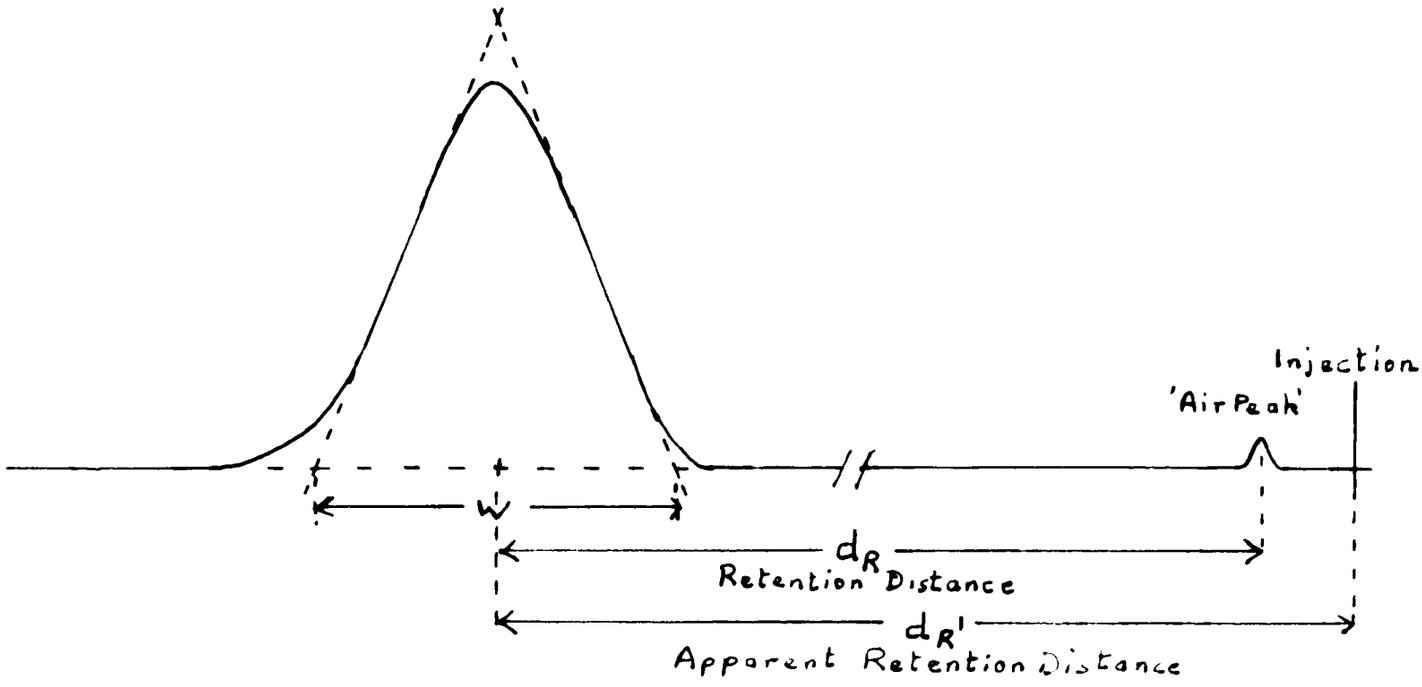
Retention values are usually measured as 'Retention Distances' on a recorder chart (d_R), which are related to 'Retention Times' (t_r) thus:

$$t_r = \frac{d_R}{c}$$

where c is the chart speed expressed in the same units of time and length.

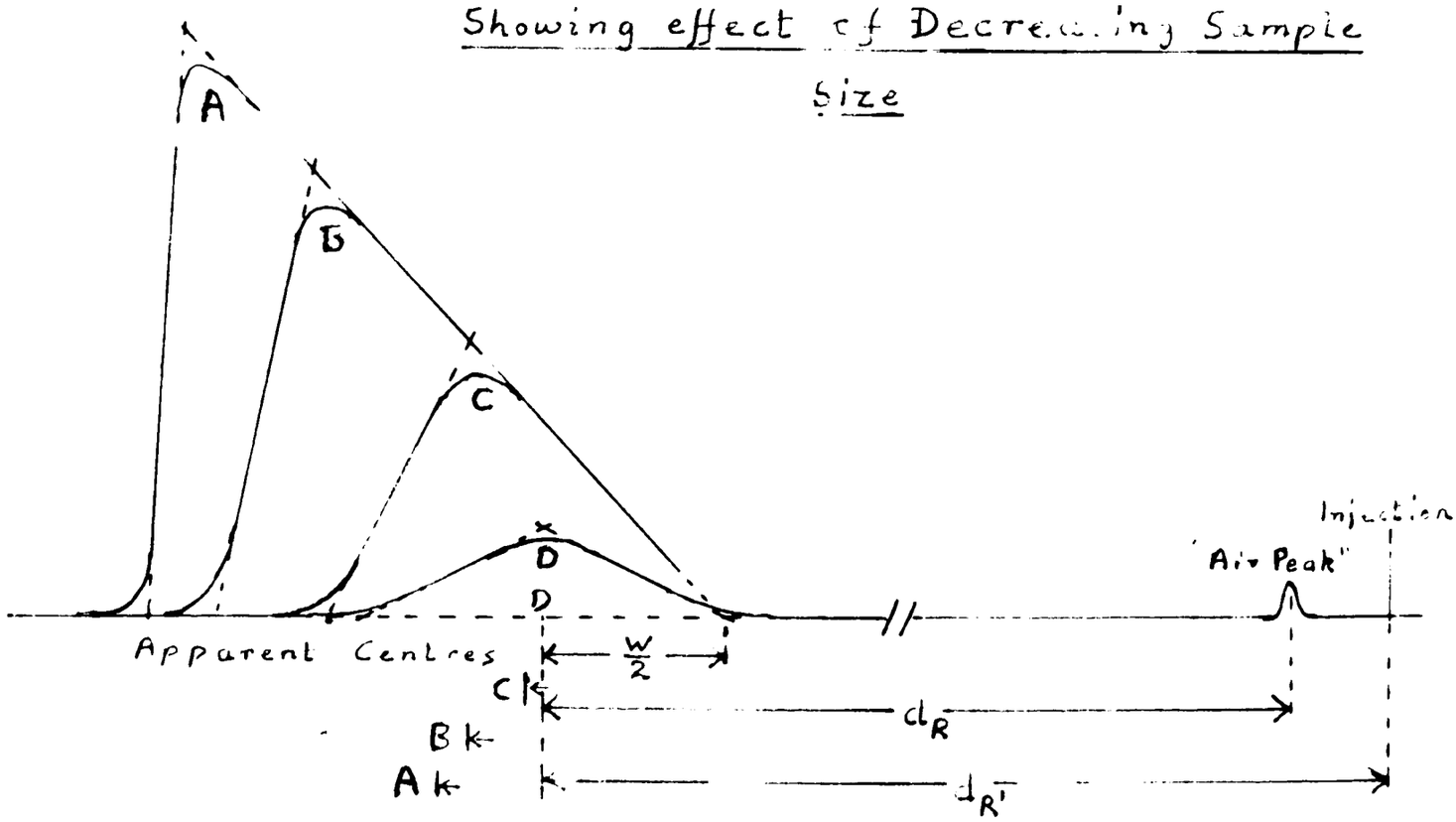
FIG. 26 Measurement of Retention Distances

A/ Symmetric Peaks



B/ Asymmetric Peaks

Showing effect of Decreasing Sample Size



In turn, these values are related to 'Retention Volumes'(V_R) thus:

$$V_R = t_r.F = \frac{d_R.F}{c}$$

where F is the flowrate expressed in the same units of time and volume.

Retention distances were measured from the air peak to the centre of symmetrical or effectively symmetrical peaks. The centre was found by bisecting the distance on the baseline between the tangents to the sides of the peaks (see Fig. 26A) rather than measuring to the peak maxima, since the relatively large volume of the density detector caused a slight delay of the maxima. Certain compounds, notably the methyl silicon and germanium chlorides, gave asymmetric peaks, particularly when present in large amounts. These peaks, characteristically, had a gradually increasing leading edge with a sharp trailing edge. Such peaks were due to the compounds concerned having higher heats of evaporation than heats of solution in the stationary phase (see Section 1.11). At small concentrations of these compounds the peaks tended to be more symmetrical (see Fig. 26B) and thus their retention distances could be measured in the normal way, but at higher concentrations such a treatment would give high retention values. The true retention distances of the asymmetric peaks could only be measured with any accuracy if the column efficiency was known.

Column efficiency is measured in 'Theoretical Plates' which may be calculated, for symmetrical peaks, in terms of the 'Apparent Retention Distance' ($d_{R'}$) measured from the injection point to the centre of the peak (see Fig.26), and the peak width, measured between the tangents on the baseline (w). The number of theoretical plates (P) is given by[5]:

$$P = 16\left(\frac{d_{R'}}{w}\right)^2.$$

Typically, on a given column, the value of P increases with retention distance with similar compounds (e.g. members of a homologous series) and it decreases slightly with increased sample size. The values of P vary somewhat with the physico-chemical nature of compounds of different series.

Since, in the absence of other effects, the value of P for compounds that lead to asymmetrical peaks should be similar to the values for compounds that give symmetrical peaks near them in the chromatograms, the theoretical half width of the peaks, measured from the front tangents (see Fig. 26), can be estimated from the approximate apparent retention distances, giving 'theoretical mid points' suitable for obtaining their retention distances. By this method it is estimated that the maximum error would be of the order of 1 - 2% (i.e. less than 0.01 log. units.).

2.72 Specific Retention Volumes (Vg)

To eliminate experimental chromatographic variables, such as weight of stationary phase, flow rate, pressures, dead volumes etc., Littlewood, Phillips and Price[10] suggested the concept of the 'Specific Retention Volume' (Vg) of a compound on a given stationary phase as a means of describing the retention characteristics of compounds on chromatographic columns and to assist in column design (e.g. stationary phase loading and operating temperatures). As it can be shown that such a function as Vg is a thermodynamic function, related to the partition coefficient of the solute between the stationary phase and gas phase, values of Vg at different temperatures can be used for calculating heats of solution and other functions.

Experimentally, a chromatograph can operate at varying temperatures, the column has a pressure drop across it, the outlet pressure can differ from atmospheric pressure, and the flowrate is usually measured with a bubble flowmeter at atmospheric temperature and pressure, whilst saturating the carrier with water vapour.

Littlewood et al.[10] defined the specific retention volume as the volume of gas, measured at 0°C, which passes through an 'ideal' column (i.e. with no compressibility effects), containing one gram of stationary phase, whilst the compound is traversing the column, with the equivalent value for an unabsorbed compound subtracted.

James and Martin[5] gave an expression for the correction of the flowrate, measured at the column outlet (F^o), at the outlet pressure (Po), to the average flowrate through the column (F'), in terms of Po and the column inlet pressure (Pi):

$$F' = F^o . \frac{3\left[\left(\frac{Pi}{Po}\right)^2 - 1\right]}{2\left[\left(\frac{Pi}{Po}\right)^3 - 1\right]} = F^o . f$$

(Tabulated values of f were used in this work[113f]).

Thus, for a column containing w gm. of stationary phase, the average volume of gas passing through the column per unit weight of stationary phase, during passage of a compound of retention distance d_R, measured on a chart, with a chart speed c, is given by:

$$\frac{F^o . f . d_R}{w . c} = Vg \text{ (by definition if } F^o \text{ is measured at } 0^oC)$$

In practice, the flowrate is not measured at the column outlet, but at the outlet of the apparatus, at atmospheric temperature (T^oK)

and pressure (Pa). If it is measured with a soap bubble flowmeter, the carrier gas will become saturated with water vapour, and, if dilute soap solutions are used, at the saturated vapour pressure of water (Pw) at room temperature. If F is the measured flowrate then:

$$F^{o} = F. \frac{Pa - Pw}{Pa} \cdot \frac{Pa}{Po} \cdot \frac{273}{T}$$

thus:

$$Vg = \frac{F \cdot f \cdot d_R}{w \cdot c} \cdot \frac{273(Pa - Pw)}{T \cdot Po}$$

In a given chromatogram, provided operating conditions remain unchanged, Vg values are proportional to retention distances. Thus if the Vg value for one compound is already known, the Vg values of other compounds in the chromatogram may be calculated.

2.73 Thermodynamics of Vg - Calculation of Heats of Solution

In an 'ideal' chromatographic column containing 1 gm. of stationary phase of density ρ, the volume of stationary phase (Vs), will be numerically equal to $\frac{1}{\rho}$. Part of the column will be occupied by the carrier gas of volume Vc.

Considering a small sample of solute so that Henry's Law is obeyed, the solute will be distributed between the gas and liquid phases according to the partition coefficient, K:

$$K = \frac{Ns/Vs}{Nc/Vc} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where Ns, Nc are the molar quantities of the solute respectively in the stationary (liquid) phase and carrier gas. Since this represents a

state of dynamic equilibrium, the average proportion of the time spent by the sample in the gas phase is $\frac{Nc}{Ns + Nc}$. Thus the average volume of gas required to transfer a sample from one end of the column to the other (the apparent retention volume, $V_{R'}$) is:

$$V_{R'} = Vc. \frac{Ns + Nc}{Nc} = Vc.(K \frac{Vs}{Vc} + 1)$$

For a sample that does not dissolve in the stationary phase, K = 0, therefore its apparent retention volume is equal to Vc. This corresponds to the conditions for the air peak. Thus the true retention volume for any solute is given by:

$$V_R = V_{R'} - Vc = K.Vs.$$

V_R as defined above is measured at the column temperature, T^oK. Since the definition of the column is that also used for defining Vg, correction of V_R to 0^oC will give Vg thus:

$$Vg = V_R . \frac{273}{T} = K. Vs. \frac{273}{T} = K. \frac{273}{\rho . T} \quad \ldots\ldots\ldots (2)$$

The partial pressure, p, of the solute in the gas phase is given by:

$$p = \frac{Nc}{Vc} RT$$

and Henry's Law may be written as:

$$\frac{Ns}{Vs} = k.p \quad \therefore \quad \frac{Ns}{Vs} = k. \frac{Nc}{Vc} RT .$$

Therefore substituting in (1)

$$K = k. RT$$

and substituting in (2)

$$Vg = k. \frac{273\ R}{\rho} .$$

As ρ can be considered to be effectively constant

$$Vg = k.\ C \quad \text{where C is a constant.}$$

The Van 't Hoff isochore may be given as:

$$\frac{d\ \ln.k}{dT} = \frac{\Delta Hs}{RT^2}$$

where ΔHs is the differential heat of solution, which differs from the heat of evaporation of the solute by the heat of mixing of solute and stationary phase. This equation may therefore be rewritten as:

$$\frac{d\ \ln.Vg}{dT} = \frac{\Delta Hs}{RT^2}$$

or on integration and change of logarithm base

$$\log.Vg' - \log.Vg'' = -\frac{\Delta Hs}{2.303\ R} \cdot \left(\frac{1}{T'} - \frac{1}{T''}\right)$$

Thus if two or more values of Vg at different temperatures are known, the heat of solution of the compound in the stationary phase may be determined.

2.74 Peak Area Measurement

For the quantitative measurements on products of the gold chloride reaction and products from the reactions carried out in stainless steel bombs, it was merely necessary to measure the relative peak areas for calculation of the relative amounts of the components. Two methods of peak area measurement were employed: The areas between the trace and baseline were cut out by razor blade and weighed. As the weights of the more significant peaks were in the range 30 - 200 mg., the limits of the method were the cutting our procedure itself, and variations in

the weight per unit area of the paper. Tests on rectangles showed that the weight of the paper usually varied by less than 2% under similar conditions of humidity. The cutting error on the large and fairly wide peaks was estimated at around 1%, with larger errors in the smaller (but less significant) peaks. Comparison between this method and the second; triangulation of peaks, showed errors only within these limits (see Table 2), as long as the peaks were not too different in basic shape. Since this second method was quicker and simpler, and enabled the traces to be preserved, it was usually employed. In the triangulation method, the area of the triangle formed by the two tangents and the baseline (see Fig. 26) was calculated from direct measurements. Although the areas of these triangles were smaller than the actual peak areas, they were proportional to them as long as the peaks had the same degree of 'tailing' etc..

Table 2

Comparison of the weighing and triangulation methods of obtaining peak areas (gold chloride reaction on Ge_3Me_8 areas referred to $GeMe_3Cl = 100$)

	MeCl	$GeMe_3Cl$	$GeMe_2Cl_2$
Areas by triangulation	8.4	100	72.2
Areas by weighing	8.(0)	100	70.6

2.75 Accuracy of Quantitative Measurements

Since the non-linearity of the density detector in the concentration range employed for all the analyses was less than +1% at 50% of any given concentration, it is seen that, apart from grease absorption effects, which were minimised in the New Apparatus, the limits of accuracy

of the measurements were imposed by the estimation of peak areas. In the measurement of any large (and significant) peak, the maximum error was estimated at around 2½%, making the maximum error in comparing two peaks 5%. Thus in the complete conversion of $SiMe_4$ to $SiCl_4$ and CCl_4 the maximum expected error would be 5% in the Si:C ratio. However in certain analyses the error in the calculated ratios would be lower, for instance in the analysis shown in Table 2 where the carbon:germanium ratio was required. In this case a 5% error in the MeCl : $GeMe_3Cl$: $GeMe_2Cl_2$ ratios would result in less than 0.5% error in the Ge : C ratio. If there were more than two major peaks the resultant error would be expected to be lower as each one would be measured within 2½% of its value. As a consequence the majority of the analyses in this work were expected to be correct within 3%, and any variations greater than this were presumed to require explanation.

2.76 Sensitivity of the Analytical System - Units used in this Work

The basic sensitivity of the analytical system of the New Apparatus was measured by injection of known quantities of benzene under the standard operating conditions. If it is assumed that, in the absence of detectable 'noise', the minimum detectable signal was ½% of full scale deflection on a 12" scale 1 mV Honeywell Brown recorder, then the minimum detectable concentration of benzene at maximum sensitivity on the basic bridge circuit (signal attenuation factor 2) was approximately 3×10^{-10} moles/ml.. This represents a density change of 1.5×10^{-3} gm./ml.. These figures would be halved if the total signal was employed (see Fig.16 Section 2.45).

The smallest peak that could be measured within 5% would have an area of about 50 mm.^{2}. This corresponds to a sample weight of about 1μg. Thus gold chloride analyses would be feasible in the 5 - 10 μg. range, apart from the difficulties experienced with hydrolysis of such small samples.

In the analyses tabulated in this work, quantities, if not expressed as percentages of mixtures, are quoted in 'molecular units' (M.U.). These units are the results obtained upon dividing the corrected peak areas by the differences in molecular weights of the samples and the carrier nitrogen. These units are proportional to the molar quantities of the components, but the proportionality constant would be expected to vary somewhat from experiment to experiment. At maximum sensitivity, 25 M.U. approximately corresponded to 1 micromole (μM). Thus at 0.200 sensitivity, 5 M.U. corresponded to 1 μM etc..

PART II

THE CHEMISTRY OF SOME SILICON AND GERMANIUM COMPOUNDS

In the interests of simplicity, compounds and their chromatographic peaks have been named from the start according to their most probable identities. The evidence for these identities is given in the appropriate sections e.g.:

The methyl germanium chlorides . . . . . Section 4.21

The chloromethyl methyl germanium chlorides . Section 4.21 and Appendix 3.1

The permethyl silanes and permethyl germanes. Sections 5.42, 5.43

The permethyl silico-germanes . . . . . Sections 6.4 - 6.9

CHAPTER THREE

PREPARATION OF THE METHYL GERMANIUM CHLORIDES

3.1 Introduction

It was necessary to prepare $GeMe_3Cl$ and $GeMe_2Cl_2$ as reactants for the proposed preparations of the permethyl germanes and the permethyl silico-germanes (see Sections 5.41 and 6.2). In addition, these compounds were required for identification of products of the gold chloride reaction and were used as parent compounds in the development of this technique (Section 4.21).

Two methods, both modifications of standard preparative procedures, were employed for the production of these compounds: The first of these methods was the 'Rearrangement Reaction' of $GeMe_4$ with $GeCl_4$. This had previously been carried out, with limited success, in sealed glass tubes, in the presence of about 7% (Molar) of $AlCl_3$ at 200°C[97]. With conventional distillation working up procedures, it was not possible to separate $GeMe_2Cl_2$ and $GeMeCl_3$. These methods had however been used with success with the higher germanium tetraalkyls[94-97], and it was felt that the use of stainless steel bombs would permit higher reaction temperatures to be used with a consequent improvement in the reaction rate of $GeMe_4$. Distillation could be used to extract the reaction mixtures if necessary, and chromatography could be used for quantitative analysis of the products and separation of samples.

The second preparative method was the 'Direct Reaction' of methyl chloride with germanium in the presence of copper[101]. It was decided, partly on account of the small quantity of MeCl available at the time,

to attempt the preparation in a stainless steel bomb rather than in a stream process.

3.2 The Rearrangement Reaction of $GeMe_4$ with $GeCl_4$

3.21 Preliminary Reactions in Stainless Steel Bombs

(Paragraph numbers pertain to the run numbers in Table 3).

1/ In the rearrangement reaction it was considered that if aluminium halides or alkyl aluminium halides[94] were genuinely catalytic, much smaller amounts than the 7% quoted in the literature[97] should suffice for reaction. As the reaction:

$$4\ Al + 3\ GeCl_4 = 4\ AlCl_3 + 3\ Ge$$

was obviously thermodynamically feasible it was decided to attempt to form traces of aluminium trichloride in situ by adding a few grains of aluminium powder to the reaction mixture. In the first reaction, only a total of 9.2% of the starting compounds had reacted at 200°C for 22 hours. Continued heating of this mixture for 69 hours at 250°C only resulted in 39% of reaction (1B).

2/ As higher yields than 1B at similar temperatures and a shorter reaction time had been reported[97], it was concluded that not much, if any, $AlCl_3$ had been formed. As this could have been due to the surface oxide layer on the aluminium, it was decided to add some mercury as well to the next reaction mixture in an attempt to break it down. With this as catalyst, virtually 100% reaction occurred at 250°C.

3/ This last experiment was repeated at 200°C, but less than 20%

Table 3

Rearrangement Reactions of $GeMe_4$ with $GeCl_4$, Carried out in Stainless Steel Bombs

Results Expressed in Molar Percentages

Reaction Conditions				Starting Compds.		Products Extracted					
Run	Catalyst	Temp. °C.	Time Hrs.	Approx. $GeMe_4$ %	Reaction Extent %	$GeMe_4$	$GeCl_4$	$GeMe_3Cl$	$GeMe_2Cl_2$	$GeMeCl_3$	Total Methyl %
1A	Aluminium	200	22	71	9.2	61.5	29.3	7.8	0.1	1.3	68
1B	(Continued)	250	69	68	39.1	42.4	18.5	26.9	1.3	10.9	64
2	Al/Hg	250	24	71	99.7	0.3		81.6	18.1	tr	70
3	Al/Hg	200	22	78	17.5	60.9	21.6	13.1	0.2	4.2	72
4	Al/Hg?	250	22	78	7.6	69.0	23.4	6.0	tr	1.6	74
5	Hg/Al?	230	65	65	72.0	24.6	3.6	40.2	5.9	25.6	64
6	Hg/Al?	250	23	81	20.9	66.9	12.2	13.5	0.1	7.3	79
7A	Mercury	250	20	50	61.9	16.9	21.2	32.9	2.6	26.4	50
7B	(Continued)	250	25	50	93.7	0.5	5.8	49.4	5.3	39.0	50
8A	None	250	21	49	10.9	43.1	46.0	5.2	tr	5.7	48
8B	(Contd.)+Hg	250	22	48	21.4	34.9	43.7	14.4	tr	7.0	47

reaction took place.

4/ It was decided to see if a mere trace of mercury on the surface of aluminium would lead to the production of a suitable catalyst. Accordingly, some aluminium powder was shaken up with mercury in an attempt to obtain some surface 'wetting'. The mercury was then decanted off. A sample of the aluminium so obtained was added to a reaction mixture, but the yields were the lowest obtained in the series of reactions.

5/ In an attempt to find out more about this last, rather surprising, result, some of the decanted mercury, which may have contained some dissolved aluminium, was added to a reaction mixture. A reasonably high yield of products was obtained under conditions effectively only slightly different from those of the previous run.

6/ On repeating this last experiment under conditions similar to run 4, only moderate yields of the products were obtained.

7/ In view of the rather conflicting results so far obtained, it was decided to see if mercury itself had any effect. Under conditions similar to runs 2, 4 and 6, a high yield was obtained and on resealing the bomb and continuing the reaction for a similar spell this was further improved (7B).

Since only small amounts of catalytic materials had so far been used, it was realised that these could be extremely prone to poisoning or promotion by minute traces of other materials such as oxygen or HCl. In addition, it was by no means certain that every last trace of the previous catalyst was removed by the cleaning procedure for the bombs, and the effects of the stainless steel, or the copper sealing ring were unknown. Accordingly one of the bombs was cleaned by a succession of

the strong acids, followed by various organic solvents, all residues being removed by wiping, and was finally baked.

8/ A reaction mixture, without catalyst was sealed up in this specially cleaned bomb and, under conditions similar to runs 2, 4, 6 and 7A, it was found that almost 11% reaction occurred, which was more than run 4. The addition of 'Analar' mercury to the products and continuation of the reaction under similar conditions had little effect, as the overall reaction was only 21%.

It was concluded that a mercury compound, possibly a chloride, could have been the active agent in run 7 and possibly in runs 5 and 6, but that it was not formed under the reaction conditions in the normal course of events (run 8B). As the reaction took place, to a certain extent, in the bomb without an added catalyst, it was decided to carry out the reactions in the absence of stainless steel by attempting to use sealed glass tubes.

3.22 Reactions in Miniature Carius Tubes

(Paragraph Numbers refer to Run Numbers in Table 4).

There was a strong possibility that ordinary sealed glass tubes would explode under the pressures of the rearrangement reactions and accordingly the miniature carius tubes, with a total usable capacity of about 0.2 ml., were developed (see Section 2.51). One prototype tube failed, probably due to insufficient annealing, but seven subsequent tubes, heated as a single batch so that they experienced identical external conditions, all survived.

9, 10/ Two 'blank reactions', with nothing added to the reaction

TABLE 4

Rearrangement Reactions of $GeMe_4$ with $GeCl_4$, Carried Out in Miniature Carius Tubes

Results Expressed in Molar Percentages.

Reaction Conditions				Starting Compds.		Reaction Products					
Run	Catalyst	Temp. °C.	Time Hrs.	Approx. $GeMe_4$ %	Reaction %	$GeMe_4$	$GeCl_4$	$GeMe_3Cl$	$GeMe_2Cl_2$	$GeMeCl_3$	Total Methyl %
9	None	250	24	49	9.3	36.2	54.5	9.0	tr	0.3	43
10	None	250	24	49	7.8	39.1	53.1	7.6	tr	0.2	45
11	Mercury	250	24	49	8.7	36.8	54.5	7.2	tr	1.5	43
12	Mercury	250	24	49	9.4	40.4	50.2	7.4	0.1	1.9	47
13	Aluminium	250	24	49	5.0	38.6	56.4	4.9		0.1	42
14	Al/Hgexcess	250	24	49	High	95	5	?	?	?	95?
15	Calomel	250	24	49	89.8	0.3	9.9	59.4	1.6	28.8	52

mixtures, were carried out. A brown deposit gradually appeared on the glass surface in contact with the liquid, and the liquid itself became slightly tinted. This was believed to be due to thermal decomposition to germanium. On opening the tubes after cooling, a small quantity of gas, which appeared to be inflammable, was liberated. Analysis of the products showed that some rearrangement had taken place in both tubes in yields only slightly less than run 8A but with a different product ratio. Thus the reaction was either autocatalytic (as are the equivalent reactions of lead[92]) or catalysed by the liberated germanium metal (cf.[97]).

11, 12/ Two reactions were carried out in the presence of mercury, run 12 containing a larger amount. In this case it is seen that the degrees of reaction were almost the same as run 9, but the product ratios were different. No marked colouration occurred and it is possible that any germanium liberated was dissolved in the mercury.

13/ A reaction was attempted in the presence of aluminium powder. In this case the products showed a marked inhibition of the reaction observed in the 'blank' runs, 9 and 10, but a similar product ratio.

14/ A reaction was carried out in the presence of relatively large quantities of mercury and aluminium. This clearly showed that formation of aluminium trichloride and/or alkyl aluminium chlorides could take place under these conditions: The mixture in the tube became dark and viscous and ultimately 'set' on cooling. Accordingly it was attempted to vacuum distil the products from the tube. On opening the tube a lot of inflammable gas was evolved and on distillation a few drops of liquid, shown to be principally $GeMe_4$, were obtained,

and some white needles sublimed just outside the tube. These needles fumed in moist air and were thought to consist mainly of $AlCl_3$. The residues in the tube appeared to be principally mercury.

15/ Some mercurous chloride was added to the reaction mixture in one of the tubes and the mixture, on heating, gradually became dark and viscous and also set on cooling. The products had to be distilled and it was found that a high degree of reaction had occurred.

A nett loss of methyl groups seemed to occur in almost every reaction unless a considerable amount of chlorine groups were abstracted to form the catalyst (see run 14). The methyl groups were presumably converted to hydrocarbons, possibly mainly ethane, which were liberated on opening the bombs or tubes.

3.23 Product Ratios, Kinetics and Catalysis

In the original work on the Rearrangement Reaction of $GeBu^n_4$ with $GeCl_4$[94-97], the following reactions were presumed to have taken place:

($R = Bu^n$)

$$GeR_4 + GeCl_4 = GeR_3Cl + GeRCl_3 \quad \text{(slow)} \quad \ldots\ldots (a)$$

$$GeR_4 + GeRCl_3 = GeR_3Cl + GeR_2Cl_2 \quad \text{(faster)} \quad \ldots\ldots (b)$$

$$GeR_4 + GeR_2Cl_2 = 2\,GeR_3Cl \quad \text{(fast)} \quad \ldots\ldots (c)$$

as neither GeR_2Cl_2 nor $GeRCl_3$ could be isolated as long as there was some GeR_4 remaining in the mixture. In addition such reactions as:

$$GeR_3Cl + GeCl_4 = GeR_2Cl_2 + GeRCl_3 \quad \ldots\ldots (d)$$

$$GeR_3Cl + GeRCl_3 = 2\,GeR_2Cl_2 \quad \ldots\ldots\ldots\ldots (e)$$

and

$$GeR_2Cl_2 + GeCl_4 = 2\,GeRCl_3 \quad \ldots\ldots\ldots\ldots (f)$$

were shown to be slower still[97], but with (e) faster than (d) and with (f)

as a slow and incomplete reaction, due to an equilibrium. Thus it was deduced that the reactivities as alkylating agents were; GeR_4 > GeR_3Cl > GeR_2Cl_2, and as chlorinating agents; GeR_2Cl_2 > $GeRCl_3$ > $GeCl_4$.

It can be seen from Tables 3 and 4 that this was not necessarily the case in this work. In most reactions appreciable amounts of $GeMeCl_3$ and, in some cases, $GeMe_2Cl_2$ were present together with $GeMe_4$ in the reaction products. In these runs it may be deduced that, compared to the reactions of $GeBu^n_4$ described above, the rates of reactions type (b) and (c) were retarded relative to type (a), or possibly reaction types (d), (e) and (f) were accelerated relative to type (a). As few of the experiments approached complete reaction, it was difficult to assess which of these possibilities was most likely, except that the low yields of $GeMe_2Cl_2$ were either consistent with reaction types (b), (d) and (e) being relatively slow compared to (a), and/or (c) and (f) being relatively fast.. Thus the most likely solution was that (b) remained slower than (c) and both were reduced in rate relative to (a).

It is seen that the effects of the various added substances were different both as regards product ratios and extent of reaction. Various trends were noticeable in the light of the previous discussion.

1/ The basic reaction carried out in glass without additives, which was either auto-catalytic or catalysed by germanium, was similar, but slower, compared with the $AlCl_3$-catalysed reaction of the literature, but with a slight retardation of (b) and (c) relative to (a).

2/ In the stainless steel bombs, relative to the above reactions, there was a slight acceleration of (a) but a considerable retardation of (b) and

(c).. There might even have been a slight acceleration of (d) and (f)..

These basic trends were modified by the addition of aluminium and mercury metals as follows:

3/ Aluminium, which could lead to a general inhibition, followed a similar trend to (1) and could reduce the effect of stainless steel.

4/ Mercury reduced the rate of (b) and (c) relative to (a) but not to the same extent as stainless steel.

5/ The presence of the chlorides of aluminium or mercury had a considerable general accelerating effect, while showing the same trends as the metals themselves.

3.24 Preparative Rearrangement Reactions

It was decided, despite the excellent yield obtained with $AlCl_3$, presumably on its own, in reaction (2) (see Table 3), to try a mixture of calomel and aluminium powder as a source of catalyst for all subsequent reactions, as this should yield a mixture of aluminium chloride and the mercury-containing catalysts.

The first preparative reaction attempted with this mixture was an attempt at the production of substantially pure $GeMe_3Cl$. This was only moderately successful (Run 16, Table 5) as there was inhibition of the reactions types (b) and (c), probably due to an excess of calomel.

The same catalytic mixture, but with a reduced calomel content, was used in an attempt to improve on the percentage of $GeMe_2Cl_2$ in the products of the direct reaction (see next Section), by addition of sufficient $GeMe_4$ to make up the methyl group deficiency, followed by rearrangement. The rearrangement reaction was then repeated on the products, after

distillation and analysis, with a fresh charge of catalyst. These runs are shown as Runs 17 and 18 in Table 5.

Table 5

Preparative Rearrangement Reactions Using Al/Hg_2Cl_2 as Catalyst: Results in Molar %, All reactions at 270°C.

Run	16		17		18	
Reaction Time	40 Hours		23 Hours		94 Hours	
	Reactants	Products	Reactants	Products	Reactants	Products
$GeMe_4$	76	14.2	12.2	-	-	-
$GeMe_3Cl$		73.4	4.5	19.7	19.7	18.8
$GeMe_2Cl_2$		11.0	65.4	67.6	67.6	69.3
$GeMeCl_3$		1.3	17.9	12.7	12.7	11.9
$GeCl_4$	24	-	-	-	-	-
% Methyl	76	75	53	52	52	52

It would seem that in runs 17 and 18 an equilibrium was being reached with the equilibrium constant, K, apparently being 18.3 in Run 17 and 21.4 in Run 18, where

$$K = \frac{[GeMe_2Cl_2]^2}{[GeMe_3Cl][GeMeCl_3]}$$

2.3 The 'Direct Reaction'

The 'Direct Reaction' offered an alternative method for the preparation of $GeMe_2Cl_2$. The original continuous stream method yielded about 10 parts of $GeMe_2Cl_2$ to one of $GeMeCl_3$ and a trace of $GeMe_3Cl$[101]. For this reaction the ratio of germanium to copper of the original reaction was chosen (4 : 1), as higher proportions of copper had been shown to give increased yields of $GeMeCl_3$[105]. A fourfold excess of germanium over the calculated amount was provided to prevent the Ge:Cu ratio from getting

too low.

The germanium was powdered to pass through a 44 mesh and a sample of 'pulverised' copper, freshly reduced in hydrogen, was mixed with it and then put in the bomb. Methyl chloride was then distilled into the bomb which was sealed and heated to 360°C for 22 hours. The bomb was cooled in liquid nitrogen, opened and fitted with a shallow blow-off through mercury. On warming up to -30°C, about 300 ml. of an inflammable gas were evolved. Further warming to room temperature led to no evolution of methyl chloride, indicating that reaction was complete. The products were distilled out and were found to have the composition: 74.5% $GeMe_2Cl_2$, 20.4% $GeMeCl_3$, and 5.1% $GeMe_3Cl$. Examination of the residues in the bomb showed no trace of exposed copper, but a fine black deposit, presumably germanium, over everything. In view of the presumed catalytic activity of germanium, or auto-catalysis in the rearrangement reaction, and the high reaction temperature employed, it was likely that these products represented equilibrium quantities, in which case the equilibrium constant K (in the previous Section) would have a value at 360°C of 53.3.

An additional effect of the long reaction time was the rather larger loss of methyl groups (7.5%) than that in the original preparation (4%).

3.4 Conclusions on the Preparative Methods

The establishment of equilibria in the rearrangement reactions of the tetramethyls and tetrachlorides is a general feature in the case of silicon[32,119] and tin[120]. These equilibria are generally in favour of the single compound rather than the two flanking members of the series and

this is accentuated by high pressures[34]. It is obvious that a similar effect is obtained with germanium as the presumed equilibrium constant for the formation of $GeMe_2Cl_2$ was found to be about 53 at 360°C but only about 21 at 270°C, both in closed systems. Similar effects had been observed in the rearrangement reactions of the higher germanium tetraalkyls, particularly in the attempted preparations of the alkyl germanium trichlorides[97]. Typically the equilibrium constant for the formation of $GeEtCl_3$ was 1.1 at 255°C and 1.7 at 280°C with reactions in sealed tubes.

Because of the existence of these equilibria the following conclusions can be drawn. $GeMe_2Cl_2$ can not be prepared at 270°C in a higher yield than 70% by the rearrangement reaction or in any reaction that results in similar conditions.

If preparation 2 may be considered to have reached equilibrium, then the equilibrium constant for the formation of $GeMe_3Cl$ would be approximately 1000 at 250°C and therefore this compound could be obtained in a yield of about 94%.

In the event, the lack of purity of these compounds was not critical for the preparations of the permethyl germanes and the permethyl silicogermanes, as apparently no branched chain compounds were produced from mixtures containing $GeMeCl_3$, and sometimes $GeMe_4$ was desirable as a marker compound. Small samples were satisfactorily purified in the preparative chromatograph for the experiments with the gold chloride reaction.

CHAPTER FOUR

DEVELOPMENT OF THE GOLD CHLORIDE ANALYTICAL TECHNIQUE

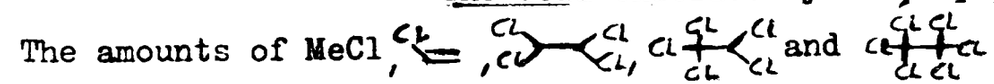
4.1 Experiments with the First Apparatus

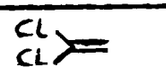
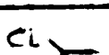
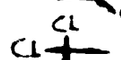
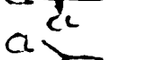
It was realised, that, when the gold chloride reaction[29-31] was applied to the alkyls of silicon and germanium, there was a much wider range of potential products than in the case of the hydrides. It was also expected that fission of Si-C and Ge-C bonds would require more rigorous conditions. The initial experiments described here were intended to find out what conditions were required for satisfactory analysis of the tetraalkyls of silicon and germanium, with the original intention of achieving complete chlorination to HCl, CCl_4 and $SiCl_4$ or $GeCl_4$. It was soon found that even under the most rigorous conditions attempted, other carbon-containing compounds were present among the products. Accordingly, samples of all the likely products had to be procured for identification purposes. The preliminary experiments were conducted without the benefit of identification, and it was subsequently found that the chromatograms had not been run for long enough for the observation of all of the possible products.

4.11 Preliminary Experiments on $SiEt_4$, EtCl and $SiMe_4$

The first set of experimental chlorinations of $SiEt_4$ were carried out with gold chloride at about 160°C and the gas reactor at about 280°C. (Such a reactor condition will henceforth be denoted thus: 160°/280°C).

TABLE 6 — Products of the Reaction of Ethyl Chloride in The Gold Chloride System, Expressed as Percentages of The Products Shown

N.B. The amounts of MeCl,  were not measured.

CELL CONDITIONS	140°/240°	160°/280°	180°/320°	190°/340°	200°/360°	210°/375°
COMPOUNDS						
CH_2Cl_2		1.2	tr			
$CHCl_3$		1.2	tr	tr		
CCl_4		7.8	tr	5.3	7.9	2.8
		0.1	20.4	53.5	72.2	28.6
			0.7	2.4	3.6	3.6
			0.7	2.2	4.8	3.6
			0.6	4.8	3.6	37.9
			tr	tr	6.5	12.9
	59.0	44.3	4.4	tr		0.4
	37.2	32.1	14.7	1.2		
	2.7	8.2	15.7	12.6		
	1.1	5.1	27.0	13.0		1.1
		?	15.7	15.8	1.4	9.3
Unidentified			~ 1 .5%	~ 1 .5%		

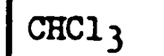
The chromatograms, run to the emergence of the parent peak, $SiEt_4$, showed either 13 or 14 product peaks and a reasonable amount of residual parent, indicating that the reaction was nowhere near completion. It was seen that the relative amounts of these products did not remain constant. The receipt of some samples of the ethyl silicon chlorides showed that the first chromatograms had not been run for long enough to observe all of them. Subsequent experiments showed that under reasonably mild conditions ($140^{\circ}/240^{\circ}C$) $SiEt_3Cl$ was the main silicon-containing product and, under the original conditions ($160^{\circ}/280^{\circ}C$), $SiEt_2Cl_2$ (see Table 7). In an attempt to discover which of the 10 remaining products did not contain silicon, ethyl chloride was reacted on the gold chloride system under a variety of conditions. These experiments (see Table 6) showed that, in fact, all of the products (with the possible exception of one), unaccounted for in the chlorination of $SiEt_4$, were chlorinated hydrocarbons, and that one of the chlorinated hydrocarbons was chromatographically coincident with $SiEtCl_3$. Subsequent identification of these compounds showed them to be derivatives of methane, ethane and ethylene, but also showed that the higher-boiling chloroethanes (sym-tetrachloroethane, pentachloroethane and hexachloroethane) had longer chromatographic retention distances than the extent to which the chromatograms had so far been run. The experiments with ethyl chloride showed that under mild conditions, progressive chlorination to ethane derivatives took place. Under more severe conditions some C-C fission occurred but this reaction was superceded, with increasing severity of the reaction, by the formation of ethylene derivatives, presumably either by elimination of Cl_2 or HCl from chloroethanes or by free radical action[121].

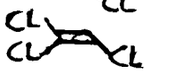
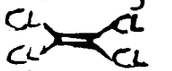
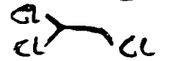
TABLE 7

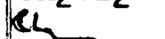
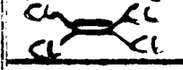
Some of the Preliminary Experiments with $SiEt_4$ & $SiMe_4$ on the Gold Chloride System: Quantitative

N.B. The higher chloroethanes were not observed and the later peaks could not be accurately measured.

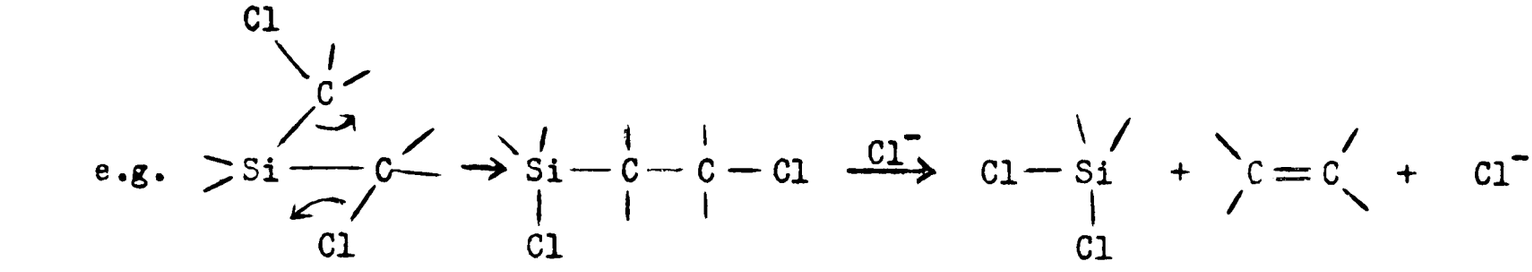
Quantities are expressed in "Molecular Units" (See Section 2.76)

Sample $SiEt_4$ Compound		Cell 140°/240° H	Si	C
HCl	38	38	-	-
EtCl	39	195	-	78
CH_2Cl_2	0.1	0.2	-	0.1
	0.7	2.8	-	1.4
$CHCl_3$	tr		-	
CCl_4	0.2	-	-	0.2
	9.1	36.4		18.2
$SiEt_2Cl_2$	3.0	30	3.0	12.0
$SiEt_3Cl$	25.4	381	25.4	152.6
TOTAL		683	28.4	263
RATIO		24.2: 1		: 9.2
ERROR		+21%		+15%

Sample $SiEt_4$ Compound		Cell 160°/280° H	Si	C
HCl	81	81	-	-
EtCl	18	90		36
	tr		-	
$SiCl_4$	0.9	-	0.9	-
	2.7	10.8	-	5.4
	tr		-	
$CHCl_3$	0.1	0.1	-	0.1
CCl_4	0.3	-	-	0.3
	26.0	104	-	52
	1	1	-	2
$SiEtCl_3$	2.5	12.5	2.5	5
	1.0	-	-	2.0
	0.4	1.2	-	0.8
$SiEt_2Cl_2$	7.5	75	7.5	30
$SiEt_3Cl$	4.0	60	4.0	24
TOTAL		436	14.9	158
RATIO		29.2:	1	:10.6
ERROR		+46%		+32%

Sample $SiMe_4$ Compound		Cell 225°/420° Si	C
HCl	Unmeasurable		
	1.3	-	2.6
$SiCl_4$	28.5	28.5	-
CH_2Cl_2	0.9	-	0.9
	0.9	-	1.8
$SiMeCl_3$	4.6	4.6	4.6
	0.9	-	1.8
$CHCl_3$	5.8	-	5.8
CCl_4	70.7	-	70.7
	5.7	-	11.4
	14.2	-	28.4
TOTAL		33.1	128.0
RATIO		1	: 3.87
ERROR			- 3%

In view of the likelihood of formation of the higher chloroethanes and the difficulty of measuring the areas of the wide and low peaks obtained from the ethyl silicon chlorides, some modification to the chromatography was clearly indicated before satisfactory analysis of ethyls could be carried out. On the other hand it was possible that the gold chloride reaction would yield lower-boiling products from $SiMe_4$. However, preliminary runs with $SiMe_4$ showed that the chloroethylenes and some of the chloroethanes could be prepared as well as the chloromethanes (see Table 7). This gave a direct indication of free-radical reactions[121] or possible group rearrangements (cf. $Si_2Me_6 \longrightarrow SiMe_3.CH_2.SiHMe_2$[45]) prior to Si-C bond fission by an elimination reaction[45]:



the last stage possibly being the chloroethylene producing step in the chlorination of $SiEt_4$.

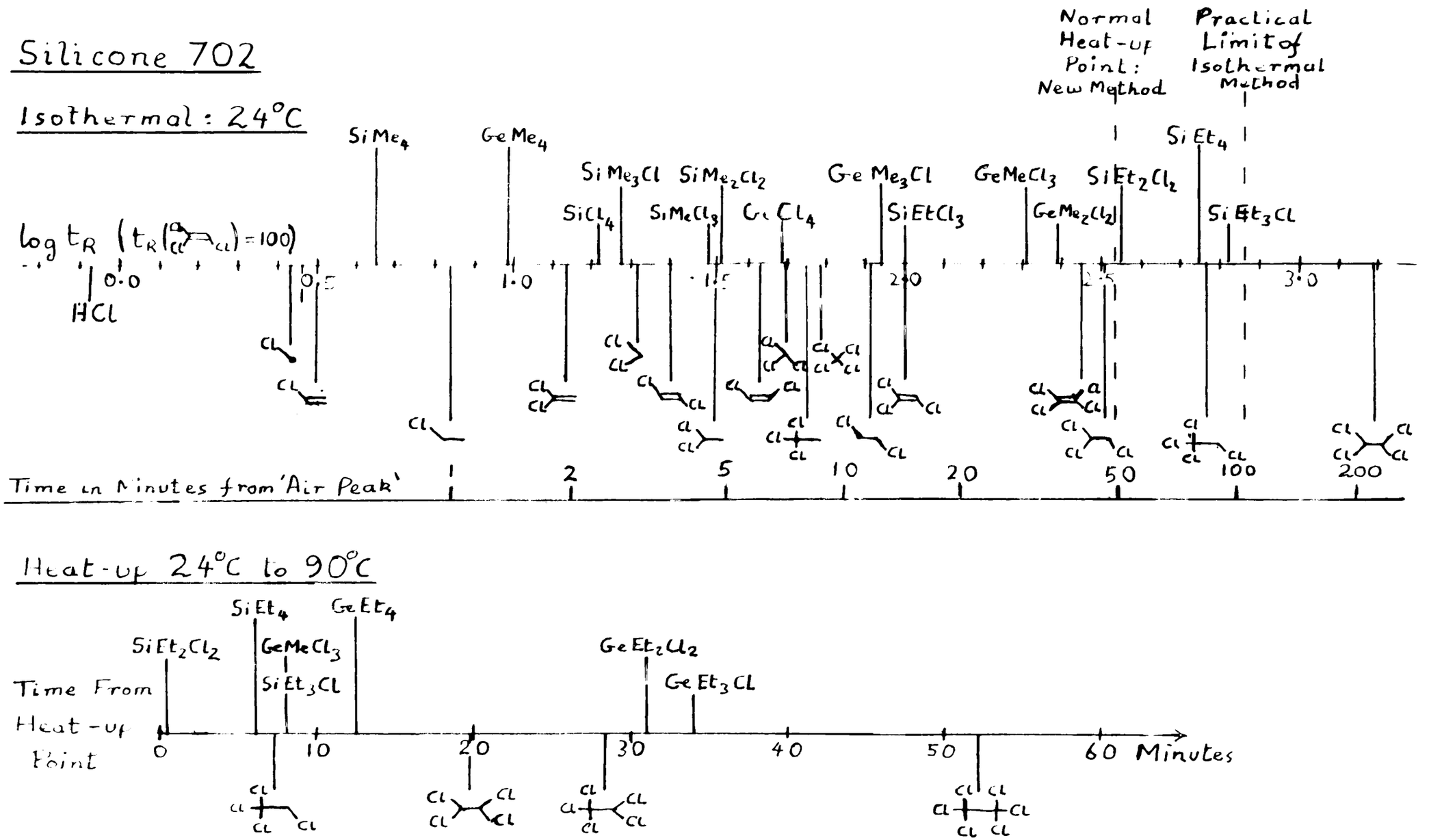
In partial support of this last possibility, there was evidence of the formation of some high-boiling compounds, in certain of the preparations, which might have been silicon compounds with chlorinated side chains. In any event, it was obvious that several types of reaction were occurring, under different conditions, in the gold chloride reactor.

4.12 First modifications to the technique

It was decided to equip the column of the gold chloride system with a heater (see Section 2.41) to enable the higher-boiling products of the

FIG. 27

First Apparatus – Chromatography of Products of the Gold Chloride Reaction



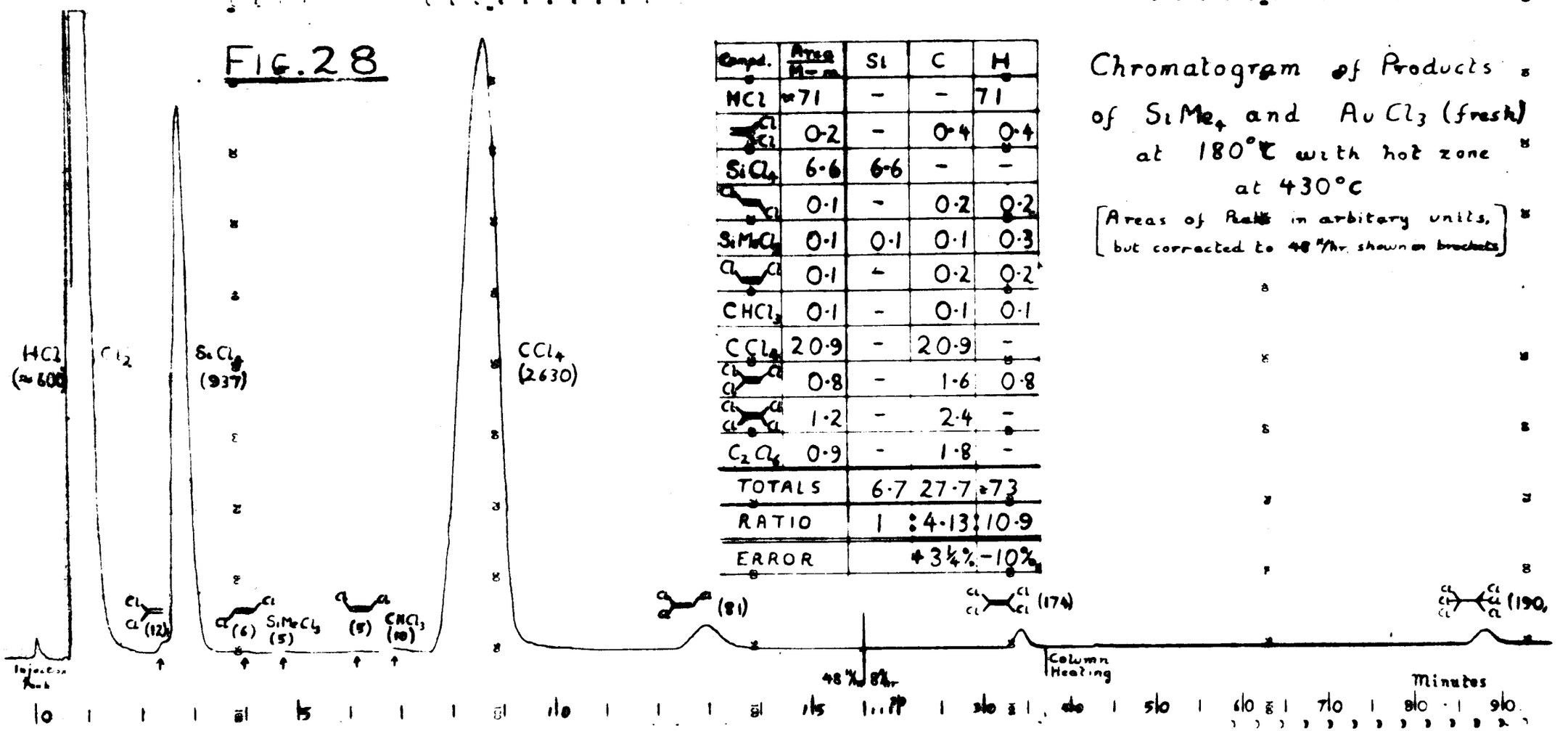
reaction to be observed and quantitatively measured with greater ease and accuracy, since the peaks would be more compact laterally and hence higher. It was decided, after a little experiment, to operate the column at ambient temperature until the peak of 1,1,2-trichloroethane (or its position) had been reached, and then to heat up the column to an equilibrium temperature of about 90°C. Allowance had to be made for the effect on the detector of the change in flowrate (see Section 2.65). By-and-large the peaks obtained after the heat-up point were sufficiently well separated for identification by inspection. Fig.27 shows the order and separation of the products of the gold chloride reaction using both the original and modified chromatographic techniques.

It was observed that in the attempts at quantitative analysis of the silicon tetraalkyls so far carried out, the silicon analyses were low and the HCl analyses high. Since this was probably due to the presence of moisture within the system, the sodium deoxidiser was fitted with a new charge. In addition it had been observed that in most of the reactions so far carried out, appreciable amounts of the parent compound remained unreacted. Examination of the charge in the cell showed that the gold had formed a hard crust over the remaining gold chloride, which was obviously preventing the evolution of chlorine once the surface $AuCl_3$ had reacted. A new charge was made up with some glass wool mixed with the gold to provide a more porous bed.

4.13 Further Experiments; with $SiMe_4$, $SiEt_4$, $GeEt_4$ and $GeMe_4$

As a result of the modifications described in the previous Section, a marked improvement in the results was observed: In particular, reactions

FIG. 28



Compd.	Area M= m	Si	C	H
HCl	≈71	-	-	71
	0·2	-	0·4	0·4
$SiCl_4$	6·6	6·6	-	-
	0·1	-	0·2	0·2
$SiMeCl_3$	0·1	0·1	0·1	0·3
	0·1	-	0·2	0·2
$CHCl_3$	0·1	-	0·1	0·1
CCl_4	20·9	-	20·9	-
	0·8	-	1·6	0·8
	1·2	-	2·4	-
C_2Cl_4	0·9	-	1·8	-
TOTALS		6·7	27·7	≈73
RATIO		1	: 4·13	: 10·9
ERROR			+ 3¼%	-10%

Chromatogram of Products of $SiMe_4$ and $AuCl_3$ (fresh) at 180°C with hot zone at 430°C

[Areas of Peaks in arbitary units, but corrected to 48 %/hr. shown in brackets]

were found to take place under milder conditions and the formation of the chloroethylenes was thus much reduced. The quantitative measurements gave results nearer the correct values (particularly after a sample of $SiCl_4$ had been passed through the gold chloride cell and the accompanying chromatograph to remove residual moisture) and the peaks of the higher-boiling compounds were measured with greater ease.

The complete chlorination of $SiMe_4$ was attempted and a similar reaction to that already shown in Table 7 was obtained with both cell temperatures some 45°C lower. The quantities of the chloroethylenes were much reduced. The results obtained, after two 'conditioning' runs are summarised in Table 8 and the chromatogram and calculation of Run 2 is shown in Fig.28. All the chromatograms were substantially similar, and it can be seen that the principal reason for the error in the hydrogen analyses was the difficulty of measuring the peaks of HCl in view of their incomplete resolution from the Cl_2 peaks.

TABLE 8

Summary of Results of the Gold Chloride Analysis of $SiMe_4$

Run	1		2		3		4	
	Ratio	Error	Ratio	Error	Ratio	Error	Ratio	Error
Total Si	1		1		1		1	
Total C	4.32	+8%	4.13	+3%	3.93	-2%	4.11	+3%
Total H	9.2	-23%	10.9	-10%	11.4	-5%	10.7	-12%

Satisfactory results were also obtained from the reaction of $SiEt_4$ in the modified gold chloride system. In particular, the calculated Si:C

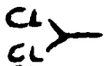
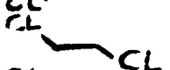
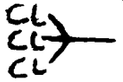
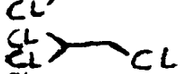
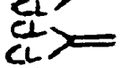
ratios were within 5% of the correct value. More severe conditions had to be employed for these analyses to guarantee that no appreciable amounts of $SiEtCl_3$ were prepared, as this compound was chromatographically coincident with trichloroethylene. The carbon-containing products were mainly ethylene derivatives in the approximate ratios as obtained from $SiMe_4$ (see Fig.28), together with about 25% of CCl_4. If the cell temperatures were increased, a loss of carbon occurred: For instance, at 215°/460°C, the main carbon products were tri- and tetrachloroethylene, and CCl_4, but the apparent C : Si ratio was reduced from 8 : 1 to 6 : 1, presumably either due to polymerisation of the ethylene derivatives or deposition of elemental carbon.

When the preliminary calibrations for the analysis of $GeEt_4$ were made, it was realised that $GeCl_4$ was almost chromatographically coincident with $CHCl_3$ (see Fig. 27). This meant that germanium analyses must be considered unreliable if either CH_2Cl_2 or CCl_4 were present in the products, as it would be expected that some $CHCl_3$ would also be present. Accordingly it was decided to see what information could be obtained by reaction under milder conditions than so far attempted. An unexpected and significant fact emerged: Reaction occurred under conditions where no detectable amounts of chlorine were evolved by the gold chloride. This implied that reaction was occurring either in the immediate vicinity of the gold chloride, or actually with the gold chloride. If reaction was taking place near, but not on the surface of the gold chloride, this would require an extremely rapid evolution of chlorine to re-establish the equilibrium amount as it was used up by the sample. As the equilibrium pressures were low at these low temperatures, recombination of chlorine

TABLE 9

Products of the Gold Chloride Reaction on $GeEt_4$

Results expressed as percentages of total Chlorinated Hydrocarbons and as percentages of total Ethyl Germanium Chlorides.

Run No.	1	2	3	4	5	6
Cell Temps.	103°/180°	114°/200°	128°/245°	137°/275°	156°/330°	170°/380°
Products						
EtCl	99.6	99.5	92.9	86.4	55.2	9.9
			1.7	3.8	10.6	25.5
	0.4	0.5	5.4	9.8	30.9	42.8
					2.7	11.4
					0.3	4.8
					0.3	5.4
						0.1
					tr	tr
$GeEt_3Cl$	55.3	53.7	43.9	39.9	9.0	
$GeEt_2Cl_2$	44.7	46.0	51.6	53.7	50.4	7.8
$GeEtCl_3$			0.7	1.0	12.4	19.4
$GeCl_4$		0.3	3.8	5.4	28.2	72.8
Empirical Ratios						
Ge	1	1	1	1	1	1
C	8.30	8.09	8.13	7.82	8.30	7.68
H	20.8	20.2	20.2	19.5	20.9	20.9

with the gold in the absence of sample would also need to be rapid. However, in the preparation of gold chloride, even with slow flowrates, some chlorine passed straight through the cell, and therefore the combination process was fairly slow. Thus it is extremely unlikely that the low temperature reactions with gold chloride occurred other than at the surface of the solid.

Some of the results of the reaction of $GeEt_4$ with gold chloride are shown in Table 9. These are expressed as percentages of the total of carbon compounds cleaved from germanium and the total of germanium compounds with at least one carbon group cleaved. In all cases there was some remaining $GeEt_4$. Comparison of these results with the results of the chlorination of EtCl (see Table 7) shows that at the lower temperatures, in the former case there was a 3 : 1 preponderance of 1,2-dichloroethane over 1,1-dichloroethane, but in the latter case the opposite was noticed; the ratio being about 1 : $1\frac{1}{2}$. This was strong evidence for some reaction taking place via side chain chlorination, preferably in the β-position, as occurs in the side chain chlorination of $SiEt_4$ by SO_2Cl_2[122]. Since no major amount of any new high-boiling compound was detected, it was assumed that fission of β-chloroethyl groups took place more readily than ethyl groups, preventing large concentrations of β-chloroethyl ethyl germanium chlorides from appearing in the products. However the presence of small amounts of products with chlorinated side chains might be indicated by the rather low germanium analyses. Under more rigorous conditions than those of Run 6 (Table 9) some chloromethane production took place and thus the analyses were no longer reliable. Subsequent reactions under conditions similar to Runs 3 and 4

gave Ge : C ratios within 2% of the correct value, usually with the amount of Ge on the low side.

A series of reactions under conditions between Runs 2 and 5 in Table 9 was carried out on $GeMe_4$ (see Table 10). It was found that even under the most severe of these conditions, there was very little loss of the second methyl group, and under more severe conditions there was confusion between MeCl and Cl_2 as well as $GeCl_4$ and $CHCl_3$, and also evidence of high-boiling compounds.

TABLE 10

Gold Chloride Reaction on $GeMe_4$: Results Calculated as Table 9

Run	1	2	3	4
Cell Temperatures:	112°/200°C	121°/230°C	135°/265°C	157°/335°C
Products (% of C and Ge volatiles)				
MeCl	100	100	100	99.7
CH_2Cl_2	-	-	-	0.3
$GeMe_3Cl$	100	100	99.2	96.8
$GeMe_2Cl_2$	-	-	0.8	3.2
Ge : C Ratio	1 : 4.04	1 : 4.11	1 : 3.91	1 : 3.88
% $GeMe_4$ Reacted	17	18	22	36

The low overall reaction may be presumed as being largely due to the low proportion of the sample that actually passed over or through the gold chloride bed. It was realised that this was a stumbling block for satisfactory low temperature gold chloride analysis where no chlorine was evolved and therefore reaction only took place at gold chloride.

Accordingly the system was redesigned (see Section 2.62) before any further work was done on the method of analysis.

4.2 Experiments Using the New Apparatus

With the redesign of the gold chloride system to include a 'plug' type of reactor (see Section 2.62) and two chromatographic columns (see Section 2.65), the actual quantitative results were expected to be more significant, since all of the sample would be expected to receive virtually the same treatment. Since runs could be carried out on both columns, identification was also expected to be simpler, and paired runs were frequently carried out for this purpose.

It was expected that progressive dechlorination of the $AuCl_3$ from run to run would alter its chlorinating properties somewhat, particularly in the low temperature reactions. Thus, in many cases, series of results were carried out in sequence of temperatures.

4.21 Experiments on $GeMe_4$, MeCl and the Methyl Germanium Chlorides

It was decided to investigate the possibilities of the gold chloride reaction under a wider range of conditions than hitherto employed. $GeMe_4$ was chosen as the subject compound. Preliminary reactions showed that a large number of high-boiling compounds, presumably the chloromethyl methyl germanium chlorides, were formed. It was therefore decided to use the method progressively on $GeMeCl_3$, $GeMe_2Cl_2$ and $GeMe_3Cl$, before it was applied to $GeMe_4$ in order that these compounds and their presumed chloromethyl derivatives could be identified, if possible. Identification of the methyl

germanium chlorides was easily effected as their main low-boiling products under mild reaction conditions were, successively, $GeCl_4$ and the previous parent compounds.

For almost all of the reactions carried out at cell temperatures in excess of 130°C, MeCl was estimated by subtraction, as it was coincident on both columns with Cl_2, unless it was obvious that none was present (i.e. The main products being CCl_4 and $CHCl_3$ with only a trace of CH_2Cl_2).

As a preliminary, the gold chloride reaction was carried out on MeCl to see what conditions were required for its chlorination and what sort of product ratios were obtained. The results of these experiments are shown in Table 11 together with a run carried out on a sample of $CHCl_3$ in approximately the same concentration and conditions as Run 3 on MeCl.

TABLE 11

Products of the Gold Chloride reaction on MeCl and $CHCl_3$ in molar percentages.

Parent:	MeCl	MeCl	MeCl	MeCl	MeCl	$CHCl_3$
Run	1	2	3	4	5	6
Cell Temp.	138°/138°	172°/375°	179°/425°	187°/425°	193°/440°	179°/425°
MeCl	100	55	12	3	0	-
CH_2Cl_2	-	38	52	26	11	-
$CHCl_3$	-	6	29	49	44	53
CCl_4	-	1	7	22	45	47

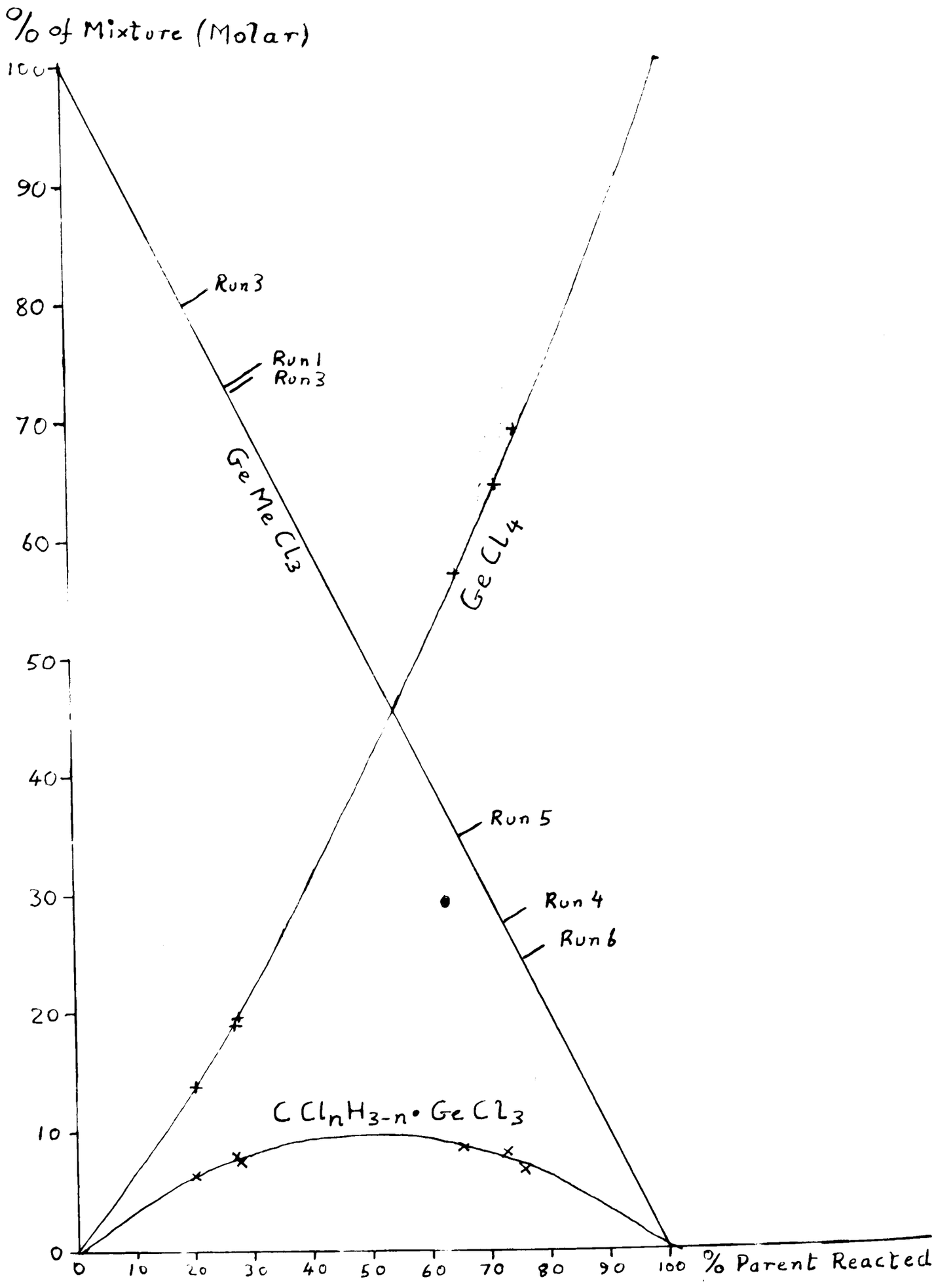
These results show that a small, but definite deactivation to chlorination occurs due to chlorine at carbon : 88% of MeCl reacts under

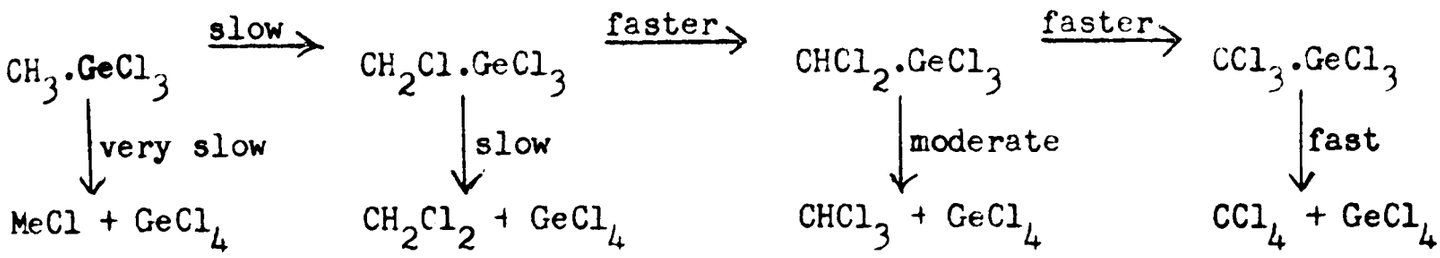
conditions where 47% of $CHCl_3$ reacts, and the product ratios of the reaction of MeCl support this.

When the gold chloride reaction was applied to $GeMeCl_3$ it was found that, in addition to $GeCl_4$ and some chloromethanes, there were 3 distinct high-boiling compounds amongst the products, with an overall yield of up to 10%. These compounds were presumed to be $CH_2Cl.GeCl_3$, $CHCl_2.GeCl_3$ and $CCl_3.GeCl_3$. On the Silicone 702 column it was presumed that these appeared in the order of their molecular weights, but this was not quite so certain on the tritolyl phosphate column (see Appendix 3.1). Tables of the retention values of these experiments are shown in Appendix 3.2 and tables of the approximate quantitative results are given in Appendix 3.3. The relative amounts of the three presumed chloromethyl compounds seemed to follow no set pattern, but were of the same order.

The quantitative analyses of the products of $GeMeCl_3$ showed that the principal carbon-containing product was CCl_4, with only a small amount of $CHCl_3$ and scarcely any CH_2Cl_2. These product ratios were vastly different from those expected from MeCl under the same reaction conditions, and even showed a higher yield of CCl_4 than would be expected from $CHCl_3$. From this, it was evident that fission of Ge-C bonds had mainly taken place by fission of $CCl_3.GeCl_3$ and, in progressively smaller amounts, from the other chloromethyl compounds. Since only small amounts of the presumed chloromethyl germanium trichlorides could be obtained, and these were, if anything, prepared in progressively decreasing amounts, an approximate kinetic scheme may be drawn up for these reactions:

FIG. 29 Gold Chloride Reaction on $GeMeCl_3$

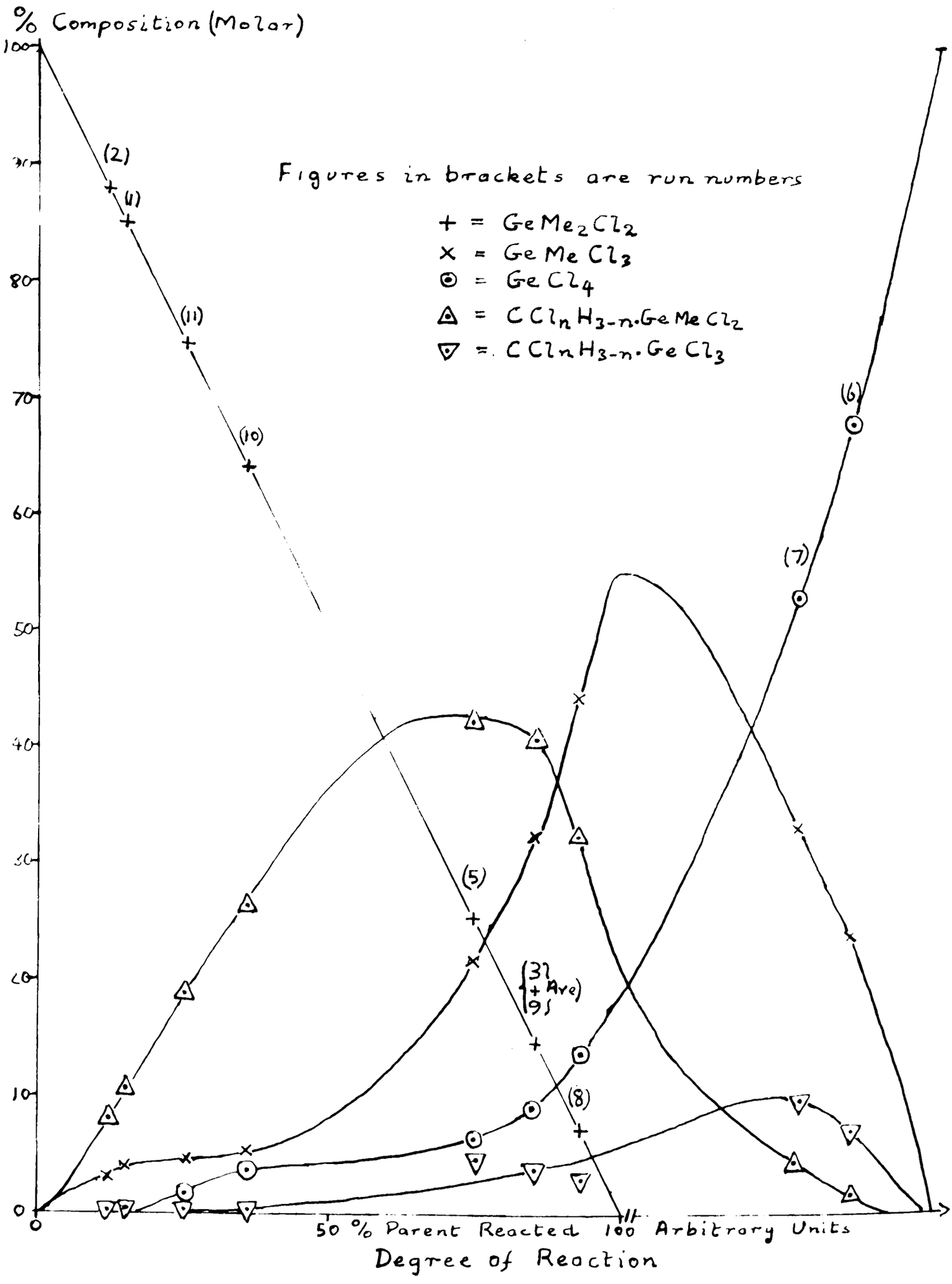




In the early experiments the $GeCl_4$ analysis was rather low and the HCl analysis rather high, probably due to hydrolysis. Fig. 2[illegible] shows the composition of the reaction products related to the degree of reaction of the parent, $GeMeCl_3$, after an allowance, based on the carbon analysis, had been made for this presumed hydrolysis. The end of the plot of the series $GeCl_3.CCl_nH_{3-n}$ must be very close to the end of the $GeMeCl_3$ plot on account of the high reactivity of these compounds.

When $GeMe_2Cl_2$ was reacted in the gold chloride system, most of the effects found with $GeMeCl_3$ were observed, (See Appendix 3.3): In particular only small amounts of CH_2Cl_2 and $CHCl_3$ relative to CCl_4 were prepared, (but not quite as small as those obtained with $GeMeCl_3$) and three new high boiling compounds, in addition to the three observed with $GeMeCl_3$, were prepared. These were possibly the chloromethyl methyl germanium dichlorides, $CCl_nH_{3-n}.GeMeCl_2$, and their chromatography followed similar trends to the previous series with the initially confusing complication that the first of these was chromatographically coincident with the second of the previous series on the Silicone 702 column, (see Appendix 3.2). Some evidence of the possible chromatographic inversion of the second and third members on the tritolyl phosphate column was afforded by the low yield, presumably of the third member, observed in the reactions under milder conditions. The total amount of this series present in the reaction products was much higher than that of the previous

FIG. 30 Gold Chloride Reaction on $GeMe_2Cl_2$



series, indicating, together with the slightly higher quantities of CH_2Cl_2 and $CHCl_3$ in the products, that the reaction of $GeMe_2Cl_2$ in the gold chloride system proceded in much the same way as $GeMeCl_3$, but with reduced kinetic trends, and probably a faster initial attack on methyl groups. The absence of detectable amounts of a third series of chloromethyl compounds would seem to indicate the following kinetics:

$$GeMe_2Cl_2 \xrightarrow{\text{slow}} CH_2Cl.GeMeCl_2 \xrightarrow{\text{faster}} CHCl_2.GeMeCl_2$$

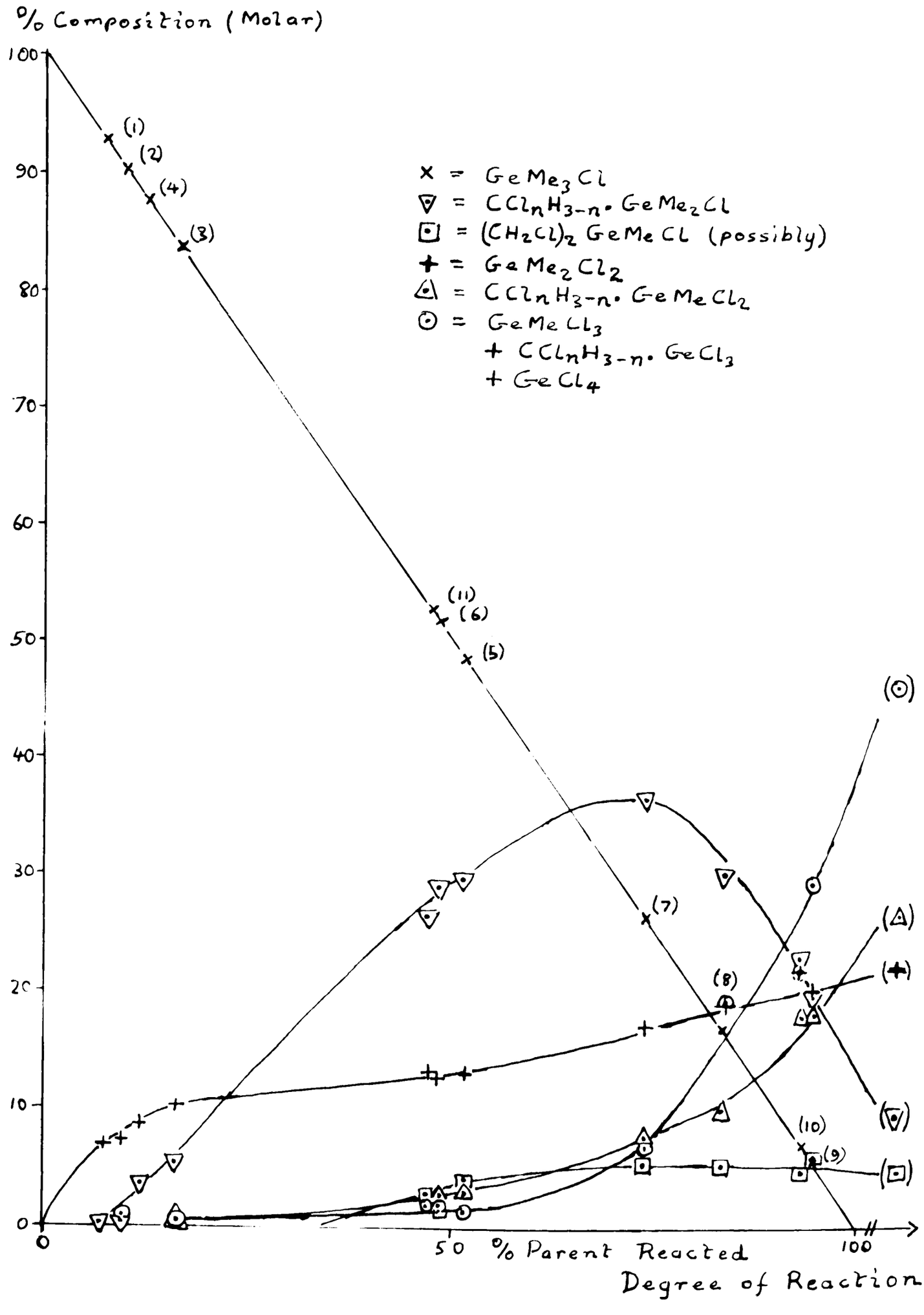
$$\Big\downarrow \text{slower}$$

$$(CH_2Cl)_2GeCl_2$$

Fig.30 shows the course of the gold chloride reaction on $GeMe_2Cl_2$, initially in terms of the percentage reacted of the parent and, after complete reaction of this, in arbitrary units. In view of the difference in the two series with chlorinated side chains, of the relative amounts from reaction to reaction, these have again been added together. From these graphs it can be seen that the major route of the chlorination of $GeMe_2Cl_2$ took place successively via the series $CCl_nH_{3-n}.GeMeCl_2$, $GeMeCl_3$, the series $CCl_nH_{3-n}.GeCl_3$ to the final product, $GeCl_4$, as suggested by the carbon analysis. The relatively lower reactivity of the $CCl_nH_{3-n}.GeMeCl_2$ series compared with their parent in contrast to the series based on $GeMeCl_3$ is shown by the large amounts of these compounds remaining after the parent had reacted completely. Retention values are tabulated in Appendix 3.2, and the quantitative values used in Fig.30, in Appendix 3.3.

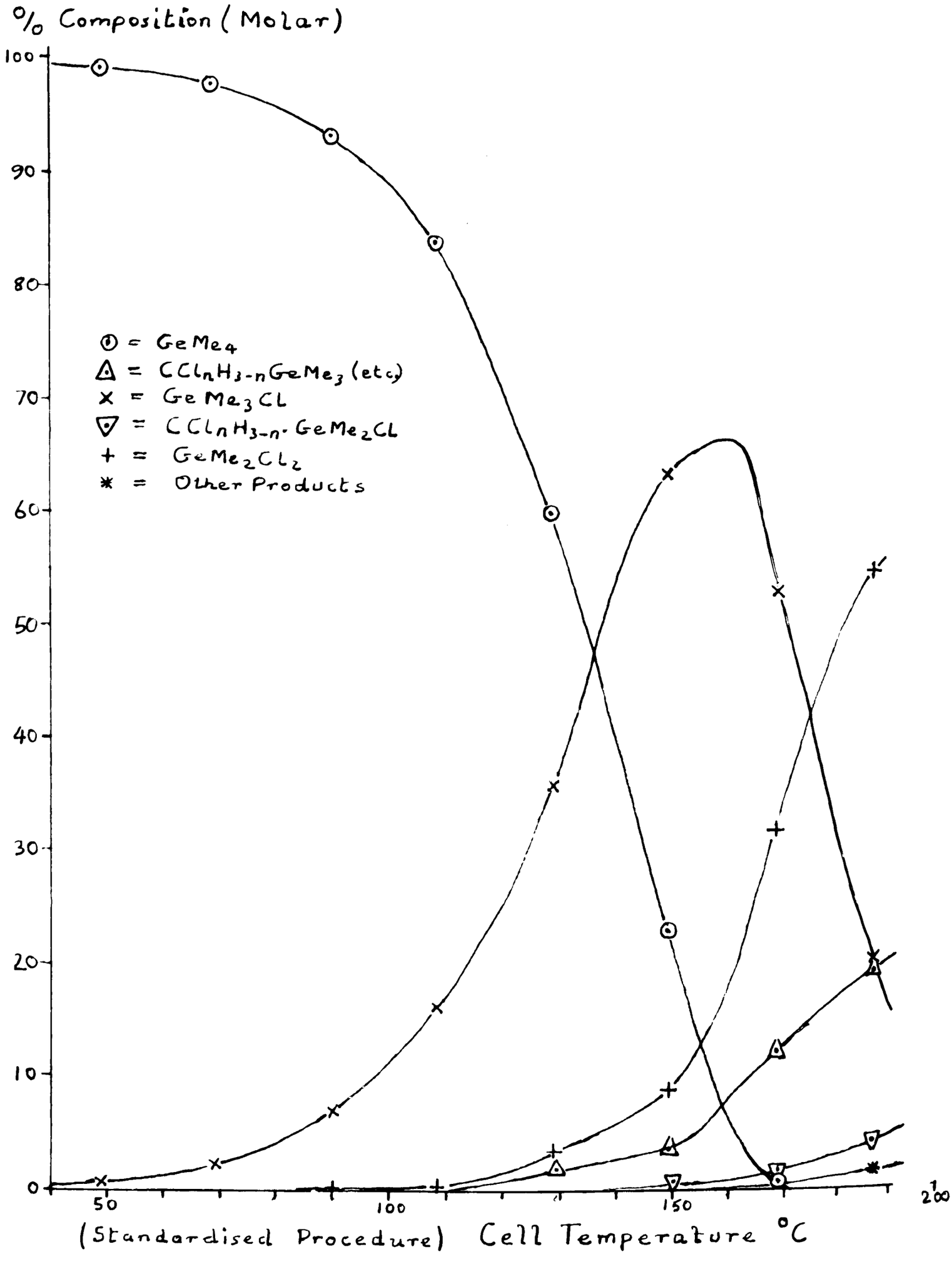
A rather different situation occurred in the reaction of $GeMe_3Cl$ in the gold chloride system, as appreciable amounts of MeCl and CH_2Cl_2 were formed, but not in the quantities that would be expected from a reaction

FIG. 31 Gold Chloride Reaction on $GeMe_3Cl$



merely involving fission of methyl groups as MeCl. In addition, fairly large amounts of at least four new compounds were prepared. Three of these fitted the expected chromatographic pattern, on both columns, (see Appendix 3.1) for the series $CCl_nH_{3-n}.GeMe_2Cl$, and the fourth, more retarded chromatographically, could possibly have been $(CH_2Cl)_2GeMeCl$. Only small amounts of the compound believed to be $CCl_3.GeMe_2Cl$ were observed, which might indicate a relatively faster loss of the CCl_3- group than the chloromethyl groups of the other members of the series, and a rate of formation not much faster than those of the other members. Fig. 31 shows a plot of the composition of the products against the percentage of $GeMe_3Cl$ reacted. From this and the carbon products analysis (see Appendix 3.3) it would seem that under mild conditions the principal reaction involved immediate loss of methyl groups as MeCl. Under slightly more intense conditions, chlorination of side groups took place, but these products were reasonably slow to react, as even when these compounds were present in large quantities, most of the detached carbon groups were present as MeCl. Under rather more vigorous conditions, when there was still little reaction of the $GeMe_2Cl_2$ prepared, the amount of CCl_4 prepared was higher than would be expected from the chlorination of MeCl, particularly in view of the lower quantities of $CHCl_3$ and CH_2Cl_2. Thus the loss of groups from the series with chlorinated side chains was principally occurring via CCl_3- groups. The compound believed to have two chlorinated side chains was slow to form and presumably slow to react. The concentration of $GeMe_2Cl_2$ did not get very high under any conditions, which would seem to indicate that its reaction via side group chlorination was more rapid than the reaction

FIG. 32 Gold Chloride Reaction on $GeMe_4$



of $GeMe_3Cl$ either by loss of methyl groups or via side chain chlorination. In Fig. 31 $GeMeCl_3$ and its subsequent products have been added together in the interests of simplicity. These last followed the expected patterns.

The reaction of $GeMe_4$ in the gold chloride system was much simpler in its early stages. Reaction took place under considerably milder conditions than those necessary for the other compounds. The results of a consecutive set of experiments are shown, plotted against the cell temperature, in Fig. 32. The initial reaction yielded $GeMe_3Cl$ and MeCl, and even under more severe conditions the reaction of the $GeMe_3Cl$ to $GeMe_2Cl_2$ initially took place with MeCl as the other product. However, under severe conditions at least three new peaks appeared on the chromatograms, which on chromatographic evidence were believed to be the series $CCl_nH_{3-n}.GeMe_3$ (Appendix 3.1), but which might have included compounds with two chlorinated methyl groups. Despite the formation of these compounds the high concentration of MeCl in the products implied that most of the Ge-C fission was yielding MeCl. This indicated that although the ease of formation of the chloromethyl derivatives may have increased slightly with methyl rather than chlorine at germanium, and although the ease of fission of methyl groups increased drastically with the number of methyl groups at germanium, the ease of fission of chloromethyl groups relative to their ease of formation decreased with methyl groups at germanium.

The analyses shown in Fig. 32 were obtained with the gas reactor at the same temperature as the gold chloride. Above 140°C gold chloride temperature, the effect of increasing the gas reactor temperature with

gold chloride constant, was to increase the relative amounts of the products believed to be chloromethyl compounds and increase the yield of CCl_4 relative to the other chloromethanes. Thus it may be presumed that the direct loss of methyl groups was due largely to reaction with gold chloride, whereas the chlorination of side chains was mainly a gas phase reaction with chlorine.

4.3 Conclusions on the Reactions with $GeMe_4$ and the Methyl Germanium Chlorides

Assuming that the two basic types of reaction mentioned above were distinct, the series of reactions of $GeMe_4$ and the methyl germanium chlorides can be explained in terms of the competition between these two types of reaction. But it has to be borne in mind that the gold chloride had the chance of reacting first.

The following trends were observed in this work: In the reaction of $AuCl_3$ with Ge-Me bonds to yield Ge-Cl bonds and MeCl, the reaction was strongly deactivated by chlorine at germanium. Thus the rates of reaction of the parent compounds were in the following order:

$$GeMe_4 > GeMe_3Cl \gg GeMe_2Cl_2 > GeMeCl_3$$

This is in accord with conventional halogenation in the absence of light with or without catalysis [35, 82, 85].

In the second type of reaction, the gas phase reaction leading to the chlorination of the methyl groups and their subsequent fission, the following conclusions were drawn:

1/ The rate of chlorination increased in the following order if chlorine was at germanium:

$$Ge\text{-}CH_3 < Ge\text{-}CH_2Cl < Ge\text{-}CHCl_2$$

and this, in particular, could have accounted for the protection of the second methyl group in $GeMe_2Cl_2$. It is also possible that the presence of a chloromethyl group would deactivate other methyl groups at germanium. These trends, however, appeared to be much reduced when there were mainly methyl groups at germanium, as it was possible that there was chlorination of second methyl groups.

2/ The rate of fission of the chloromethyl groups increased in the following order:

$$(\ Ge\text{-}CH_3\ ) < Ge\text{-}CH_2Cl < Ge\text{-}CHCl_2 < Ge\text{-}CCl_3$$

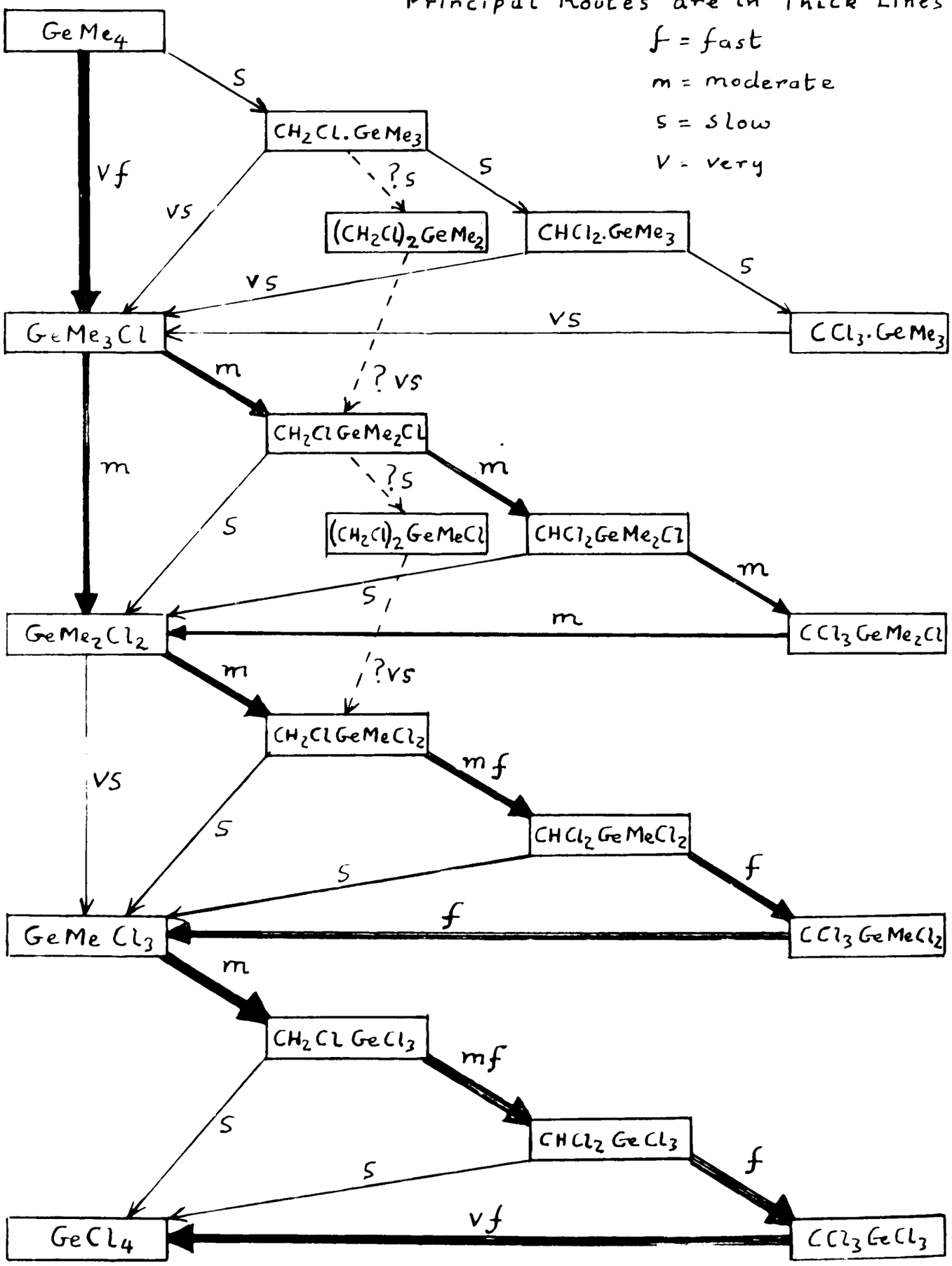
Loss of a methyl group may be included in this Table of the gas reaction, as in cases where reaction could only have been occurring in the gas reactor, no MeCl was produced. The strange effect in the chlorination of $GeMe_2Cl_2$ where both MeCl and CCl_4 were the principal carbon products is explained by the competition of this effect with the direct loss of methyl groups by reaction with gold chloride itself.

3/ The rate of fission of chloromethyl groups compared with their rate of formation from methyl groups was reduced by methyl groups at germanium or was increased by chlorine. Thus only low yields of the series $CCl_nH_{3-n}.GeCl_3$ (10%) could be obtained, whereas much higher yields of the chloromethyl methyl germanium dichloride and dimethyl germanium chloride series could be obtained, despite the competing direct demethylation reaction in the latter case.

The relative rates of the gold chloride and gas phase reactions were determined by the following factors:

At low gold chloride temperatures (up to 120°C) no detectable evolution

FIG. 33 **Proposed Scheme for the Gold Chloride Reaction on $GeMe_4$ and the Methyl Germanium Chlorides**



of chlorine occurred, therefore any reaction must have taken place with the gold chloride only. There was consequently little effect on the reaction if the gas reactor was heated or not. These conditions were sufficient for much chlorination of $GeMe_4$ and a small amount of $GeMe_3Cl$.

At temperatures above 140°C, detectable evolution of chlorine occurred, and therefore the degree of reaction in the gas reactor depended on the temperature, as long as there was an excess of chlorine, and on the gold chloride temperature if there was not. In cases where there was a lack of chlorine and a high gas reactor temperature there was a tendency for some of the carbon to appear as ethylene derivatives, as noticed in the early experiments on the gold chloride method, where these conditions undoubtedly occurred.

The direct demethylation of $GeMe_2Cl_2$ and $GeMeCl_3$ was almost prohibitively slow under the normal gold chloride temperatures so that the only reaction occurring with these compounds was the gas phase reaction.

Fig.33 shows the proposed course of the reactions of $GeMe_4$ and the methyl germanium chlorides. The reactions involving demethylation (to the left of the figure) are favoured at low temperatures and the gas phase reactions (to the right of the figure) are favoured under severe conditions; thus at high temperatures, despite the more rapid demethylation, $GeMe_4$ will form its chloromethyl derivatives in quantities up to 20% of the products. If this reaction was allowed to progress further, the much slower dechloromethylation reaction would, perforce, become a minor route of the reaction of $GeMe_4$ to $GeMe_3Cl$. The reactivities of the various stages marked in Fig.33 do not necessarily refer to the Table as a whole, but refer to the relative reactivities of the various reactions

between adjacent methyl germanium chlorides.

The trends deduced in the gas phase reaction on the methyl germanium chlorides are in agreement with those observed in the free-radical chlorination of the methyl silicon chlorides[122], in liquid or gas phase, using ultra violet light and promoted by peroxides or metallic chlorides etc., or using such agents as sulphuryl chloride. In particular it had been found that there was a slight accelerating effect with methyl groups rather than chlorine at silicon[123] and that $-CH_2Cl$ and $-CHCl_2$ groups were attacked more readily than $-CH_3$[124]. Similar, but not so exhaustive, work with germanium compounds indicated that, as found in this work, the relative rates of chlorination of $-CH_3$, $-CH_2Cl$ and $CHCl_2$ groups were more pronounced than with silicon, particularly with $.GeCl_3$ groups[125]. The chlorination of MeCl showed the reverse trend and only occurred under more rigorous conditions.

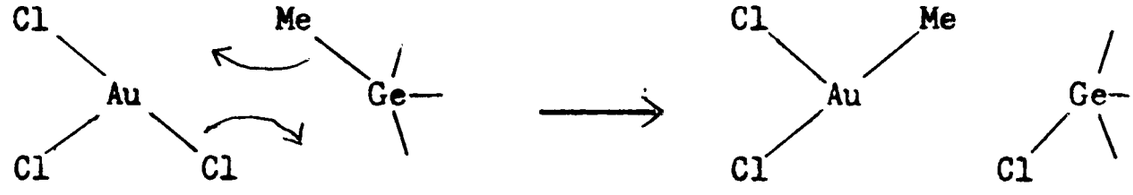
The gas phase fission of the $Ge-CCl_3$ bonds is possibly similar to the hydrolysis of $Si-CCl_3$ compounds in alkali[45, 124] where the reaction is via a nucleophilic attack on Si, and $Si-CCl_3$ is attacked far more readily than $Si-CHCl_2$. In this case the reaction would take place by Cl^- (or incipient Cl^-) on germanium. However, the fission could also be considered in terms of a free-radical reaction, since the high reactivity of compounds with chlorine at both carbon (trend 2 above) and germanium (trend 3 above) could be explained in terms of electron withdrawal from the Ge-C bond, increasing the likelihood of homolytic fission.

The reaction with gold chloride seems to bear considerable resemblance to the halogenation of silicon and germanium alkyls by halogen catalysed by aluminium trihalides[35, 45, 84, 85, 126], or the reaction with aluminium

trihalides[34, 45, 127] (or other metallic halides[127, 128]) with the exception, that chlorinated hydrocarbons were liberated in the gold chloride reaction. It is therefore possible to postulate several schemes for the reaction of $AuCl_3$ e.g:

$$2\ AuCl_3 \longrightarrow AuCl_4^- + AuCl + Cl^+$$

followed by attack on carbon by Cl^+, or attack on silicon or germanium by $AuCl_4^-$ (or Cl^- derived from this). Alternatively, a similar reaction to the $AlCl_3$ reaction is possible:



followed by loss of MeCl from $AuMeCl_2$.

4.4 The Gold Chloride Reaction as a Method of Analysis

It was concluded that the gold chloride reaction was sufficiently quantitative, after precautions against hydrolysis and with a high efficiency product collection trap, to be used for quantitative analysis. In the general applicability of chlorination to the field of silicon and germanium volatiles, this reaction is almost certainly more suitable than some of the other techniques involving micro-reactors and gas chromatography that have been described in the literature[129, 130].

In view of the large number of products that can be obtained, due to side chain chlorination, with reactions at intermediate temperatures, it seemed best to use this method either under very severe conditions so that chlorination was virtually complete, or under mild conditions when

only the weaker bonds were broken. The latter conditions were expected to result in retention of configuration of major parts of the structures of the parent compounds, and therefore structural analysis should be possible. For the projected work on the permethyl silanes and germanes, it was considered that this type of structural information would enable isomeric forms to be detected. It was expected from the literature that Si-Si and Ge-Ge bonds would be selectively broken in the presence of Si-Me and Ge-Me bonds (see Section 1.33), and reaction should, therefore be attempted at temperatures below 50°C, provided that this was adequate for fission of all Si-Si and Ge-Ge bonds, as little loss of methyl groups would be expected at this temperature. However, if operationally necessary, higher temperatures could be used, as long as they were under 100°C, as the absence of any chlorine liberated would enable the amount of MeCl formed to be measured.

CHAPTER FIVE

THE PERMETHYL SILANES AND PERMETHYL GERMANES.

5.1 Introduction

This chapter is concerned with the preparation of the permethyl silanes and permethyl germanes by modified Wurtz-Fittig reactions (see Section 1.31 for references) on the methyl silicon and germanium chlorides carried out in stainless steel bombs. The lower members of both series were subsequently identified by the low temperature gold chloride reaction as part of the development programme of that technique. At the time of the preliminary coupling experiments on the methyl silicon chlorides, the products were only identified by chromatography. In these experiments permethyl siloxanes were present in the reaction products, both as a result of their being in the reactants and as a result of hydrolysis during the experimental manipulations. In the early experiments these were retained and the chromatograms of the products were compared with 'blank' reactions, where the experiments were duplicated but with the reacting metal omitted. Some of the siloxanes were identified by deliberate preparation, and it was found that, as expected, the major siloxane products were the straight chain and ring compounds. In the reaction mixtures there were, however, some compounds which appeared to belong neither to the siloxane series or the permethyl silane series: Their chromatographic properties indicated the latter, and their removal by concentrated sulphuric acid indicated the former. It must be concluded that these were compounds with some Si-Si bonds but

TABLE 12

Coupling Experiments with Silicon Trimethyl Chloride

Run	Metal	Temperature	Time	Si_2Me_6%
1	K	110°C	24 Hrs.	75 - 85
2	Na	150°C	22 Hrs.	30 - 40
3	Zn + Al + Mg	180°C	25 Hrs.	0.8 - 1.2
4	Zn + Al + Mg + Hg	190°C	40 Hrs.	5 - 6
5	Mg + Hg	190°C	24 Hrs.	No Product
6	Al + Hg	190°C	22 Hrs.	No Product
7	Zn + Hg	190°C	24 Hrs.	No Product
8	Li	200°C	21 Hrs.	No Product
9	Li	300°C	24 Hrs.	No Product

also terminal chlorine or siloxane links.

In the later work, after preliminary quantitative chromatography on small samples, the products were 'washed' for a few minutes with cold H_2SO_4 to remove the siloxanes and residual chlorosilanes, but not for so long as to allow extensive demethylation of the permethyl silanes[131, 132] (although there was always a slight evolution of methane), followed by washing with water and drying with $CaSO_4$. Samples of the products were then chromatographed and the results were compared with the original chromatogram to see which products were unaffected by this treatment.

5.2 Preliminary Coupling Experiments with $SiMe_3Cl$

For the Wurtz-Fittig reaction on trialkyl silicon halides it has been shown that iodides react more readily than chlorides[72, 73] and that $SiEt_3Cl$ reacts more readily than $SiMe_3Cl$[70, 72] although this is not so marked if the iodides are used[73]. As a result, only the more reactive metals can be used for the coupling of $SiMe_3Cl$; K or Na/K[72, 74] or Na in decalin at 160-180°C[133]. In particular it was shown that Mg, Al, Cu, Zn and Hg did not react[73].

In the preliminary coupling experiments in this work, the First Apparatus was used for the chromatography of products. As the preparative chromatograph was fitted with a katharometer as detector, only approximate analyses were obtained. A summary of the results is given in Table 12.

These results, with the exception of Runs 3 and 4, agree, in general, with the published results. Comparing the results of Runs 3 and 4 with Runs 5, 6 and 7, it is seen that at least two metals were involved in the

FIG. 34 Retention Values on Silicone Rubber, 64·5°C

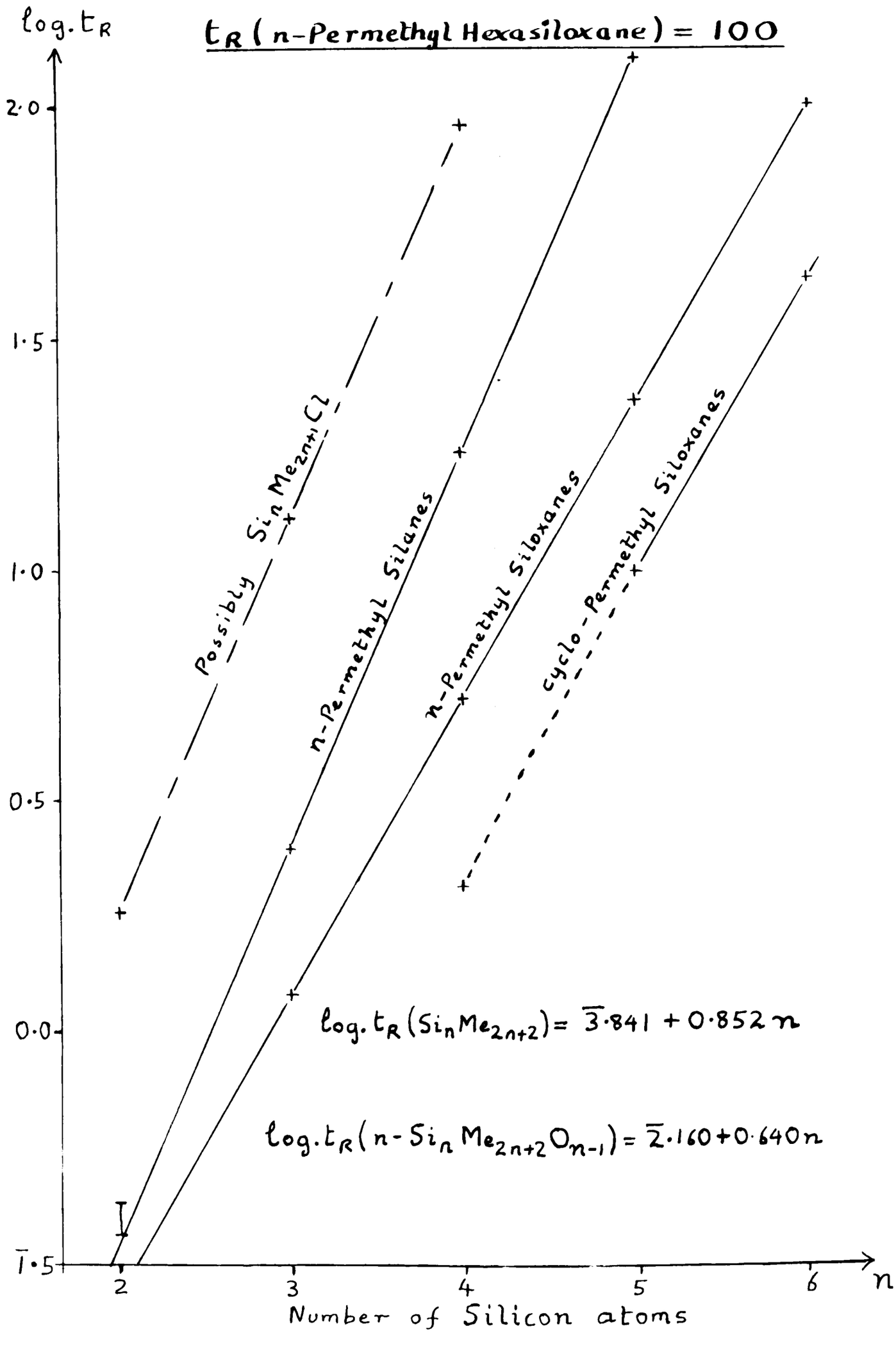


FIG. 35 Retention Values on Silicone Rubber, 100°C

t_R (n-Permethyl Hexasiloxane) = 100

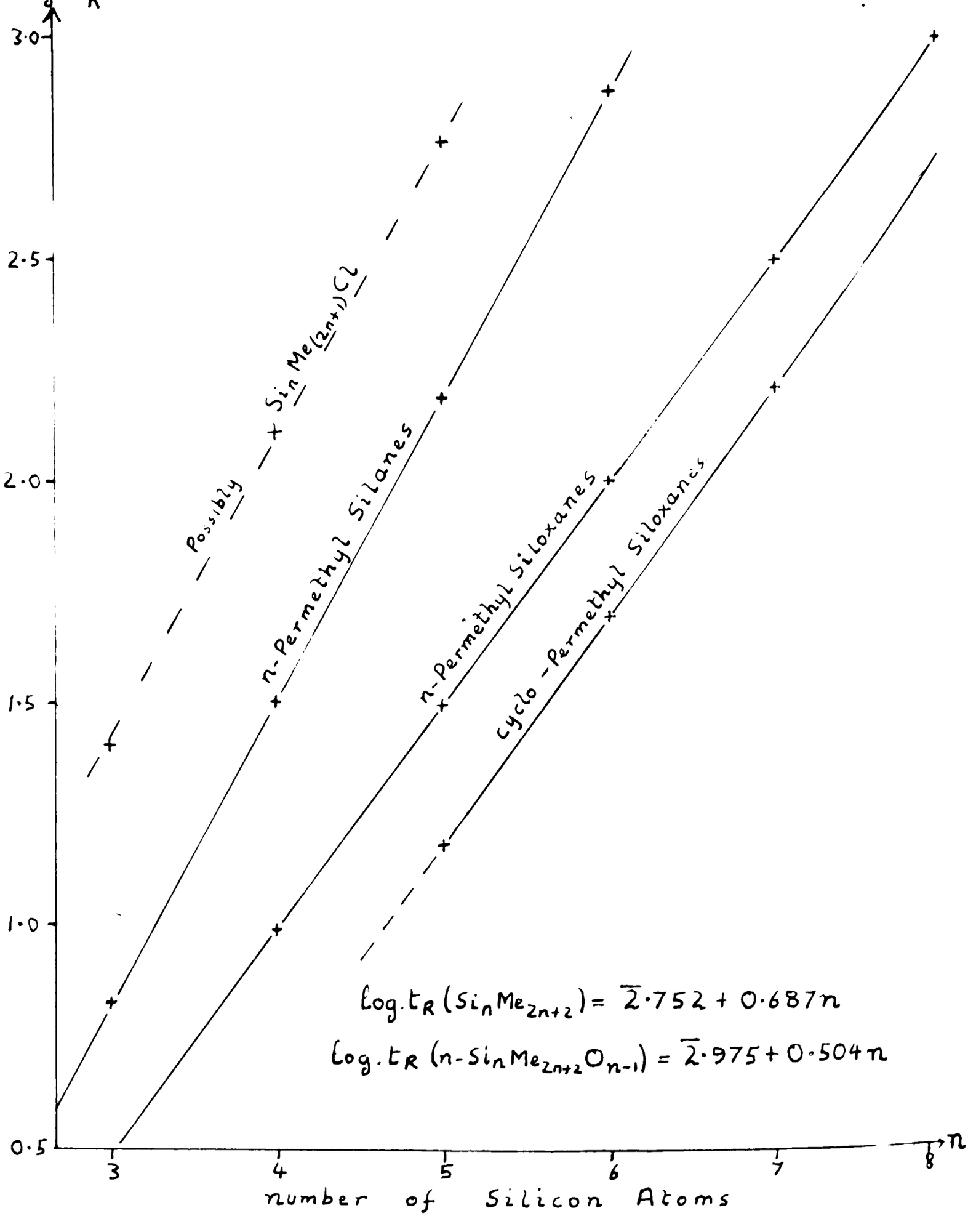
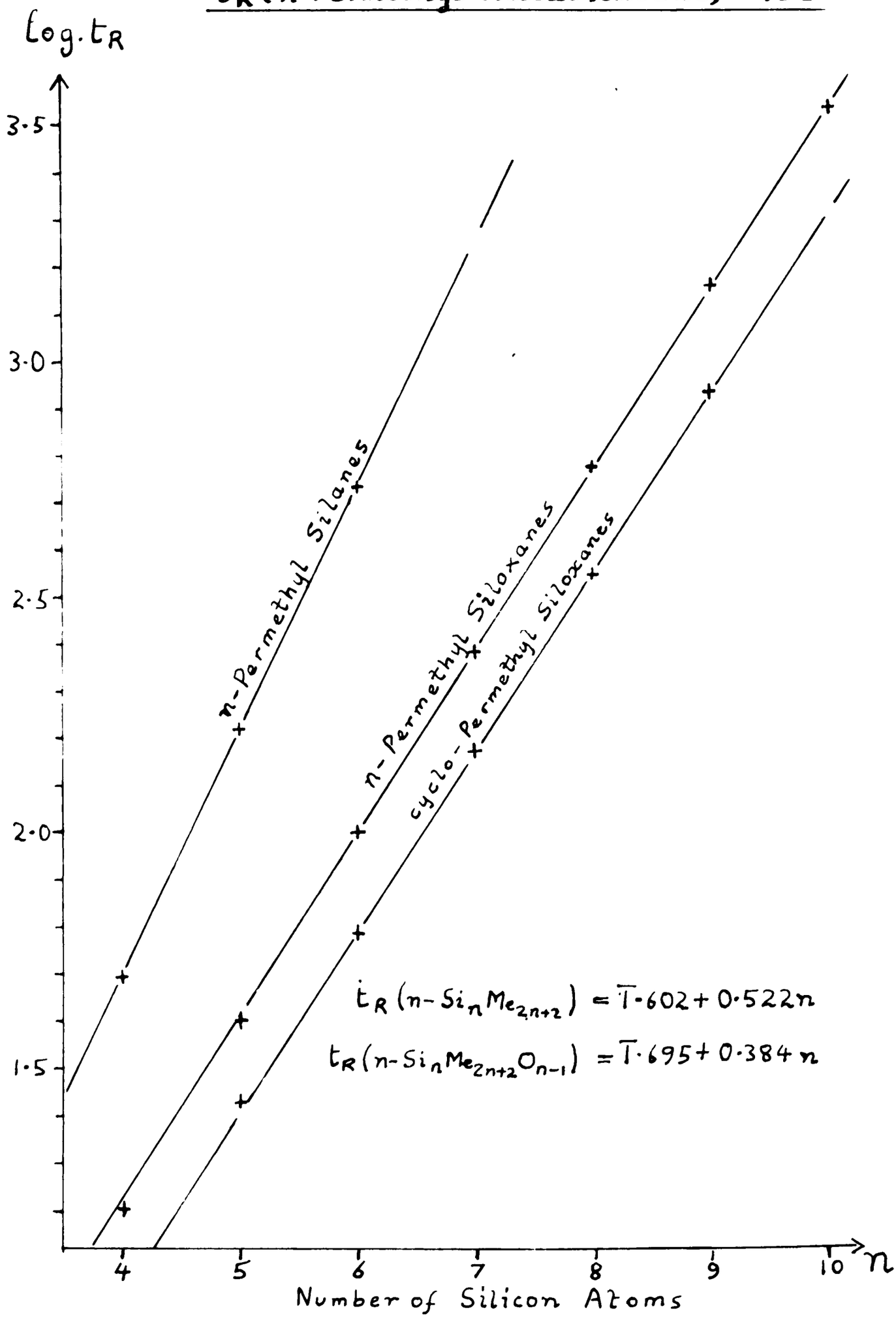


FIG. 36 Retention Values on Silicone Rubber, 140°C

t_R (n-Permethyl Hexasiloxane) = 100

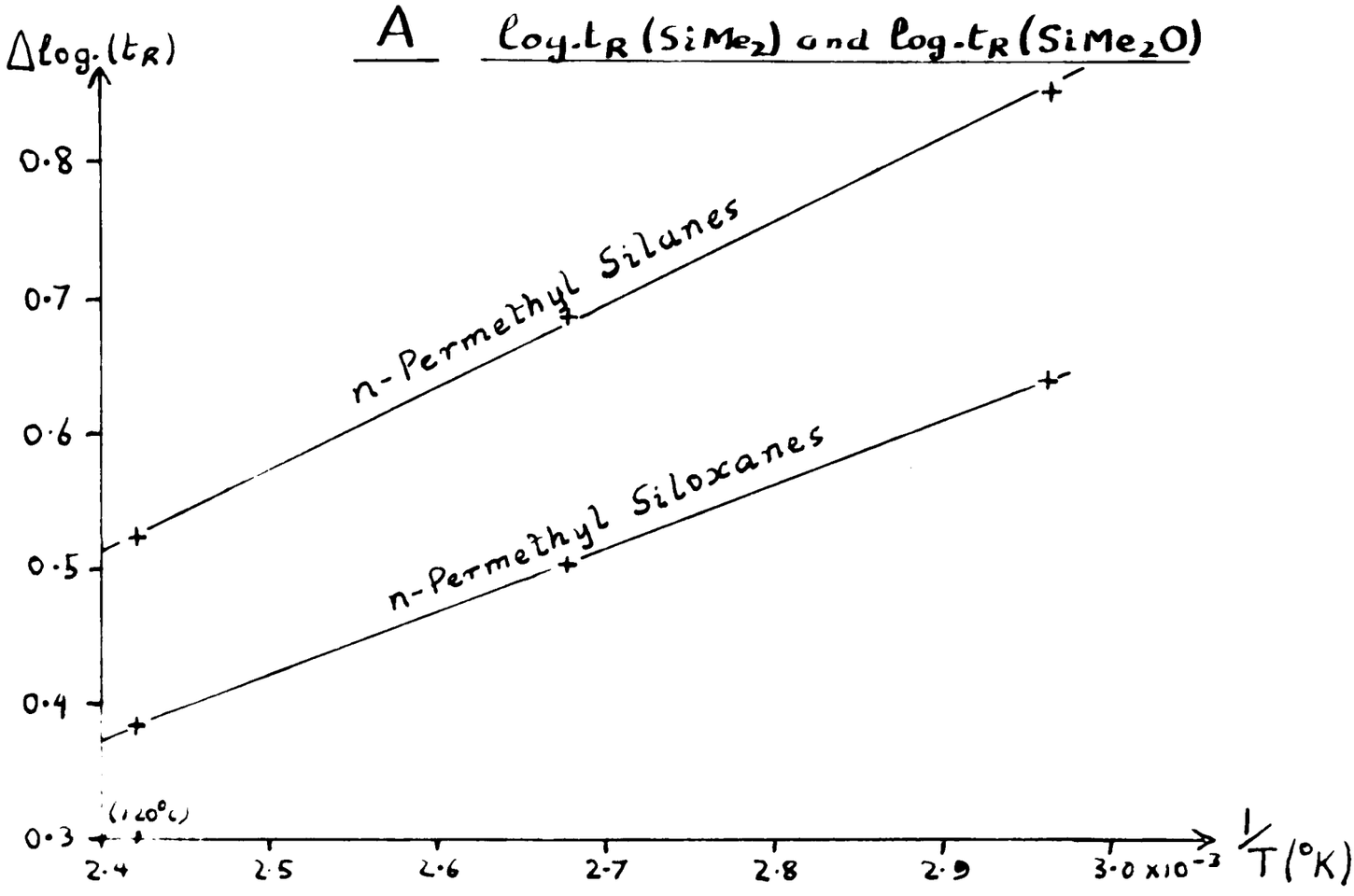


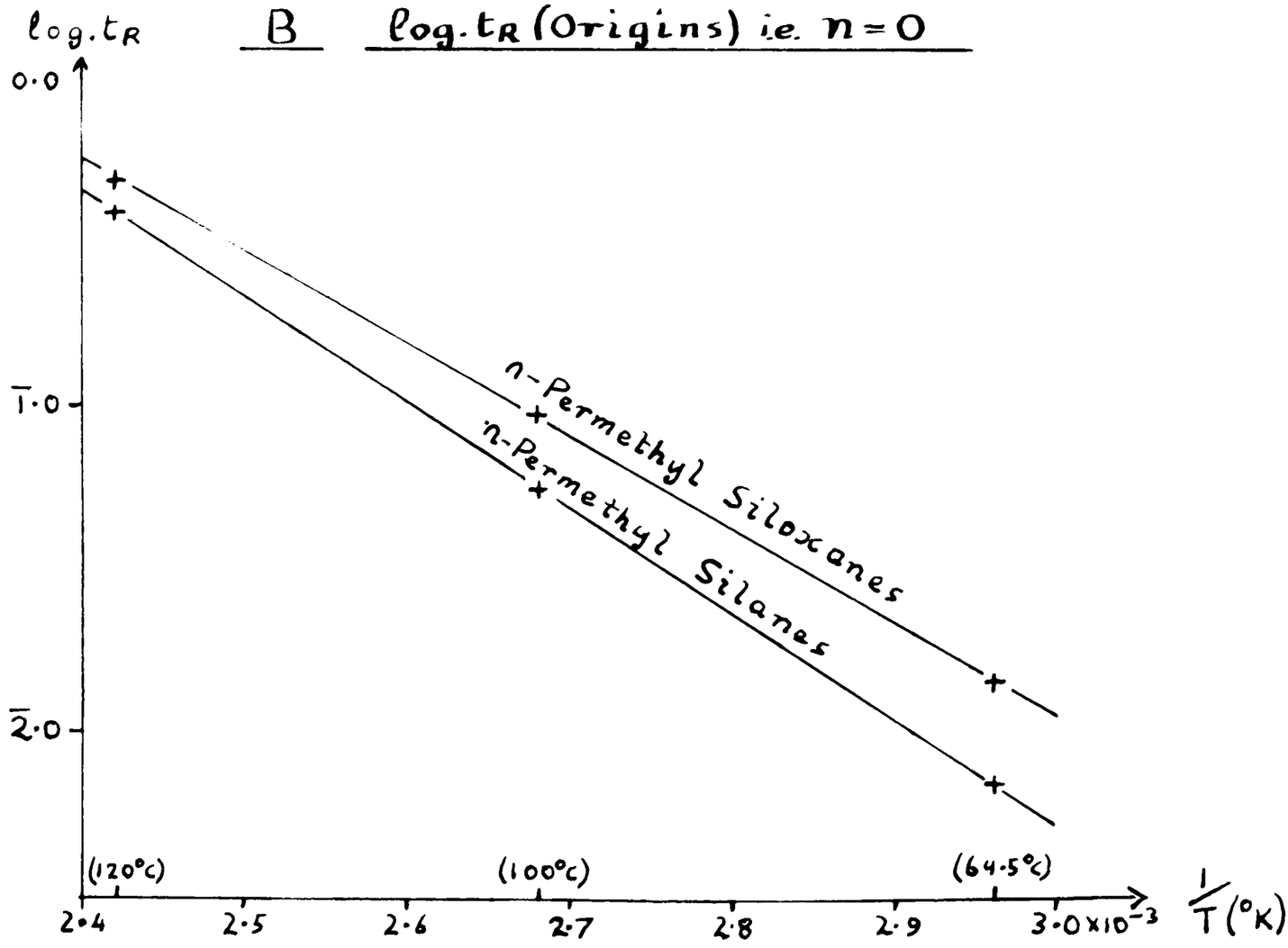
coupling reaction, and that the mercury was probably assisting the reaction by amalgamating the metal surfaces (cf. Section 3.22).

5.3 Coupling Experiments with Mixtures of $SiMe_3Cl$ and $SiMe_2Cl_2$

Since potassium gave a better yield than sodium in the coupling reactions of $SiMe_3Cl$, it was decided to repeat the experiments of Kumada et al.[24] and Andrews[32] on the coupling of mixtures of $SiMe_3Cl$ and $SiMe_2Cl_2$, but using potassium instead of sodium. The preliminary chromatography of products was carried out on the first apparatus, but this was found to be suitable only for the compounds up to and including n-Si_4Me_{10} (see Appendix 2). A commercial chromatograph (Perkin-Elmer Model F11) equipped with a flame ionisation detector was available. This was fitted with a column containing a silicone elastomer as the stationary phase. The products of the coupling reactions and their 'blank' runs were chromatographed on this instrument. Runs were carried out at successively higher temperatures, their approximate quantitative patterns being used for identification between runs at the different temperatures. Plots of the $\log.t_R$ values (n-permethyl hexasiloxane, $t_R = 100$) of the more significant products against the supposed number of silicon atoms in their chains are shown in Figs. 34, 35, 36. (The identities of the N- and cyclo-permethyl siloxanes being established by synthesis). As a check for these assumptions the values of $\log.t_R(-SiMe_2-)$ for the permethyl silanes and $\log.t_R(-SiMe_2.O-)$ for the n-permethyl siloxanes were plotted against $\frac{1}{T}$ ($^oK.$), see Fig. 37A, and the t_R values of the extrapolated origins (i.e. Si_o) for both series were plotted

FIG. 37 Silicone Rubber Column - Comparative Results





against $\frac{1}{T}$, see Fig. 37B. The first of these plots should give straight lines, the slopes of which would be equal to the difference in heats of solution of adjacent homologues of the two series (see Section 2.73), and would therefore imply correct identification of the separate homologous series. The second plots should similarly give straight lines, based on subtraction of heats of solution between the series, and any discontinuity would imply an incorrect identification within a series, e.g. Si_4Me_{10} instead of Si_5Me_{12}. It can be seen therefore that the results plotted in Figs. 34, 35, 36 are self consistent. A sample of Si_2Me_6 from one of the preparations in the previous section was used to identify Si_2Me_6 on Fig. 34.

Thus the permethyl silanes up to Si_6Me_{14} appeared to be present in the reaction mixtures investigated, but Si_7Me_{16} did not appear to be present. This could have been due to an inadequate distillation temperature or inadequate vacuum in the extraction of the products from the stainless steel bombs.

Approximate quantitative results were obtained from the chromatograms, by dividing the peak areas by the number of carbon atoms in the molecules. The values, in molar percentages of the volatile permethyl silanes, are given in Table 13A, Runs 1 and 2. In each of the reactions a certain amount of brown polymeric material was found. This would explain the apparent loss of $SiMe_2$ groups in these results.

It was found that, contrary to the coupling reactions using sodium[24,32], where successive products with longer chains were prepared in decreasing amounts, in the reactions described here, Si_3Me_8 was prepared in lower amounts than n-Si_4Me_{10}. This may be due to the reported higher reactivity

TABLE 13

Products of Wurtz Reactions on Mixtures of Methyl Silicon and Germanium Chlorides Expressed as Percentages of Permethyl Silanes and Germanes Extracted By Vacuum Distillation ½ hr. at 150°C.

A. $SiMe_3Cl$ + $SiMe_2Cl_2$ with Potassium

Experiment	1	2	3
$SiMe_3Cl$: $SiMe_2Cl_2$	4 : 1	2 : 1	1 : 1
Temperature	110°C	150°C	125°C
Time	23 hrs	24 hrs	36 hrs
Approx. Percentage of Silanes in Volatile Products	80-85	85-90	90
$SiMe_4$	?	?	tr
Si_2Me_6	85.5	59.0	38.1
Si_3Me_8	3.5	7.5	6.9
n-Si_4Me_{10}	10.6	30.0	50.0
n-Si_5Me_{12}	0.4	3.4	5.0
n-Si_6Me_{14}	0.02	0.1	tr?

B. $GeMe_3Cl$ + $GeMe_2Cl_2$ + $GeMeCl_3$ with Potassium ($GeMe_4$ Marker)

Experiment	1	2
$GeMe_3Cl$: $GeMe_2Cl_2$: ($GeMeCl_3$)	6.6:1:0.12	1.2:1:0.15
Temperature	125°	125°
Time	24 hrs	36 hrs
Ge_2Me_6	84.9	54.1
Ge_3Me_8	14.4	36.7
Ge_4Me_{10}	0.7	9.2
Ge_5Me_{12}		Possibly tr.
Approx. Percentage of Germanes in Volatile Products	97	99

of Si_2Me_5Cl than $SiMe_3Cl$ to potassium[134], as the former compound was a possible intermediate and would be required for the formation of both compounds, whereas with the overall lower reactivity to sodium this effect might not be so noticeable.

Unfortunately, further investigations using the Perkin-Elmer chromatograph were not possible as deposits of silica and similar materials on various components of the detector had a deleterious effect on its performance and ultimately lead to an electrical insulation breakdown, despite efforts to remove the deposits from the detector. As replacement was expensive, further work was deferred until such time as the New Apparatus was completed, when accurate quantitative measurements would also be possible.

5.4 Experiments Using the New Apparatus

5.41 Preparation of the Permethyl Silanes and Germanes

A further coupling experiment was carried out using potassium on an approximately equimolar mixture of $SiMe_3Cl$ and $SiMe_2Cl_2$ in an attempt to obtain higher yields of the higher-boiling permethyl silanes. The products were analysed on the analytical system of the New Apparatus and the results are shown on Table 13A, Run 3.

In this run, and all the later preparative runs described in this and the next chapter, for the quantitative analysis of the products, a chromatographic technique similar to that used for the gold chloride analyses was employed since it offered easy measurement of the peaks of

both the lower and higher-boiling compounds. This was repeated on the 'washed' products and the results were compared with isothermal chromatograms carried out at column temperatures of 60° or 90°C for identification by logarithmic retention measurements.

The volatile products of this preparation (Table 13A, Run 3) contained about 10% of impurities, largely the n- and cyclo-permethyl siloxanes and some $SiMe_3Cl$ but no $SiMe_2Cl_2$. Again, there was a reasonable amount of polymeric material as indicated by the product ratio. A small yield of a product believed to be $SiMe_4$ was obtained. This rather unexpected result is discussed in Section 5.5.

A similar coupling reaction was attempted with the methyl germanium chlorides. This type of mixed reaction with germanium had not been previously reported. As all the reactions for the preparation of the methyl germanium chlorides described in Chapter 3 had resulted in mixtures, it was decided to use a mixture containing some $GeMe_4$ as a marker compound for the reaction. This mixture had the following composition: 14.2% (Molar) $GeMe_4$, 73.4% $GeMe_3Cl$, 11.1% $GeMe_2Cl_2$ and 1.3% $GeMeCl_3$. After reaction with excess potassium for 24 hours at 125°C a mixture with the following composition was recovered: 29.2% $GeMe_4$, 57.3% Ge_2Me_6, 9.7% Ge_3Me_8, 0.5% n-Ge_4Me_{10}, 3.3% $GeMe_3Cl$. There were no other products in measurable amounts, and only the $GeMe_3Cl$ was removed by the 'washing' technique. These results, expressed in terms of the total yield of permethyl germanes, are given as Run 1 in Table 13B. Assuming that no $GeMe_4$ was formed in the reaction (but see Section 5.5) these results are consistent with formation of polymer, from about 16% of the methyl germanium chlorides, having an average empirical formula

$(GeMe_3)_9.(GeMe_2)_9.(GeMe)_2$. It is seen that no product corresponding to iso-Ge_4Me_{10} was prepared from the $GeMeCl_3$ and that therefore all of this chloride had presumably reacted to form polymer. This is discussed in Section 5.5.

A second coupling experiment was carried out on a mixture with a higher proportion of $GeMe_2Cl_2$ (and $GeMeCl_3$) in an attempt to obtain higher yields of the tri- and tetragermanes. Using a longer reaction time, reaction was virtually complete, with only a trace of $GeMe_3Cl$ remaining. Only one extra compound was observed, which was believed for a while to be iso-Ge_4Me_{10}, but was subsequently found to disappear on 'washing' the mixture. This was present only to the extent of about 0.6%. The analysis of the products is shown as Run 2 on Table 13B, which can be fairly directly compared with the silicon Run 3 (Table 13A). Again, on the basis of a $GeMe_4$ marker, it can be deduced that about 46% of the methyl germanium chlorides, including all of the $GeMeCl_3$, reacted to form a polymer, the average empirical formula of which was $(GeMe_3)_2.(GeMe_2)_4.GeMe$..

The polymeric products of these reactions appeared as brown waxy flakes on reaction of the residual potassium in the bombs with water.

5.42 Analysis of Some Permethyl Silanes and Permethyl Germanes

Samples of the permethyl silanes and permethyl germanes were purified in the preparative system of the New Apparatus, in each case by a four stage operation on alternate columns. The samples obtained in this way were of the order 1 to 25 mg.. In accordance with the conclusions of Section 4.4, these samples were reacted in the gold chloride system under

TABLE 14

The Gold Chloride Analysis of Si_2Me_6 and Si_3Me_8

A. Si_2Me_6

Run : Column	1.TTP	2.TTP	3.702
Cell Temperatures	30°/30°C	31°/31°C	32°/32°C
Sample Size (μM)	3.6	3.5	3.6
Sensitivity	0.200	0.200	0.200
Products (M.U.) -			
MeCl	3.3	2.0	2.1
$SiMe_3Cl$	35.8	34.9	35.2
$SiMe_2Cl_2$	0.6	0.4	1.4
Empirical Ratios -			
Si = 1 Me:	3.07	3.05	3.01

B. Si_3Me_8

Run : Column	1.TTP	2.TTP	3.TTP	4.702
Cell Temperatures	32°/32°C	32°/32°C	33°/33°C	32°/32°C
Sample Size (μM)	2.7	3.6	3.5	3.9
Sensitivity	0.250	0.125	0.125	0.125
Products (M.U) -				
MeCl	0.5	0.2	0.2	0.3
$SiMe_3Cl$	33.8	22.6	21.9	22.3
$SiMe_2Cl_2$	11.3	8.1	8.2	11.0
Empirical Ratios -				
Si = 1 Me:	2.76	2.74	2.74	2.68
Si = 3 Me:	8.28	8.23	8.20	8.04

mild conditions so that both empirical and structural formulae could be deduced. As the preparation and identification of these parent compounds had already been reported (see Section 1.31), these analyses were treated, to an extent, as part of the development of the analytical method, to see what conditions would be required for the analysis of the new series of permethyl silico-germanes (see Section 6.4 ff). In principle, the tritolyl phosphate column offered the best separation of the methyl silicon chlorides (see Fig. 25, Section 2.65) and therefore this column was initially selected for the analysis of the products from the permethyl silanes. However other operational requirements, described below, showed that this was not a suitable column for this work and it was mainly used for qualitative analysis of the products.

Treatment of the compound believed to be Si_2Me_6 in the gold chloride system under mild cell conditions showed that the major product was $SiMe_3Cl$, with $SiMe_2Cl_2$ and MeCl as minor products (see Table 14A). No other products were observed. The first two runs, carried out on the tritolyl phosphate column showed that considerably more MeCl than $SiMe_2Cl_2$ was apparently produced, the third run on the Silicone 702 column showing a similar, but much reduced, effect. This was believed to be due to the presence of moisture in the columns which would be expected to react with both of the silicon compounds, but to a greater extent with $SiMe_2Cl_2$[45]. The larger amount of this compound in the analysis on the Silicone 702 column was originally thought to be due to the presence of less moisture. As a result of this effect, the methyl : silicon ratios obtained using the tritolyl phosphate column were about 2% higher than would be expected for a compound with the formula Si_2Me_6, but the ratio

obtained using the Silicone 702 column was much closer to the expected value. The presence of $SiMe_3Cl$, a compound chromatographically distinct from the parent compound, as the sole major product, clearly indicated that $SiMe_3$- groups were the only structural feature of the parent compound, and in view of the tetravalency of silicon the only possible structure of the parent was $SiMe_3.SiMe_3$.

The compound believed to be the next homologue in the permethyl silane series, Si_3Me_8, on treatment in the gold chloride system yielded the same three products. However, in this case, $SiMe_2Cl_2$ was a major product (see Table 14B). The yields of $SiMe_2Cl_2$ relative to $SiMe_3Cl$ obtained when the products were chromatographed using the tritolyl phosphate column were again lower than the yield when the Silicone 702 column was employed, despite the prior passage of large samples of $SiMe_2Cl_2$ through both columns. As a result, the ratio of methyl groups to silicon was apparently between 2½% and 3½% higher than would be expected for a parent compound Si_3Me_8 when the tritolyl phosphate column was used, but only ½% higher than expected using the Silicone 702 column. Structurally, the formulae apparently obtained using the tritolyl phosphate column were in the range $(SiMe_3)_{2.8-3.1}.SiMe_2$ and using the silicone column, $(SiMe_3)_{2.1}.SiMe_2$. However, it is impossible to visualise a compound with only $SiMe_3$- and -$SiMe_2$- structural units with a ratio of $SiMe_3$- to -$SiMe_2$- groups greater than 2 : 1 and the compounds with this ratio are $SiMe_3.SiMe_2.SiMe_3$.

From this analysis and the analysis of Si_2Me_6, it is seen that the Silicone 702 column enabled the more accurate results to be obtained. In view of the conditioning runs with $SiMe_2Cl_2$ it was unlikely that much

TABLE 15

The Gold Chloride Analysis of n-Si_4Me_{10}

Run : Column	3.TTP	4.TTP	5.702
Cell Temperatures	95°/95°C	95°/95°C	94°/94°C
Sample Size (μM)	1.9	3.1	3.5
Sensitivity	0.250	0.250	0.250
Products (M.U) -			
MeCl	0.7	0.8	0.8
$SiMe_3Cl$	23.0	37.7	36.4
$SiMe_2Cl_2$	15.3	26.9	35.6
(Possibly) Si_2Me_5Cl	tr	tr	-
Empirical Ratios -			
Si = 1 Me:	2.62	2.59	2.52
Si = 2 Me:	5.23	5.19	5.03

moisture would have remained in the system, although it was possible that some might have been introduced with the sample of parent from the preparative system. On these grounds it was presumed that actual reaction of $SiMe_2Cl_2$ was taking place to a certain extent with the column material in the tritolyl phosphate column and, therefore, in spite of all precautions it would be impossible to obtain much more than qualitative analyses using this column.

In preliminary experiments with the gold chloride reaction on the compound believed to be n-Si_4Me_{10} it was found that under similar reactor conditions to those employed for the analyses of the two previous compounds, in addition to the major products $SiMe_3Cl$ and $SiMe_2Cl_2$ and the minor product MeCl, there were small amounts prepared of three other compounds, distinct from the parent compound, appearing between the major products and the parent on the chromatograms. In view of the incomplete bromination of Si_4Me_{10}, achieved by zu Stolberg[109] under mild conditions, giving $SiMe_3.SiMe_2Br$, $SiMe_3.SiMe_2.SiMe_2Br$ and $BrSiMe_2.SiMe_2Br$, it was believed that the products obtained in these runs were the chloro equivalents. Accordingly the cell temperature was raised until only a trace of the most persistent of the three compounds was prepared, before attempting quantitative analysis. The results (Table 15) showed that low $SiMe_2Cl_2$ analysis were again obtained using the tritolyl phosphate column, although the effect was reduced if large samples were used. Analysis on the Silicone 702 column, however, was consistent with an empirical formula Si_2Me_5 although, as before, the methyl analysis was a little low. The approximate equality of the amounts of the two major products indicated a 1 : 1 ratio of $SiMe_3$- to - $SiMe_2$- groups in the parent.

TABLE 16

The Gold Chloride Analysis of Ge_2Me_6 and Ge_3Me_8

A. Ge_2Me_6

Run : Column	1.TTP	2.702	3.702	4.702
Cell Temperatures	46°/72°C	46°/72°C	30°/30°C	30°/30°C
Sample Size (μM)	1.1	1.3	1.8	2.8
Sensitivity	0.250	0.250	0.250	0.250
Products (M.U.) -				
MeCl	1.20	1.46	1.33	2.61
$GeMe_3Cl$	12.24	14.72	20.24	32.00
$GeMe_2Cl_2$	1.30	1.73	1.80	3.08
Empirical Ratios -				
Ge = 1 Me:	2.99	2.99	2.98	2.99

B. Ge_3Me_8

Run : Column	1.702		2.702		3.TTP	
Cell Temperature	30°/30°C		30°/30°C		30°/30°C	
Sample Size (μM)	1.0		1.1		1.0	
Sensitivity	0.250		0.500		0.500	
Products (M.U.) -	(Δ)	(W)	(Δ)	(W)	(Δ)	(W)
MeCl	0.72	2.0	1.33	3.4	1.55	4.4
$GeMe_3Cl$	11.99	34.3	26.48	78.4	21.52	60.8
$GeMe_2Cl_2$	6.28	16.6	16.62	47.6	14.40	40.7
Empirical Ratios -						
Ge = 1 Me:	2.69	2.71	2.65	2.65	2.65	2.65
Ge = 3 Me:	8.09	8.14	7.94	7.95	7.93	7.93

Although both the empirical formula and the structural evidence would be equally applicable to $SiMe_3.SiMe_2Cl$ or n-Si_4Me_{10}, the chemical evidence, in particular the immunity of the parent to the 'washing' procedure, and the chromatographic evidence, clearly pointed to the second of these possible structures.

In all the permethyl silane analyses there was a certain amount of demethylation, indicated by the presence of MeCl among the products. This was sufficiently low not to affect the structural discussions. As this was taking place under milder cell conditions than those expected for the demethylation of either of the methyl silicon chlorides, it was concluded that it took place before the completion of the Si-Si bond fission.

When gold chloride analysis was carried out, under similar conditions to those employed for the analysis of Si_2Me_6, on the compound believed to be Ge_2Me_6, it was found that a slightly higher degree of demethylation took place. In this case, however, the quantities of $GeMe_2Cl_2$ were in better agreement with the MeCl analyses, whichever column was used. The fact that the amounts of $GeMe_2Cl_2$ were slightly higher than those of MeCl was probably due to a lower trapping efficiency for small amounts of the latter. The results obtained (Table 16A) were in good agreement with an empirical formula $GeMe_3$ and, even without allowance for demethylation, with a structural formula $GeMe_3.GeMe_3$.

The gold chloride analyses of the compound believed to be Ge_3Me_8 showed similar trends (see Table 16B). The results were calculated both by triangulation of peaks ($\triangle$) and by cutting out the peaks and weighing them (W). This was carried out as a check that the former method, which

was easier and enabled the chromatograms to be preserved, would be an adequate method for the analyses of the permethyl silico-germanes. Comparison of the results obtained using these two methods of measurement (see Section 2.74) showed only small relative variations (maximum $\pm 3\%$). The results of the analyses showed that the empirical formula of the parent was Ge_3Me_8. The presence of a ratio of $GeMe_3Cl$ to $GeMe_2Cl_2$ of just less than 2 : 1, as would be expected from the demethylation mainly occurring at $GeMe_3$- groups, as indicated by the absence of measurable quantities of $GeMeCl_3$, clearly showed that the structure of the parent compound was $GeMe_3.GeMe_2.GeMe_3$.

It is therefore seen that there was possibly slightly more demethylation in the gold chloride analysis of the permethyl germanes than in that of the permethyl silanes but apparently no reaction of $GeMe_2Cl_2$ with the tritolyl phosphate column. This latter effect, when compared with the reaction of $SiMe_2Cl_2$ might be explained in view of the lower reactivity of the germanium chlorides to ionic types of reaction, particularly hydrolysis[40].

5.43 Identification by Chromatography

The linear nature of the plots of logarithmic retention data against the number of atoms in the chain has already been demonstrated for the permethyl silanes (Section 5.3). Similar plots, showing both the permethyl silanes and permethyl germanes (as well as the permethyl silico -germanes) are shown in the next Chapter as Figs. 41, 42, and 47.

In the two series, the following members were identified by the gold chloride analytical technique:

$SiMe_4$, Si_2Me_6 , Si_3Me_8 and n-Si_4Me_{10}

$GeMe_4$, Ge_2Me_6 and Ge_3Me_8 .

Other compounds prepared in the respective preparations of the two series were similarly unreactive to the washing by concentrated sulphuric acid and their logarithmic retention values were very close to those predicted by extrapolation of the plots obtained with the known compounds, on both columns, and at all suitable column temperatures employed. Whilst this was only evidence of the heats of solution and solution vapour pressures of these compounds, the fact that the values were close to the predicted values on two columns of different polarity strengthens the evidence that the compounds in question were the next homologues in the two series.

On this basis, there is strong evidence that the following compounds were also present in the products of the reactions described in sections 5.3 and 5.41:

n-Si_5Me_{12} , n-Si_6Me_{14} and n-Ge_4Me_{10} , n-Ge_5Me_{12} .

5.5 Conclusions on the Coupling Reactions

It has been shown that the hitherto unknown Wurtz-Fittig coupling by potassium of mixtures of $GeMe_3Cl$ and $GeMe_2Cl_2$ gave appreciable yields of the permethyl germanes in amounts decreasing with increase of chain length in much the same way as the coupling by sodium of $SiMe_3Cl$ and $SiMe_2Cl_2$[24, 32]. The coupling of these silicon compounds by potassium, however, gave low yields of Si_3Me_8 and high yields of Si_4Me_{10}. This can be explained in terms of the observed high reactivity to potassium of

Si_2Me_5Cl compared with $SiMe_3Cl$[134] (see Section 5.3). The products of both of these preparative reactions, if incomplete, contained unreacted trimethyl chlorides only, indicating that the dimethyl dichlorides were more reactive to potassium. This would be expected from comparison of the conditions required for the coupling by sodium of $SiMe_3Cl$[72] and $SiMe_2Cl_2$[76]. The higher reactivity of the dimethyl dichlorides would explain the formation of polymer and the lower proportion of $-SiMe_2-$ and $-GeMe_2-$ groups found in the volatile products, compared to the proportion of the dimethyl dichlorides in the reactants; thus the initial stage of the reaction would be predominantly the formation of polymer consisting of $-SiMe_2-SiMe_2-$ and $-GeMe_2-GeMe_2-$ chains with occasional $SiMe_3-$ and $GeMe_3-$ end groups. This discussion is expanded in Section 6.21. The higher reactivity of $GeMe_2Cl_2$ compared to $GeMe_3Cl$ is supported by the apparently complete reaction of the $GeMeCl_3$, present in the reactants, to form polymer. It can therefore be assumed that this last compound was more reactive still.

In the third preparation of the permethyl silanes (Section 5.41), there was strong chromatographic evidence for the formation of some $SiMe_4$. This would not have been observable in the previous preparations, because of the high temperatures employed for the chromatography, and because the various impurities were not removed. A similar reaction may have taken place in the permethyl germane preparations, in which case the conclusions about the polymeric products of these reactions need not necessarily be correct. If such a reaction did take place, and there was strong evidence of this in the permethyl silico-germane preparations (see Section 6.2), then it was possibly due to the formation of some

potassium methyl which could react with $SiMe_3Cl$.

CHAPTER SIX

THE PERMETHYL SILICO - GERMANES

6.1 Introduction

The first member of the series of permethyl silico-germanes, $SiMe_3.GeMe_3$, was prepared (together with Si_2Me_6 and Ge_2Me_6) in 1965 by Mironov and Kravchenko[35], by the coupling of a mixture of $GeMe_3Br$ and $SiMe_3I$ with potassium. Identification was carried out 'by chromatography'. This work followed the preparation of $SiEt_3.GeEt_3$, using a similar method by Shackleford et al. in 1963[64].

Wurtz-Fittig coupling of mixtures of $SiMe_3Cl$ and $SiMe_2Cl_2$[24, 32] has been shown to prepare the n-permethyl silanes up to n-$Si_{12}Me_{26}$[27] and, in this work, a similar reaction with $GeMe_3Cl$ and $GeMe_2Cl_2$ has been shown to prepare the n-permethyl germanes, up to n-Ge_5Me_{12} at least. It was therefore considered probable that mixtures of $SiMe_3Cl$, $SiMe_2Cl_2$, $GeMe_3Cl$ and $GeMe_2Cl_2$ would be coupled by potassium to yield the general series $Si_nGe_mMe_{2(n+m)+2}$ consisting of the permethyl silanes (m = 0), the permethyl germanes (n = 0) and the permethyl silico-germanes. Omission of one or more of these reactants should lead to the preparation of sub-groups within the general series, having the appropriate omission of structural units, providing that no exchange of alkyl groups took place.

It was apparent that a particular form of isomerism would occur within the permethyl silico-germane series as each position in the chains could be occupied by either a silicon or a germanium atom: Thus there would be four possible isomers with the formula n-$Si_2Ge_2Me_{10}$. These are given

below together with their diagrammatic structures which have been chosen, in the interests of brevity and clarity, as suitable abbreviations for the text:

$SiMe_3.GeMe_2.GeMe_2.SiMe_3$ = O–●–●–O

$SiMe_3.SiMe_2.GeMe_2.GeMe_3$ = O–O–●–●

$SiMe_3.GeMe_2.SiMe_2.GeMe_3$ = O–●–O–●

$GeMe_3.SiMe_2.SiMe_2.GeMe_3$ = ●–O–O–●

This form of isomerism will be called 'Positional Isomerism'.

Conventional analytical methods would suffice for the determination of the molecular formulae of the permethyl ailico-germanes, provided they were obtainable in reasonable yields, but would be unable to determine their structures, with the exception of O–●. On the other hand, the low temperature gold chloride technique as employed on the permethyl silanes and permethyl germanes (see Section 5.42) would be able to determine the empirical formulae of all the possible permethyl silico-germanes with up to four atoms in the chain, with the exception of the pair of compounds, O–O–●–● and O–●–O–●. The structures of any branched chain compounds prepared could similarly be determined. The gold chloride technique had the additional advantage over conventional analytical methods that three separate structural determinations, as well as a 'conditioning' run and a sample purity check, could be carried out on a total sample of around 3 micromoles (approximately 1 mg. of $Si_2Ge_2Me_{10}$). Therefore compounds prepared in concentrations of the order of 0.5% in reaction mixtures could be separated and identified from total samples of 250 mg. after allowing for wastage of 25% in the purification procedure.

TABLE 17

Wurtz-Fittig Reactions of Potassium on Methyl Silicon Chlorides and Methyl Germanium Chlorides.

Run	1	2	3
Approximate Initial Composition (Molar %)			
$SiMe_3Cl$	74.0	-	21.4
$SiMe_2Cl_2$	-	43.6	19.4
$GeMe_4$	1.4	4.7	2.0
$GeMe_3Cl$	11.4	32.9	24.9
$GeMe_2Cl_2$	11.6	16.3	28.4
$GeMeCl_3$	1.6	2.5	3.9
Reaction Conditions	130°C 25 hrs.	130°C 28 hrs.	130°C 24 hrs.
Approximate % Reaction	90-93	92-95	90-95
Products in Molar % of Volatiles			
O	2.4	9.0	12.6
●	4.3	45.4	19.7
O-O	59.1	1.0	8.3
O-●	27.9	1.6	5.6
●-●	0.3	20.6	23.2
O-O-O	0.4	0.3	2.0
O-●-O	1.6		0.6
O-O-●		1.2	6.5
O-●-●	0.9		1.3
●-O-●		10.5	3.1
●-●-●	0.3	4.1	8.1
O-O-O-O	0.3	0.4	1.1
O-O-●-O	tr		0.6
O-O-O-●		0.4	1.2
O-●-●-O	1.5		0.2
(O-O-●-●)			
(O-●-O-●)			1.2
●-O-O-●		3.1	1.1
O-●-●-●	0.2		0.4
●-O-●-●		1.5	1.2
●-●-●-●	0.8	0.9	2.0

6.2 Preparation of the Permethyl Silico-Germanes

Preparations were carried out using similar techniques to those employed for the preparation of the permethyl silanes and permethyl germanes (see Sections 2.51, 5.3 and 5.41). Small samples of the products were chromatographed on both columns in the analytical system. The products were 'washed' using the technique of Section 5.1 and samples were again chromatographed. On comparing the two sets of chromatograms, little or no relative loss was observed of the permethyl silanes, permethyl germanes and the products subsequently shown to be the permethyl silico-germanes. The relative amounts of these products were estimated from several chromatographic runs, as the minor products were not always observed in measurable quantities on the low-sensitivity runs required for accurate measurement of the major peaks. The results obtained for the three preparations carried out are shown in Table 17.

In the first preparation it was intended to attempt the preparation of the permethyl silico-germanes with silicon in a terminal position only, using a reaction mixture essentially consisting of 6 parts of $SiMe_3Cl$ to one part each of $GeMe_3Cl$ and $GeMe_2Cl_2$. The excess of $SiMe_3Cl$ was added in an attempt to minimise permethyl germane formation in the event of this being a preferred reaction to the formation of Si-Ge bonds. The expected products up to Ge_4Me_{10} were:

O-O, O-●, ●-●, O-●-O, O-●-●, ●-●-●, O-●-●-O, O-●-●-● and ●-●-●-●.

On chromatography of the products of the reaction, peaks that would be expected to correspond to compounds of these complexities (see Section 6.3) were found, but in addition there were traces of $SiMe_4$, Si_3Me_8 and Si_4Me_{10}, the latter two indicating that $-SiMe_2-$ or $SiMe_3.SiMe_2-$ intermediates

were formed. It was also uncertain whether the increased proportion of $GeMe_4$ in the products, compared with the reactants, was entirely due to the reduction in the quantity of volatile products because of polymer formation, or whether a similar reaction to that leading to $SiMe_4$ formation had taken place. If the formation of $SiMe_4$ (and possible $GeMe_4$) had taken place, as suggested in Section 5.5, via potassium methyl, the formation of this compound from $SiMe_3Cl$ or Si_2Me_6 could leave intermediates suitable for the preparation of the higher permethyl silanes. The implication of this type of reaction was that in addition to the expected permethyl silico-germanes in these preparations, their positional isomers would also be expected to be present in small amounts. This was found to be the case (see Section 6.5 ff.). In the first preparation it was estimated that almost all of the $GeMe_3Cl$, but only about 20% of the $GeMe_2Cl_2$ (and none of the $GeMeCl_3$), had reacted to form volatile products.

In the second preparation it was intended to produce the permethyl silico-germanes with silicon as $-SiMe_2-$ groups only. The expected products were therefore:

●–●, ●–O–●, ●–●–●, ●–O–O–●, ●–O–●–O and ●–●–●–●.

In view of the success of the first reaction, a high proportion of the methyl germanium chlorides was used; the reaction mixture effectively consisted of about 3 parts of $SiMe_2Cl_2$ to 2 of $GeMe_3Cl$ to one of $GeMe_2Cl_2$.

Peaks corresponding to the complexities of the anticipated products were found on the chromatograms, but in addition there appeared to be a large amount of $SiMe_4$ and smaller quantities of the other permethyl silanes, some of the compound believed to be O–●, some of a compound with the expected complexity Si_2GeMe_8 (but not the compound prepared in reaction 1)

which was therefore probably O–O–●, and some of a presumed Si_3GeMe_{10} isomer, probably O–O–O–●. Thus it appeared that the presumed action of potassium methyl was accentuated in this reaction and it would therefore be expected that in addition to the desired silico-germanes there would be an appreciable amount of their positional isomers present. This was confirmed in the structural analyses of these compounds.

In the third preparation it was decided to produce the entire range of compounds, as this was the only possible way of producing all the permethyl silico-germanes not deliberately obtained as major products in the two previous preparations. These compounds were:

O–O–●, O–O–O–●, O–O–●–O, O–O–●–● and O–●–O–●.

The four main reactants were present in approximately equal amounts, but on examination of the products it was found that the following compounds, as they were subsequently identified, were prepared in relatively small amounts:

O–●–O, O–●–●, O–O–●–O, O–●–●–O, O–●–●–● and possibly O–●–O–●, i.e. all the compounds with $-GeMe_2-$ groups with the possible exception of O–O–●–● and with the exception of ●–●–●, ●–O–●–● and ●–●–●–●. Although it could be seen that all the compounds prepared in small quantities could be considered to be derived from O–●– units, some study of the course of the coupling reaction was required to see why this should be so (see next Section).

In this third preparation there appeared to be a considerable amount of reaction to form $SiMe_4$, and in this case, almost certainly some $GeMe_4$. It would appear that the amount of $SiMe_4$ prepared in each of the reactions was roughly proportional to the proportion of methyl germanium chlorides.

This would be indicated by the very small extent to which this was presumed to happen in the purely permethyl silane preparation (see Section 5.5), and could be explained in terms of an easier fission by potassium of Ge-Me bonds compared with Si-Me bonds.

6.21 A Tentative Explanation of the Yields Obtained from the Mixed Coupling Reaction

The treatment described here omits the postulated action of potassium methyl. It can be seen that although this type of action was undoubtedly significant, when related to the coupling as a whole, including polymer formation, it probably represented less than 10% of the reactions that took place. The effect on product ratios of this type of action would be expected to be particularly small in the third preparation, since all four reactants of interest were present in approximately equal amounts.

As has already been suggested in Section 5.5, the governing factor in the preparation of the permethyl silanes and permethyl germanes is likely to be the formation of polymer, principally in the early parts of the reactions. If it can be assumed that the coupling reactions take place effectively in stages, which would be the case as long as any intermediates with more than one silicon or germanium atom were not vastly more reactive than the methyl silicon and germanium chlorides, then a reasonable estimate of the reactions may be made. In this treatment, only the intermediates with one or two silicon or germanium atoms are considered. These intermediates could be radicals, potassium compounds or chlorides, or mixtures of these. A modified form of the structural shorthand used so far is employed here to describe them: Thus O– indicates

Me_3SiCl and/or Me_3SiK and/or $Me_3Si^{\bullet}$, and -●-●- indicates (K,Cl or $^{\bullet}$) $-GeMe_2-GeMe_2-$(K,Cl or $^{\bullet}$) and all possible mixtures.

In the preparation of the permethyl silanes, the following intermediate schemes may be considered, where R represents any methyl silane intermediates:

1/ -0- $\xrightarrow{+R}$ Products

2/ -0- + -0- $\longrightarrow$ -0-0- $\xrightarrow{+R}$ Products

3/ 0- + -0- $\longrightarrow$ 0-0- $\xrightarrow{+R}$ Products

4/ 0- $\xrightarrow{+R}$ Products.

If it is considered that the reactions of type 1 mainly represent the first stages of 2 and 3, the following reactions between intermediates with one or two silicon atoms can take place.

a/ -0-0- + -0-0- $\longrightarrow$ -0-0-0-0- $\longrightarrow$ Mainly polymers

b/ -0-0- + -0-0 $\longrightarrow$ -0-0-0-0 $\longrightarrow$ Polymers and high-boiling volatiles

c/ -0-0- + -0 $\longrightarrow$ -0-0-0 $\longrightarrow$ Polymers and high-boiling volatiles

d/ 0-0- + -0-0 $\longrightarrow$ 0-0-0-0 Volatile

e/ 0-0- + -0 $\longrightarrow$ 0-0-0 Volatile

f/ 0- + -0 $\longrightarrow$ 0-0 Volatile

The order of reactivity to potassium, $SiMe_3Cl < SiMe_2Cl_2$, is possibly reflected in a reduced trend 0-0- < -0-0- . Since the former compounds presumably react via intermediates of the same type as the latter, and since Si_2Me_5Cl has been shown to react somewhat more rapidly than $SiMe_3Cl$ with potassium[134], a possible reactivity order of the four types of intermediates considered is:

$$0- \ll 0\text{-}0- < -0\text{-}0\text{-}0- < -0-.$$

This would give an initial rate of reaction order

$$f < e < d \sim c < b < a$$

as the intermediates with two silicon atoms would be formed rapidly. Since the faster reactions, tending to form polymers, would use a higher proportion of $SiMe_2Cl_2$ than $SiMe_3Cl$, and the concentration of -0-0- would probably fall off according to $[SiMe_2Cl_2]^2$ whereas that of 0-0- would fall off according to $[SiMe_2Cl_2]$, the rates of the reactions relative to (f) should be reduced in the following order:

$$a > b > c \sim d > e .$$

Consequently the volatile permethyl silanes would be progressively formed in relatively greater yields compared to the polymers until such time as effectively all the $SiMe_2Cl_2$ had been used up, when (f) would become the sole reaction. This is supported by the fact that only $SiMe_3Cl$ remained unreacted in reactions over 90% complete.

In the preparations of the permethyl silanes, only small amounts of polymer were formed, and high yields of Si_4Me_{10} (and the higher volatiles) compared to Si_3Me_8 were obtained. This would be supported by a reactivity order:

$$0- \ll 0\text{-}0- < -0\text{-}0\text{-}0- < -0- .$$

However, in the preparations of the permethyl germanes, the high degree of polymer formation, and low yields of the higher members of the volatile series would support the reactivity order:

$$\bullet- < \bullet\text{-}\bullet- < -\bullet\text{-}\bullet\text{-}\bullet- < -\bullet- .$$

In the preparations of the mixed silicon-germanium series, it was probable that higher yields of polymer than those prepared in either of

the two separate series, were obtained. Total yields of the three and four membered chains compared to the two membered chains were in ratios between those obtained in the two separate series. Certain compounds (see previous Section) were obtained in low yields and in the third preparation the permethyl silanes appeared in considerably lower yields than the permethyl germanes.

Since the concentrations of the four reactants of interest were approximately equal in the third preparation of the mixed series, this preparation is used as the basis of the following discussion:

Comparison of the proportions of the reactants with the proportions of the appropriate groups in the volatile products gives the following result:

Reactants (%) $SiMe_3Cl$ 21, $GeMe_3Cl$ 25, $SiMe_2Cl_2$ 19, $GeMe_2Cl_2$ 28.

Products (%) $SiMe_3$- 32, $GeMe_3$- 57, -$SiMe_2$- 13, -$GeMe_2$- 11.

Therefore, as polymer formation is presumed to be the primary reaction, the reactivity order would be expected to be:

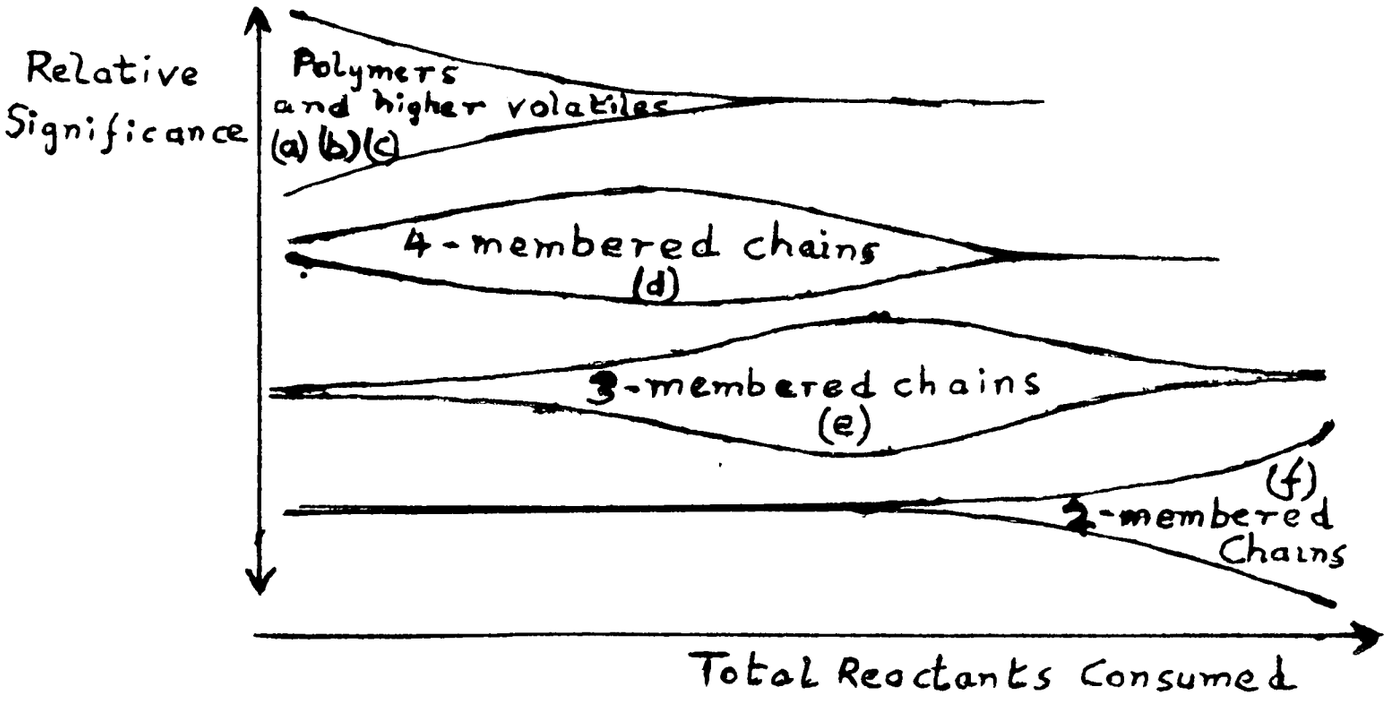
$$GeMe_3Cl < SiMe_3Cl < SiMe_2Cl_2 < GeMe_2Cl_2 .$$

This is not contradicted by the evidence obtained from the separate series and is in agreement with the fact that more $GeMe_3Cl$ than $SiMe_3Cl$ remained at the end of the reaction.

The preparation of the two membered chains has been postulated as mainly taking place towards the end of the reaction. In the third preparation, despite the lower amount of $SiMe_3Cl$ compared to $GeMe_3Cl$ that must have been present at the later stages of the reaction (see above), only a low yield of O-●, relative to O-O and ●-●, was obtained. This could be indicative of a generally higher affinity of silicon for silicon, and

germanium for germanium, than silicon for germanium. If this last hypothesis is accepted, then the relative yields of the products of the third preparation can be approximately explained.

The coupling reaction of the permethyl silanes and germanes has been already explained in terms of the relative rates of reactions types (a) to (f) where the slower reactions become progressively more significant as the dimethyl dichlorides are used up. Thus the reaction as a whole takes place in a series of overlapping stages, each slower than the previous one, which is shown in a crude form below:-



The polymer formation has been shown to consume the bulk of the $GeMe_2Cl_2$, rather less of the $SiMe_2Cl_2$, a smaller amount of the $SiMe_3Cl$ and only a little of the $GeMe_3Cl$. At this stage, the formation of the intermediates -O-O-, -O-● and -●-● would be expected to become relatively insignificant and the formation of O-O-, O-●, ●-O- and ●-● would become important. The relative amounts of reactants would be in the order:

$$GeMe_2Cl_2 < SiMe_2Cl_2 < SiMe_3Cl < GeMe_3Cl$$

and their reactivities, apart from the postulated Si-Si and Ge-Ge affinities, would be in the reverse order. Under these conditions it would be expected that ●-●- would be produced in the greatest amount, with approximately equal (and smaller) amounts of O-O- and ●-O- and a smaller amount still of O-●- . All of these intermediates would be expected to be more reactive than $SiMe_3Cl$ and $GeMe_3Cl$ (see above)[134] but since they resemble the trimethyl chlorides rather than the dimethyl dichlorides, they would be expected to have a similar order of reactivity:

●-●- ∽ O-●- < ●-O- ∽ O-O- .

Combining these two effects to obtain approximate rates of reaction, it can be seen that the intermediates would fall into three classes: ●-●- ; large amounts but relatively slow, ●-O- and O-O-; intermediate amounts but faster, O-●-; small amounts and slow. These three classes are denoted in the table below as +, o and - respectively. The postulated preferences of Si for Si and Ge for Ge over Si for Ge are denoted by + and - respectively. For the preparation of the four membered chains empirical values have been assigned as follows:

For the intermediates, + = 1.3, o = 1.0, - = 0.4,

and for the preferences + = 1.2, - = 0.8.

The products of these values are shown and compared with the actual yields obtained (figures in brackets).

Product	●-●-	-●-●	Preference	Prediction	Actual Yield
0-0-0-0	o	o	+	1.2	(1.1%)
0-0-0-●	o	o	+	1.2	(1.2%)
0-0-●-0	o	-	-	0.3	(0.6%)
0-0-●-●	o	+	-	1.0	(1.2% incl.0-●-0-●)
0-●-0-●	o	-	-	0.3	(1.2% incl.0-0-●-●)
●-0-0-●	o	o	+	1.2	(1.1%)
●-0-●-●	o	+	-	1.0	(1.2%)
0-●-●-0	-	-	+	0.2	(0.2%)
0-●-●-●	-	+	+	0.6	(0.6%)
●-●-●-●	+	+	+	2.0	(2.0%)

It can be seen that there is a good correspondence between predictions on this basis and the actual yields obtained, with the exception of 0-0-●-0.

The reactions between the two membered intermediates will be in competition with reactions between them and $SiMe_3Cl$ and $GeMe_3Cl$ (and derived intermediates). Although, as has been already indicated, this tends to become significant only in the later stages, the same values as those used above still give a reasonable prediction when considered together with the 0- and ●- intermediates. At this stage of the reaction there would be a large concentration of ●- (+) and a lower concentration of more reactive 0- (-). Assigning empirical values of 5.0 and 1.8, the following table is obtained:

Product	●-●-	-●	Preference	Prediction	Actual Yield
0-0-0	o	o	+	2.2	(2.0%)
0-0-●	o	+	-	4.0	(6.5%)
	o	o	+	2.2	
●-0-●	o	+	-	4.0	(3.1%)
0-●-0	-	o	-	0.6	(0.6%)
0-●-●	-	+	+	2.4	(1.3%)
	+	o	-	1.9	
●-●-●	+	+	+	7.8	(8.0%)

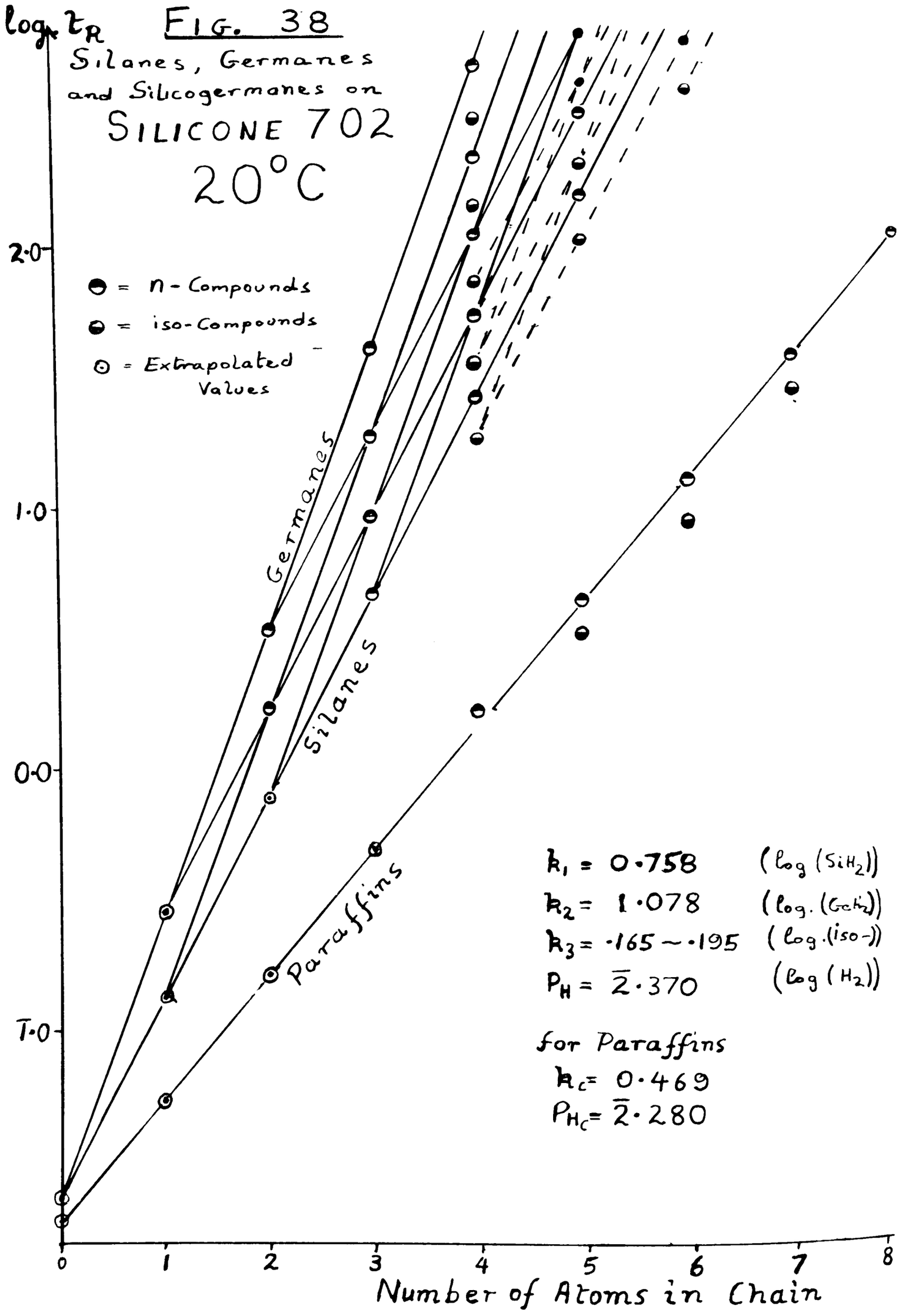
As can be seen, this is a reasonable prediction with the exception of 0-●-● where the prediction is three times the yield obtained. This is possibly explained by the fact that the reactions near the bottom of the table are those expected to be slow, and that at the stage of the reaction represented there might be very little 0-●- remaining.

The discussion and values may be applied to the formation of the two membered chains, but here the empirical values do not give very good results probably due to the late stage of the reaction:

Product	0-	-0	Preference	Prediction	Actual Yield
0-0	o	o	+	3.9	(8.3%)
0-●	o	+	-	7.2	(5.6%)
●-●	+	+	+	30.0	(23.2%)

These last results would seem to show that, as expected, significant amounts of Si_2Me_6 are prepared before much $SiGeMe_6$ or Ge_2Me_6 is formed.

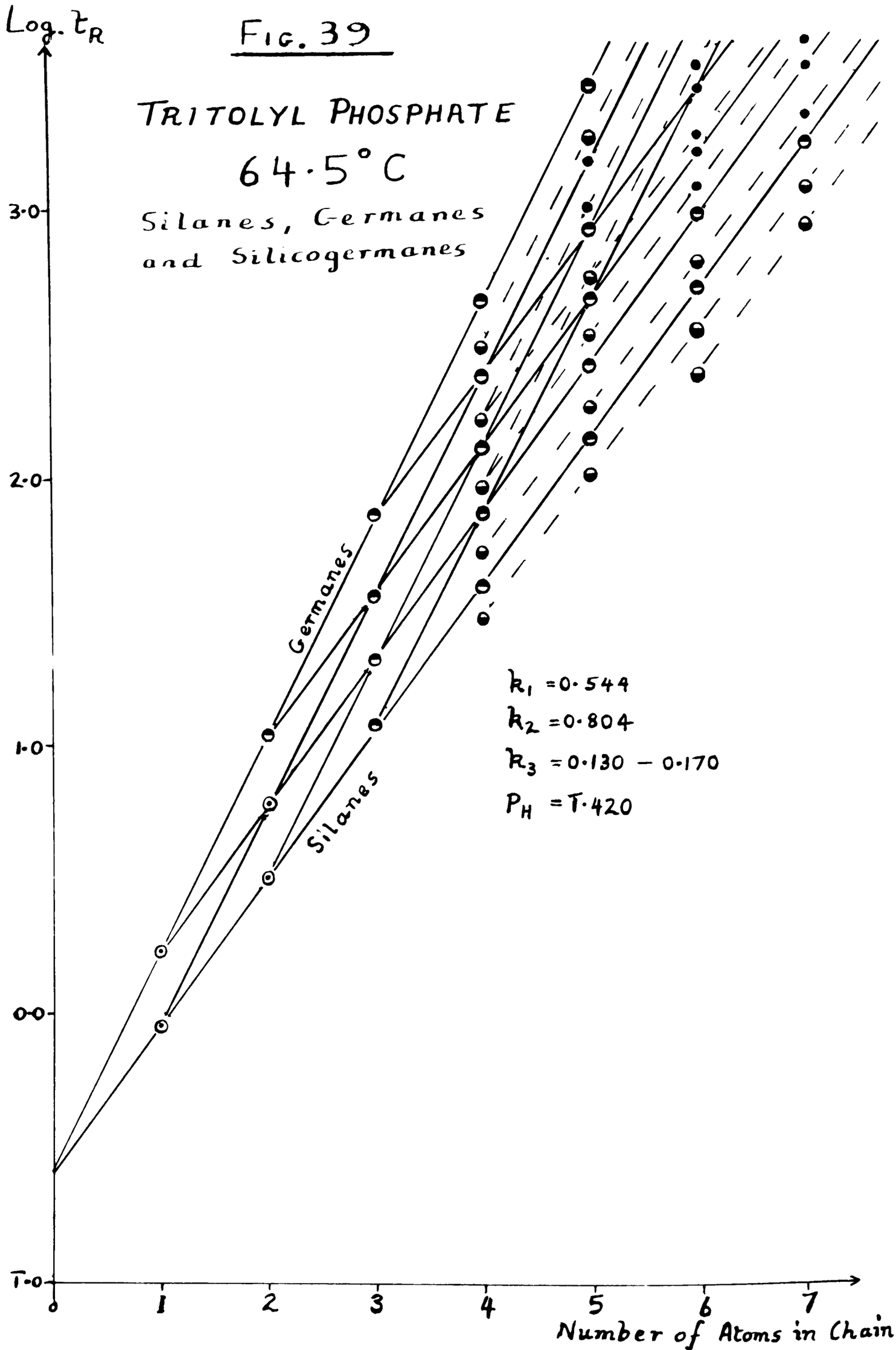
In conclusion it is seen that despite a static approach to a dynamic problem, reasonable predictions of the relative yields of the members of the mixed series may be made. The hypothesis of the way in which the


log. t_R
FIG. 38
Silanes, Germanes and Silcogermanes on
SILICONE 702
20°C
= n-Compounds
= iso-Compounds
= Extrapolated Values
Germanes
Silanes
Paraffins
2·0
1·0
0·0
T·0
0
1
2
3
4
5
6
7
8
Number of Atoms in Chain
k_1 = 0·758 (log (SiH_2))
k_2 = 1·078 (log. (GeH_2))
k_3 = ·165 ~ ·195 (log. (iso-))
P_H = $\bar{2}$·370 (log (H_2))
for Paraffins
k_c = 0·469
P_{H_c} = $\bar{2}$·280

overall reactions proceed seems to be borne out by the limited amount of experimental evidence.

6.3 Chromatography of the Silanes, Germanes and Silico-Germanes, and their Permethyl Derivatives

In the original work carried out by Timms and the Author[29-31] and the subsequent work by Andrews[32, 50] on the silicon-germanium hydrides, it was realised that these compounds together with the silanes and the germanes comprised a general series, $Si_nGe_mH_{2(n+m)+2}$, where, in their chromatographic behaviour in particular, they formed a near perfect 'Mixed Homologous Series': The straight line graphs obtained by plotting $\log.t_R$ or log.Vg values against the number, n, of atoms in the chains for both the series n-Si_nH_{2n+2} and the series n-Ge_nH_{2n+2} had a common origin (n = 0) at a 'Theoretical Hydrogen Point' (i.e. subtraction of $-SiH_2-$ from SiH_4 and $-GeH_2-$ from GeH_4). This was not an isolated phenomenon as it was found to apply to retention on different columns and at different temperatures (see Figs. 38, 39). This appears to be a unique phenomenon: It can be seen from Fig.38 that the 'Theoretical Hydrogen Point' (P_H) was not shared with the n-paraffins. The implications of the common origin for the silane and germane series were extensive: It was shown that the $\log.t_R$ or log.Vg values of the silico-germanes plotted against their chain lengths fell almost exactly on the predicted intermediate values between the silanes and germanes of the same chain length. Therefore all the possible homologous series within the general series had linear logarithmic plots parallel to either those of the


Log. t_R
FIG. 39
TRITOLYL PHOSPHATE
64·5° C
Silanes, Germanes
and Silicogermanes
3·0
2·0
1·0
0·0
T·0
Germanes
Silanes
k_1 = 0·544
k_2 = 0·804
k_3 = 0·130 – 0·170
P_H = T·420
0
1
2
3
4
5
6
7
Number of Atoms in Chain

silanes or those of the germanes, depending on whether the chains were increased by the addition of $-SiH_2-$ or $-GeH_2-$ units. In addition, in the type of rule that was suggested by this behaviour there appeared to be no stipulation as to the order in which these units were added to the chain, and therefore it was to be expected that positional isomers would be chromatographically coincident. This was subsequently shown to be the case, with a high degree of accuracy, in several instances. The branched chain compounds formed a similar, and almost equally regular, series, with plots almost parallel to those of the normal series, with retention times between 64% and 75%, depending on temperature and column, of their normal isomers.

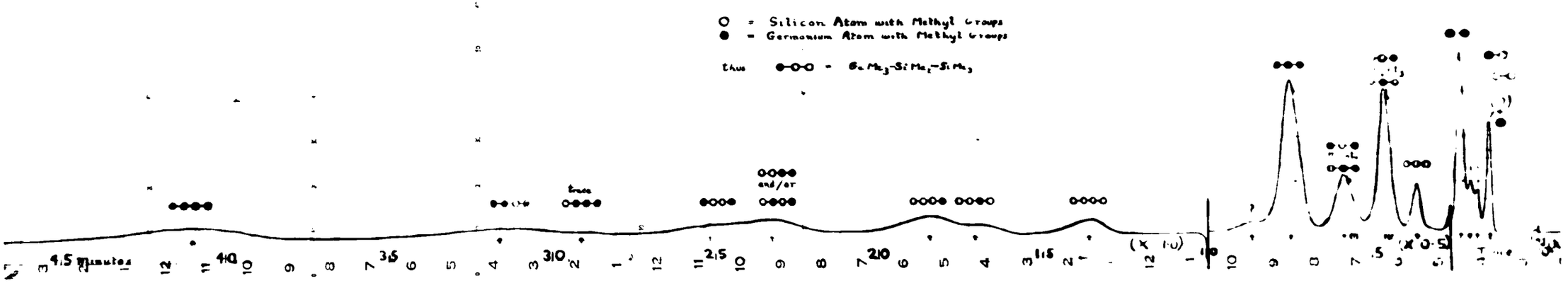
The other principal physical implication of such a series was that the Si-Ge bonds in such units as $SiH_3 \cdot GeH_3$ and $-SiH_2-GeH_2-$ were virtually non-polar, and thus the electronegativities of silicon and germanium in the hydrides were practically identical, as any difference in the Si-Ge polarity compared with Si-Si and Ge-Ge should have been detectable on the polar phase at least. Supporting evidence of this was that the melting points of the silico-germanes were almost exactly intermediate between the appropriate silanes and germanes, and presumed mixtures of positional isomers did not appear to have depressed melting points.

It was considered to be a possibility that such an effect as that observed with the hydrides was a general feature of silicon and germanium chemistry; if this was so, then it would be expected that the silanes and permethyl silanes would form a similar series with a 'Theoretical minus-Silicon Point' as the common origin, but this was shown not to be the case (see Appendix 2). It was still a possibility, however, that

FIG. 40

Chromatogram of the products of Si/Ge Bomb reaction 3

after washing with concentrated H_2SO_4, on TRITOLYL PHOSPHATE 90°C



the permethyl silanes and permethyl germanes would form a similar series to the hydrides, with the permethyl silico-germanes in intermediate positions and positional isomers chromatographically coincident. However it was shown that the 'Theoretical Ethane points' ($-SiMe_2-$ from $SiMe_4$ and $-GeMe_2-$ from $GeMe_4$) of the two series were not coincident. In particular the separations of these points obtained from results on the tritolyl phosphate column, were 0.225 (logarithmic units) at 60°C, 0.150 at 90°C and 0.060 at 120°C. It was therefore expected that the retention values of the permethyl silico-germanes could not be predicted with any great accuracy, and that positional isomers would not be chromatographically coincident. Fig.40 is a photocopy of one of the chromatograms obtained showing most of the members of the series. (The lines had to be manually thickened to make them visible on a reduced copy). It is seen that positional isomers were partly resolved from each other.

For the prediction of the retention values of the n-permethyl silico-germanes, in the first instance, mean values between the n-permethyl silanes and n-permethyl germanes of the same length were the only reasonable basis, thus:

$$\log.Vg(Si_nGe_mMe_{2(n+m)+2}) = \frac{n}{n+m}.\log.Vg(Si_{n+m}Me_{2(n+m)+2}) + \frac{m}{n+m}.\log.Vg(Ge_{n+m}Me_{2(n+m)+2}) \quad . \; . \; (1)$$

The values obtained using this interpolation method are shown as horizontal lines in Figs. 41, 42 and 47. These values are compared with the results actually obtained for the specific permethyl silico-germanes, from precision chromatographic runs. Points marked in brackets had to be obtained from other runs as they were not sufficiently well resolved from their isomers

FIG. 41 n-Permethyl-Silanes, -Germanes and -Silicogermanes; Tritolyl Phosphate 60°C

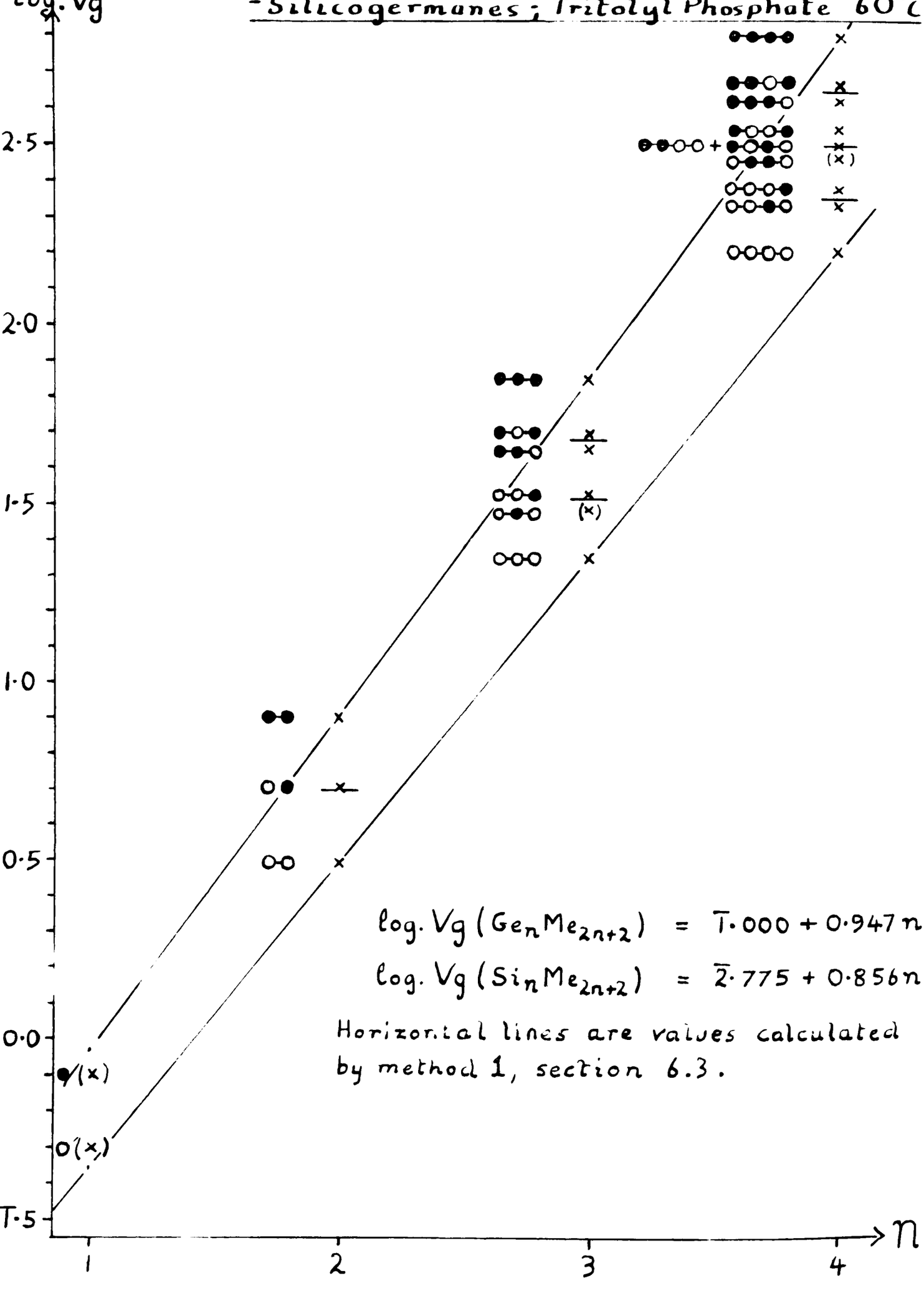
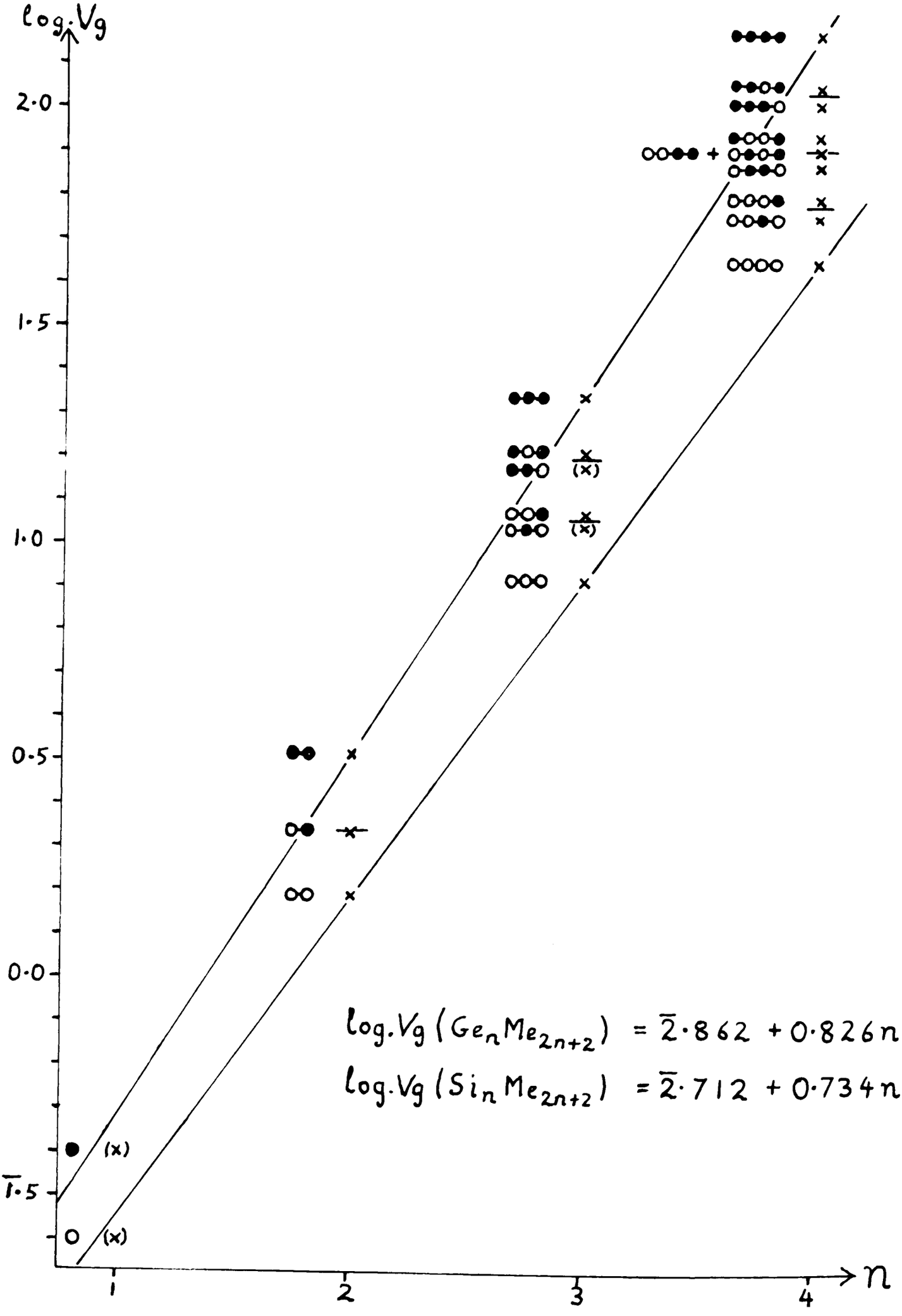


FIG. 42 Tritolyl Phosphate 90°C



$\log. V_g\,(Ge_nMe_{2n+2}) = \bar{2}\cdot862 + 0\cdot826n$

$\log. V_g\,(Si_nMe_{2n+2}) = \bar{2}\cdot712 + 0\cdot734n$

for precision measurements in these runs. The results obtained on the Silicone 702 column were not quite so consistent, as the column efficiency was deliberately rather low (see Section 2.3) and therefore the retention distances were difficult to measure precisely, but they showed the same general trends as outlined below. Some tables of retention results obtained on both columns are shown in Appendix 4.1.

In the chromatograms of the first permethyl silico-germane preparation, where silicon was expected as terminal groups only, it was found that the peaks of the major compounds subsequently proved to be permethyl silico-germanes had retention distances from about 5% to 10% less than the values predicted from equation 1 (see above), with the exception of $SiMe_3GeMe_3$ which appeared approximately as predicted.

In the chromatograms of the second preparation, where silicon was expected as $-SiMe_2-$ groups only, and therefore all terminal groups were expected to be $GeMe_3-$, the three major products were retarded from 3% to 10% more than expected.

In the third preparation these trends were confirmed, the chromatograms showing isomer pairs with retention values either side of the predictions, including one early and one late n-Si_3GeMe_{10} isomer. But the chromatograms also contained a peak, having approximately the predicted n-$Si_2Ge_2Me_{10}$ value, which was subsequently shown to that of either or both of the asymmetric isomers, O–O–●–● or O–●–O–●.

Thus it is seen that the compounds with the least symmetrical structures: O–●, O–O–●–● and/or O–●–O–●, had retention values very close to the predictions. Otherwise, in the sets of positional isomers, the ones with fewer $-SiMe_2-$ groups were less retarded than predicted values,

TABLE 18

Log.Vg. Values of Permethyl Silico-Germanes Compared with Values Predicted by the Two Empirical Methods in Section 6.3.

	Tritolyl Phosphate 60°C.					Tritolyl Phosphate 90°C.				
	Log.Vg.	Calc.1	Error	Calc.2	Error	Log.Vg.	Calc.1	Error	Calc.2	Error
0-0	0.488	-	-	-	-	0.190	-	-	-	-
0-●	0.704	0.692	+.012	0.692	+.012	0.335	0.347	-.012	0.347	-.012
●-●	0.896	-	-	-	-	0.515	-	-	-	-
0-0-0	1.343	-	-	-	-	0.914	-	-	-	-
0-●-0	1.48	1.509	-.03	1.493	-.01	1.04	1.056	-.02	1.021	+.02
0-0-●	1.521		+.012	1.568	-.047	1.067		+.011	1.074	-.007
0-●-●	1.652	1.676	-.024	1.617	+.035	1.18	1.198	-.02	1.180	.00
●-0-●	1.693		+.017	1.692	+.001	1.210		+.012	1.233	-.023
●-●-●	1.842	-	-	-	-	1.340	-	-	-	-
0-0-0-0	2.199	-	-	-	-	1.648	-	-	-	-
0-0-●-0	2.327	2.347	-.020	2.317	+.010	1.753	1.778	-.025	1.752	+.001
0-0-0-●	2.372		+.025	2.376	-.004	1.793		+.015	1.803	-.010
0-●-●-0	2.47	2.494	-.02	2.435	+.03	1.869	1.907	-.038	1.855	+.014
0-0-●-●) 0-●-0-●)	2.494		.000	2.494	.000	1.904		-.003	1.907	-.003
●-0-0-●	2.536		+.032	2.553	-.017	1.937		+.030	1.959	-.022
0-●-●-●	2.616	2.642	-.026	2.612	+.004	2.010	2.037	-.027	2.011	-.001
●-0-●-●	2.656		+.014	2.671	-.015	2.049		+.012	2.062	-.013
● ●-●-●	2.789	-	-	-	-	2.166	-	-	-	-

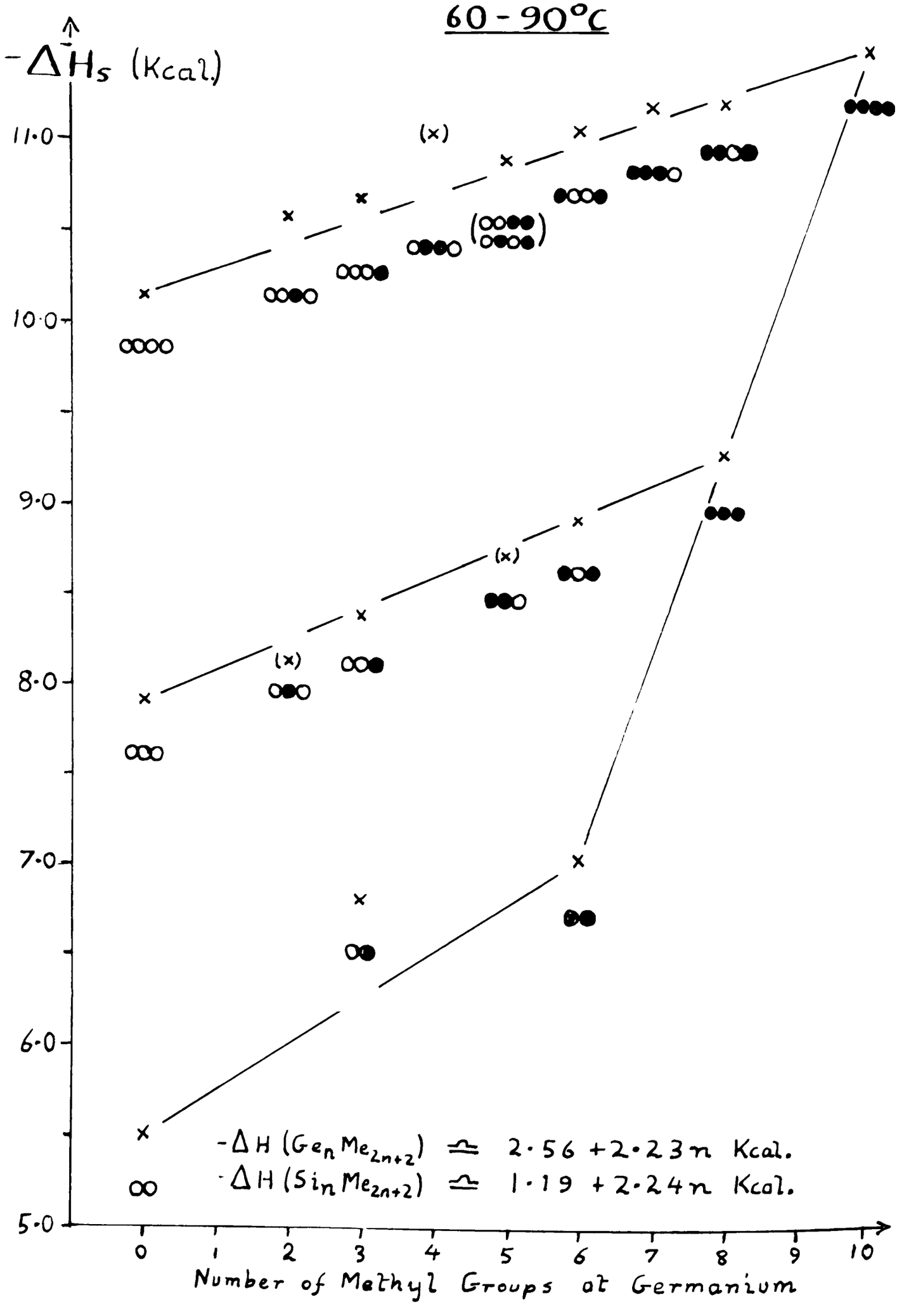
and the isomers with fewer $-GeMe_2-$ groups were more retarded. This would seem to indicate that the relative numbers of methyl groups attached to silicon and germanium atoms could be used as a basis for the prediction of log.Vg values: For instance, O–●–● has 3 methyl groups attached to silicon and 5 to germanium. On this basis the calculation would be

$$\log.Vg(O\text{–}\bullet\text{–}\bullet) = \tfrac{3}{8}.\log.Vg(O\text{–}O\text{–}O) + \tfrac{5}{8}.\log.Vg(\bullet\text{–}\bullet\text{–}\bullet) \quad . \quad . \quad . \quad . \quad (2)$$

Predictions based on this and the previous type of calculation, together with some experimental values, are shown in Table 18. It can be seen that calculations according to equation 1 make no allowance for structure, but calculations according to equation 2 overemphasise the positional effects but do not make enough allowance for the silicon-germanium chain effect, or more correctly, the molecular weight effect.

The heats of solution of the permethyl silanes, permethyl germanes and permethyl silico-germanes were calculated by the method described in Section 2.73. Since these calculations involve subtraction of log.Vg values, errors of the order of 1% in measurement of retention distances (a reasonable error for the later peaks) would lead to errors of up to $\pm$0.15 Kcal. The earlier compounds might be expected to show greater errors. The values obtained with the tritolyl phosphate column are shown plotted against the number of methyl groups attached to germanium in Fig. 43. It is seen that, bearing in mind the likely errors, these values, with the exception of that of O–●, which was very difficult to measure (see Fig.40) and O–●–●–O, which required values obtained from separate chromatograms (as did O–●–O and O–●–●), are in reasonable agreement with a linear increment of the heat of solution with the number of methyl groups attached to germanium. The values obtained for the heats of

FIG. 43 Heats of Solution in Tritolyl Phosphate 60 - 90°C



solution of the permethyl silanes and permethyl germanes, shown in equation form at the bottom of Fig.43, show the rather unusual effect of approximately the same regular increment between homologues of both series, only the origin being different. This is in complete contrast to the hydrides, where the origins were the same but the increments for the two series were different.

If the observed heat of solution effects are in fact real, the implication is that the heat of solution of a member of the general series $Si_nGe_mMe_{2(n+m)+2}$ is determined by two factors only: The first is that there is a certain value for the heat of solution for each methyl group in the molecule, implying an almost total screening of the silicon-germanium chain by the methyl groups. The second factor, which is added to the first, is a constant plus a proportion of another constant, the proportionality factor being the ratio of methyl groups attached to germanium to the total number of methyl groups. This can only be expressed as the proportionate 'silane-germane nature' as shown by the number of bonds to methyl groups. Thus the heat of solution of a permethyl silico-germane with x methyl groups attached to silicon and y attached to germanium would have the following heat of solution on tritolyl phosphate at around 75°C:

$$-\Delta H_{soln.} = -1.05 + 1.12(x+y) + 1.37\frac{y}{x+y} \quad \text{Kcal.}$$

If the heats of solution are additive in this way, the implication is that at high temperatures, the log.Vg values of the permethyl silico-germanes would tend to those predicted by calculations similar to equation 2 and at low temperatures they would tend to those predicted by equation 1.

6.4 Determination of the Structures of the Permethyl Silico-Germanes

There were three main sources of evidence used for the elucidation of the formulae and structures of the permethyl silico-germanes:

1/ Chromatography: The results obtained from this technique were used in three principal ways:

a) To enable the complexities, i.e. molecular formulae of the permethyl silico-germanes to be estimated by reference to the previously identified permethyl silanes and permethyl germanes which were present in the samples (see Section 6.3, equation 1).

b) To enable the results of different preparations to be compared.

c) As a check on the structural determinations by means of the variations in retention times and the hypothesis based on these described in Section 6.3, (equation 2 et seq.).

2/ The method of preparation: By the variations in the reaction mixtures, described in Section 6.2, it was expected that sub-groups of compounds with specific structural features would be prepared. As has been seen this was invalidated to a certain extent by the evidence of group exchange, but nevertheless it was anticipated that this would result in only relatively small amounts of isomers of the compounds deliberately prepared.

3/ The low-temperature gold chloride technique: In view of the earlier successful application of this technique to the analysis of the permethyl silanes and permethyl germanes, it was expected that it would enable both empirical and structural formulae to be obtained. For structural analysis, it was necessary to minimise fission of Me-Si and Me-Ge bonds whilst ensuring that all Si-Si, Si-Ge and Ge-Ge bonds were

chlorinated. In practice, it was found that an increased degree of Ge-Me bond fission, compared to that encountered in the permethyl germane analyses, occurred in these analyses. As the extent of this increased progressively it was not certain whether there was any activation of methyl germanium groups by the presence of methyl silicon groups or whether the initial increase was due to the general trend. Because of this progressively higher reactivity, the analyses have been discussed in sequence. On the other hand, there was found to be little or no chlorination of Si-Me groups in the early analyses and it was presumed that this fact could be used for estimating positional isomerism, whenever it was impossible to do so from the germanium products.

In view of the reactivity of $SiMe_2Cl_2$ on the tritolyl phosphate column (see Section 5.42) most runs were carried out using the Silicone 702 column. A table of the retention data obtained in these runs is given in Appendix 4.2. It was found that the only products observed in measurable quantities in these analyses were: MeCl, $SiMe_3Cl$, $SiMe_2Cl_2$, $GeMe_3Cl$, $GeMe_2Cl_2$, $GeMeCl_3$ and $GeCl_4$.

For the gold chloride analyses, the individual permethyl silico-germanes were initially crudely separated from approximately 70-100mg. samples of the reaction mixtures in the preparative system. For some of the compounds only present in small amounts, as many as 6 of these runs had to be made. The impure compounds were then purified by successive preparative chromatography on the two columns in turn, four stages usually being carried out, prior to transfer to the analytical system. When it was necessary to extract minor products from their positional isomers, even more intricate procedures were required and these are described in

the appropriate sections. In view of the very small quantities available of some of the products (0.2% in a total sample of 500-600 mg.) it was decided to standardise on a technique, using small samples only, so that all results could be more directly compared. A series of five runs, consisting of a sample purity check, a 'conditioning run' and three analytical runs was carried out on most of the compounds, but on some, when only very small samples were available, the sample purity checks, and in one case the 'conditioning run', were not carried out. The effect of absorption in the tap grease was clearly seen, as even after prolonged purging of the gold chloride system, after the introduction of a new sample and [redacted] the 'conditioning run', some 'memory' of the previous compound remained. In addition, the sizes of the samples obtained from a series of evaporations under practically identical conditions became successively larger. Retention values for the products of the analyses shown in Tables 19 to 24 are given in Appendix 4.2.

6.5 Analysis of the Products of the First Preparation

These compounds would be expected to contain silicon as $SiMe_3$- groups only, but were possibly contaminated with small amounts of their positional isomers.

The 'predicted' chromatographic values in this and the succeeding Sections refer to equation 1, Section 6.3 unless otherwise stated.

6.51 The Product Believed to be $SiMe_3.GeMe_3$

This was obtained as a major product in the first preparation (27.9%)

TABLE 19

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B		
Parent Compound	$SiMe_3GeMe_3$			$SiMe_3GeMe_2SiMe_3$		
Gold Chloride Run	1	2	3	1	2	3
Column	TTP	702	702	TTP	702	702
Cell Temperature	33°/33°C	35°/35°C	34°/34°C	33°/33°C	33°/33°C	33°/33°C
Evaporation Temperature	-21°C	-26°C	-16°C	22°C	22°C	22°C
Evaporation Time (Min.)	4	4	4	3½	3½	3½
Sample Size (μM)	2.0	1.0	4.5	1.7	2.7	3.0
Sensitivity	0.250	0.250	0.250	0.400	0.250	0.250
Products (M.U.) -						
MeCl	2.20	0.50	4.67	1.0	1.7	2.2
$SiMe_3Cl$	11.98	5.93	27.9	33.6	33.9	37.5
$SiMe_2Cl_2$					0.25	0.25
$GeMe_3Cl$	11.08	4.57	21.3	0.86	0.7	0.7
$GeMe_2Cl_2$	3.47	1.17	7.26	17.25	13.7	14.45
$GeMeCl_3$	tr		tr	2.30	2.5	3.1
$GeCl_4$					0.1	0.1
Empirical Ratios -						
Si	1	1	1	2	2	2
Ge	1.22	0.97	1.02	1.21	1.00	0.97
Me	6.54	5.79	5.98	8.46	7.96	7.91

and was also a product of the second (1.6%) and third (5.6%) preparations. Its peak occurred on chromatograms at about half the logarithmic distance between the peaks of Si_2Me_6 and Ge_2Me_6, and it was therefore almost certainly the compound described by Mironov and Kravchenko[35], as $SiMe_3GeMe_3$. Apart from a low silicon analysis using the tritolyl phosphate column (run 1), the gold chloride analyses (Table 19A) gave an empirical formula $SiGeMe_6$. The major products were $SiMe_3Cl$ with rather less $GeMe_3Cl$. $GeMe_2Cl_2$ and a smaller amount of MeCl were present as minor products. It may therefore be deduced that the parent compound was $SiMe_3.GeMe_3$, and that approximately 25-30% of the $GeMe_3$ groups were demethylated to yield $GeMe_2Cl_2$. The MeCl analysis would seem to confirm this. It was particularly noticed that despite this extensive demethylation of $GeMe_3$ groups there was very little secondary demethylation, and at the same time there appeared to be no demethylation of $SiMe_3$ groups to $SiMe_2Cl_2$.

6.52 The Product Believed to be $SiMe_3.GeMe_2.SiMe_3$

This product was obtained in a yield of 1.6% in preparation 1 and 0.6% in preparation 3. Its chromatographic behaviour was consistent with a formula Si_2GeMe_8 but it was retarded rather less than predicted by formula 1, Section 6.3. A rather low silicon analysis was obtained in the first gold chloride run (Table 19B) which was carried out on the tritolyl phosphate column, but the succeeding runs on the Silicone 702 column gave results consistent with an empirical formula Si_2GeMe_8. The major products were $SiMe_3Cl$ and $GeMe_2Cl_2$ in a ratio of about $2\frac{1}{2}$: 1. However, reasonable amounts of $GeMeCl_3$ and MeCl were also present, indicating 15-18% demethylation of the original $GeMe_2$ groups sufficient to make the

above ratio approximately 2 : 1. It was presumed that the small amount of $SiMe_2Cl_2$ was derived almost entirely from $-SiMe_2-$ groups, and the presence of $GeMe_3Cl$, indicated some $GeMe_3$ groups. It was therefore concluded that the parent compound was $SiMe_3.GeMe_2.SiMe_3$ containing around 5% of another compound, probably its positional isomer, $SiMe_3.SiMe_2.GeMe_3$. (The low $SiMe_2Cl_2$ analysis on this basis was consistent with the rather low values obtained in Section 5.42 on the Silicone 702 column and the small size of the sample).

6.53 The Product Believed to be $SiMe_3.GeMe_2.GeMe_3$

This product was obtained in a yield of 0.9% in preparation 1 and 1.3% in preparation 3. It was also probably present in the products of preparation 2 (see Section 6.61). Its chromatographic retention was slightly less than the predicted value for $SiGe_2Me_8$. The first gold chloride run (Table 20A) gave a low germanium analysis, probably because of traces of the previous compound. The other gold chloride runs were consistent with an empirical formula $SiGe_2Me_8$. Three major products were obtained: $GeMe_2Cl_2$ was present in the largest amount with rather less $SiMe_3Cl$ and a smaller amount of $GeMe_3Cl$. In addition, appreciable amounts of MeCl and $GeMeCl_3$ were present. These quantities could be explained by a partial demethylation of $GeMe_3$ groups to form $GeMe_2Cl_2$ and a lower extent of demethylation of $GeMe_2$ groups. In this case there would have been approximately equal amounts of $SiMe_3$, $GeMe_3$ and $GeMe_2$ groups in the parent. Thus, it may be concluded that the parent was $SiMe_3.GeMe_2.GeMe_3$, the presence of a trace of $SiMe_2Cl_2$ possibly indicating contamination (1-2%) with its isomer.

TABLE 20

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B		
Parent Compound	$SiMe_3GeMe_2GeMe_3$			$SiMe_3GeMe_2GeMe_2SiMe_3$		
Gold Chloride Run	1	2	3	1	2	3
Column	702	702	702	702	702	702
Cell Temperature	33°/33°C	33°/33°C	33°/33°C	47°/33°C	48°/33°C	48°/33°C
Evaporation Temperature	22°C	31°C	29°C	46°C	52°C	51°C
Evaporation Time (Min.)	3½	3½	3½	5	7½	10
Sample Size (μM).	0.6	3.5	3.1	0.8	2.3	3.1
Sensitivity	1.000	0.500	0.500	0.500	0.250	0.500
Products (M.U.) -						
MeCl	1.19	5.8	12.0	3.8	6.2	12.6
$SiMe_3Cl$	13.87	42.6	37.1	19.5	27.5	75.1
$SiMe_2Cl_2$		0.4	0.4	0.3	0.2	0.4
$GeMe_3Cl$	10.46	36.8	28.9	0.4	0.8	2.8
$GeMe_2Cl_2$	13.61	45.7	40.4	15.5	20.6	57.6
$GeMeCl_3$	1.78	4.3	5.3	5.6	6.3	17.8
$GeCl_4$		0.1	0.1	0.3	0.3	0.4
Empirical Ratios -						
Si	1.07	0.99	1.00	1	1	1
Ge	2	2	2	1.10	1.01	1.04
Me	7.99	7.83	7.95	5.08	5.02	5.03

On the basis of these conclusions it can be calculated that the extent of the demethylation of germanium groups in the latter two runs, assuming little secondary demethylation had taken place, was as follows:

Run 2: $GeMe_3$- ⟶ $GeMe_2Cl_2$ 15% -$GeMe_2$- ⟶ $GeMeCl_3$ 10%

Run 3: $GeMe_3$- ⟶ $GeMe_2Cl_2$ 24% -$GeMe_2$- ⟶ $GeMeCl_3$ 15%

These figures are approximately in the ratio (3 : 2) that would be expected from statistical attack, followed by deactivation to further attack, on methyl groups at germanium in the parent compound. They do not correspond to the product ratios expected from attack on mixtures of $GeMe_3Cl$ and $GeMe_2Cl_2$ (see Section 4.21). The inhibition of secondary attack is clearly seen in the analyses in the two previous Sections. Thus in all subsequent work this conclusion was used as a basis for detecting the source of any $GeMe_2Cl_2$. (An extension of this would have also been used for detecting branched chain compounds, had these been formed, by the proportion of $GeCl_4$ to $GeMeCl_3$).

6.54 The Product Believed to be $SiMe_3.GeMe_2.GeMe_2.SiMe_3$

This product was prepared in a 1.5% yield in the first preparation and in a much smaller yield (0.2%) in the third. Its chromatographic retention was somewhat less than the predicted value for $Si_2Ge_2Me_{10}$. The first gold chloride analysis (Table 20B) gave a slightly high germanium analysis, probably due to traces of the previous compound, but the subsequent runs were well in agreement with an empirical formula $SiGeMe_5$. In view of the rather high evaporation temperatures that were necessary to obtain reasonable sized samples, the gold chloride cell was heated to a higher temperature than had been used for the previous analyses to

prevent possible condensation of the sample. The products contained $SiMe_3Cl$ as the major product with about $\frac{3}{4}$ of this amount of $GeMe_2Cl_2$ and about $\frac{1}{4}$ of $GeMeCl_3$. The absence of a large concentration of $GeCl_4$ and the presence of MeCl in a rather lower concentration than the $GeMeCl_3$ showed that the origin of most, if not all, of this last compound was $-GeMe_2-$ groups. On this basis the structure was deduced as being $SiMe_3.GeMe_2.GeMe_2.SiMe_3$. The presence of small amounts of both $GeMe_3Cl$ and $SiMe_2Cl_2$ indicated some contamination, probably by other $Si_2Ge_2Me_{10}$ isomers, to the extent of about 6%.

6.55 The Product Believed to be $SiMe_3.GeMe_2.GeMe_2.GeMe_3$

This product only appeared in low yields in the first and third preparations (0.2% and 0.4%). Its chromatographic properties indicated the molecular formula $SiGe_3Me_{10}$, but it was slightly less retarded than the predicted value. In view of the very small sample that was finally separated, considerable preflushing of the apparatus was done, since there was not considered to be enough sample for a purity test or a conditioning run, prior to the analyses. It was estimated that the total sample size was only about 2 micromoles (0.8 mg.). This was a considerably smaller amount than had previously been handled. The three analytical runs carried out (Table 21A) were not very consistent and on average indicated a lower silicon content than would be expected for $SiGe_3Me_{10}$. Examination of the products, after allowance for approximately 35% demethylation of $GeMe_3-$ groups and approximately 25% demethylation of $-GeMe_2-$ groups indicated a parent with 2 $GeMe_2$ groups to one each of $SiMe_3$ and $GeMe_3$ groups. It was concluded that the parent was predominantly

TABLE 21

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B		
Parent Compound	$SiMe_3GeMe_2GeMe_2GeMe_3$			$GeMe_3SiMe_2GeMe_2$		
Gold Chloride Run	1	2	3	1	2	3
Column	702	702	702	702	702	702
Cell Temperatures	49°/34°C	49°/34°C	49°/34°C	34°/34°C	34°/34°C	34°/34°C
Evaporation Temperature	51°C	51°C	51°C	30°C	30°C	30°C
Evaporation Time (Min.)	5	5	5	3½	4	3¼
Sample Size (μM)	0.4	0.6	0.8	2.5	3.5	3.1
Sensitivity	1.000	1.000	1.000	0.500	0.500	0.500
Products (M.U.) -						
MeCl	4.9	14.4	22.7	17.5	26.3	25.7
$SiMe_3Cl$	9.6	13.4	19.5	6.5	8.3	6.2
$SiMe_2Cl_2$	0.2	0.5	0.6	23.2	33.0	30.3
$GeMe_3Cl$	4.6	12.1	15.5	40.1	53.7	42.0
$GeMe_2Cl_2$	17.1	29.6	44.1	21.5	32.2	33.6
$GeMeCl_3$	6.1	7.1	8.8	0.4	0.7	0.8
$GeCl_4$	0.2	0.2	0.2			
Empirical Ratios -						
Si	1.05	0.85	0.88	0.96	0.95	0.95
Ge	3	3	3	2	2	2
Me	9.45	10.28	9.88	7.97	7.93	7.82

$SiMe_3.GeMe_2.GeMe_2.GeMe_3$ but, in view of the presence of $SiMe_2Cl_2$, in the products, probably contaminated with its isomer, and possibly even Ge_4Me_{10}.

6.6 Analysis of the Products of the Second Preparation

The permethyl silico-germanes produced by the second preparation (see Section 6.2) were expected to contain silicon as $-SiMe_2-$ groups only. However, there was evidence for an even more extensive rearrangement of groups in this reaction than in the previous preparation, and therefore it was expected that these compounds would be contaminated with their isomers to a larger extent than the compounds so far analysed. It was not initially appreciated just how difficult it was to obtain a good isomer separation in this series of compounds, and so despite 'chopping' of the earlier parts of the peaks of the set of compounds described in this Section, it was not until the third compound was purified that a reasonable separation was attained. The technique finally employed is described in Section 6.7.

In the event, high purity was not required for establishing the structural formulae of the major components, and the presence of isomers did not upset the calculation of empirical formulae.

6.61 The Product Believed to be $GeMe_3.SiMe_2.GeMe_3$

This product was obtained in yields of about 10.5% from preparation 2 and about 3.1% from preparation 3. It was believed to be present in trace amounts in the products of preparation 1 (see Section 6.53), in an amount around 0.02%. Its chromatographic behaviour suggested the

formula $SiGe_2Me_8$, but it was not the compound described in Section 6.53 as it appeared on chromatograms later than the predicted value. In the gold chloride analysis (Table 21B) it would seem that the empirical formula obtained was $Si_{0.95}Ge_2Me_{7.9}$. This was probably due to the loss of some of the $SiMe_2Cl_2$ that was obtained as a major product. A low $GeMeCl_3$ analysis showed that the major source of the $GeMe_2Cl_2$ was $GeMe_3$-, which would indicate a ratio of over 2 parts of $GeMe_3$- groups to one of -$SiMe_2$- groups. The presence of $SiMe_3Cl$ and evidence of at least some -$GeMe_2$- groups would account for some of the apparent excess of $GeMe_3$- groups, indicating an 18-20% contamination of the obvious major product, $GeMe_3.SiMe_2.GeMe_3$, with its isomer $SiMe_3.GeMe_2.GeMe_3$. The loss of around 4% of the $SiMe_2Cl_2$ was expected with peaks of this size from the work on the permethyl silanes (Section 5.42) on the Silicone 702 column.

6.62 The Product Believed to be $GeMe_3.SiMe_2.SiMe_2.GeMe_3$

This product was obtained in yields of about 3.1% and 1.1% in preparations 2 and 3 respectively. On chromatograms it appeared rather later than was predicted for a compound with the formula $Si_2Ge_2Me_{10}$, in contrast with the compound described in Section 6.54. Initially the gold chloride analysis was carried out at temperatures similar to those already employed on the suspected four-membered chain compounds (Sections 6.54 and 6.55) but in view of the large amount of apparent demethylation at germanium in the first two runs, it was decided, despite the risk of condensation, to carry out the third run at lower cell temperatures. In this way it was hoped to reduce demethylation so that

TABLE 22

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B		
Parent Compound	$GeMe_3SiMe_2SiMe_2GeMe_3$			$GeMe_3SiMe_2GeMe_2GeMe_3$		
Gold Chloride Run	2	3	4	1	2	3
Column	702	702	702	702	702	702
Cell Temperatures	49°/33°C	49°/33°C	35°/33°C	35°/35°C	35°/35°C	35°/35°C
Evaporation Temperature	54°C	54°C	53°C	54°C	54°C	64°C
Evaporation Time (Min.)	7½	7½	7½	5	5	5
Sample Size (μM)	1.5	1.3	0.5	0.2	0.4	0.7
Sensitivity	0.500	0.500	0.500	1.000	1.000	1.000
Products (M.U.) -						
MeCl	35.3	25.8	6.3	0.7	8.3	13.5
$SiMe_3Cl$	3.3	2.9	1.1	0.6	0.6	1.1
$SiMe_2Cl_2$	28.6	26.2	9.6	3.5	9.0	14.8
$GeMe_3Cl$	8.4	9.6	5.5	9.9	10.8	23.0
$GeMe_2Cl_2$	23.9	20.7	5.7	6.8	17.6	26.3
$GeMeCl_3$	5.4	1.3	0.2	0.4	1.0	1.0
$GeCl_4$	0.1	tr			tr	
Empirical Ratios -						
Si	0.84	0.92	0.93	0.72	0.98	0.95
Ge	1	1	1	3	3	3
Me	4.78	5.01	4.97	9.33	9.87	10.08

the structural results were more unequivocal. This proved to be successful and so the milder cell conditions were also used for some of the other high-boiling compounds. In the gold chloride analyses of this parent compound (Table 22A), the quantities of silicon compounds were again lower than expected, but not too low for an empirical formula other than $SiGeMe_5$ to be deduced. The second run indicated that most of the $GeMe_2Cl_2$ was derived from $GeMe_3$ groups, but only on the third run, carried out under mild conditions, was the $GeMe_3Cl$ analysis greater than half the $SiMe_2Cl_2$ analysis, clearly showing there to have been more than one $GeMe_3$ group to every two $-SiMe_2-$ groups. The presence of about 10% of the Silicon as $SiMe_3Cl$ again indicated extensive contamination by isomeric products, but there was no doubt that the major component was $GeMe_3.SiMe_2.SiMe_2.GeMe_3$, contaminated to the extent of 15 to 20% with its isomers, O–O–●–●, O–●–O–● and, less likely, O–●–●–O.

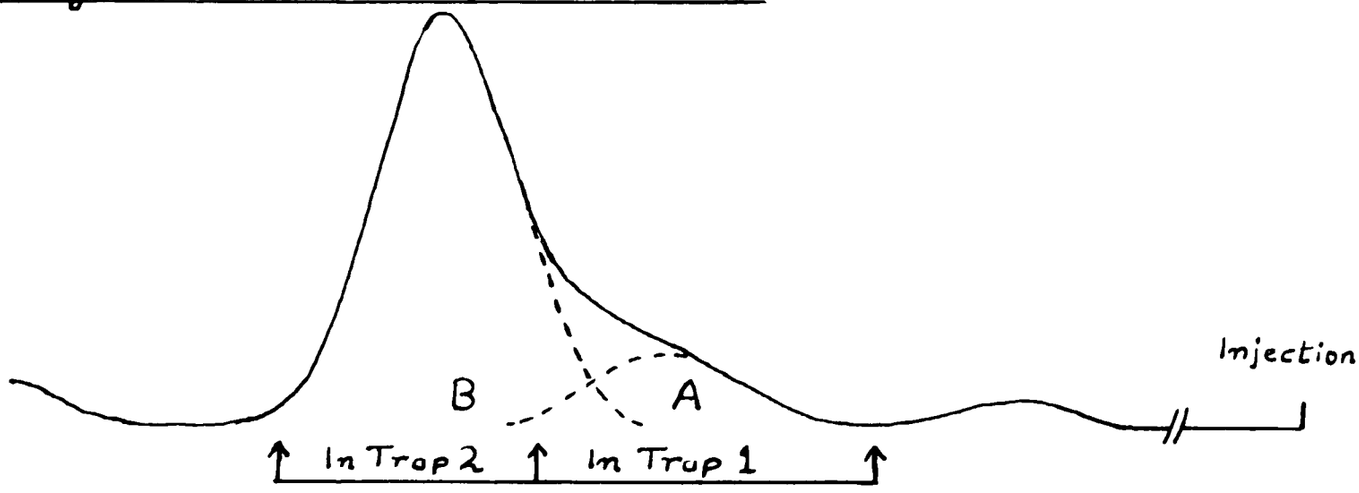
6.63 The Product Believed to be $GeMe_3.SiMe_2.GeMe_2.GeMe_3$

This product was obtained in yields of about 1.5% and 1.2% in preparations 2 and 3 respectively and was believed to be a contaminant of the $SiGe_3Me_{10}$ isomer prepared in run 1. Its chromatographic retention was somewhat greater than was expected for a compound with the formula $SiGe_3Me_{10}$. In attempts to obtain the compound prepared in run 2 reasonably free from its isomer, which in the light of previous experience was expected to be present, most of the sample was lost, and consequently only a small amount was available for the gold chloride work. The first gold chloride run (Table 22B) gave a very low silicon analysis, but otherwise, despite the low sample sizes, the other runs were well in agreement with a molecular

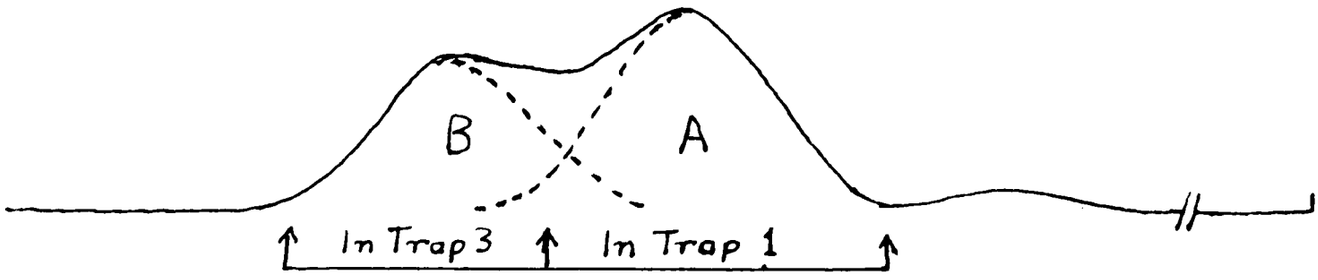
FIG. 44 **Preparative Chromatography**

Showing a method of obtaining a reasonable Isomer separation of a minor component; A

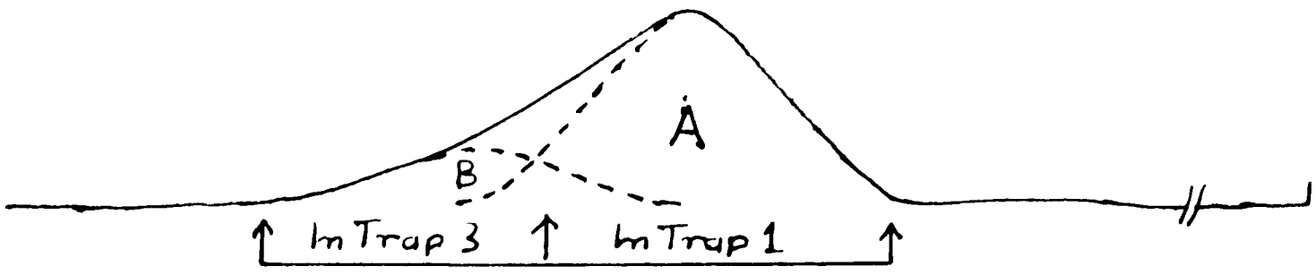
Stage 1 : Initial Preparative Run



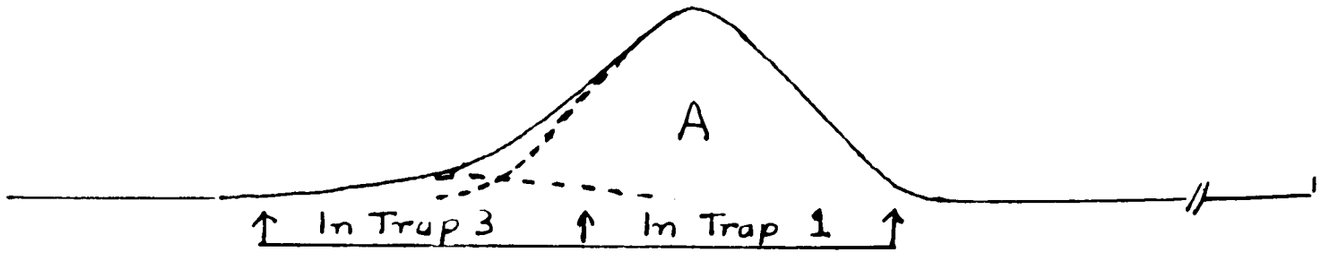
Stage 2 : Contents of trap 1 (Increased Sensitivity)



Stage 3 : Contents of trap 1



Stage 4 : Contents of trap 1



formula $SiGe_3Me_{10}$ although, on a purely empirical basis, the methyl analysis was rather doubtful. The yields of $GeMe_3Cl$, 1 to 1½ times as large as those of $SiMe_2Cl_2$ indicated a probable 2 : 1 ratio of $GeMe_3$- groups to -$SiMe_2$- groups and the large amount of $GeMe_2Cl_2$ together with some $GeMeCl_3$ indicated a -$GeMe_2$- group as well. Thus it was deduced that the parent compound was $GeMe_3.SiMe_2.GeMe_2.GeMe_3$, and the presence of some $SiMe_3Cl$ probably indicated contamination by about 6% of its isomer.

6.7 Analysis of Products of the Third Preparation

As the third preparation was expected to produce a mixture of all the possible permethyl silico-germanes, the extraction of the compounds to be analysed was expected to be very difficult in view of the need to achieve a reasonable separation of positional isomers, which were present in comparable quantities. In most cases the separation of the chromatographic peak maxima of positional isomers was only 0.040 logarithmic units. The most difficult type of separation was the purification of the minor components of an isomer pair: The principle of the method employed is shown in Fig. 44. It is seen that the major component had to be removed in stages in order to prevent excessive loss of the minor component. In practice the reduction in quantity of the original major component between each stage was not as great as suggested by the diagram, partly on account of the difficulty of judging the trap changeover points from the recorder trace at the time of the experiment, partly because of the need to 'condition' traps and taps, and partly

because of sample diffusion within the apparatus.

It had been noted in the work in the previous Sections and in Section 5.42, that even using the Silicone 702 column, about 4% of large samples (and larger percentages of small samples) of $SiMe_2Cl_2$ were apparently being removed from the gold chloride reaction mixtures. This was happening despite preflushing of the analytical system with various methyl silicon chlorides, and the precautions to remove moisture and oxygen from the analytical system's carrier gas. It was accordingly thought possible that some moisture must have come from the preparative system with the samples. The presence of moisture in the preparative system had not been definitely established, but it was conceivable that it could be present and accordingly the system was treated with a sample of $SiCl_4$ before carrying out the purification of the last set of compounds. It is considered that some improvement was obtained.

6.71 The Product Believed to be $SiMe_3.SiMe_2.GeMe_3$

This was the major permethyl silico-germane product (6.5%) in preparation 3 and was apparently present in preparation 2 (about 1.2%). Its chromatographic properties were consistent with a molecular formula Si_2GeMe_8, and because it appeared slightly later than predicted, it was not expected to contain $-GeMe_2-$ groups (see Section 6.3). The gold chloride analysis (Table 23A) clearly indicated a molecular formula Si_2GeMe_8. Examination of the products showed that $SiMe_3Cl$ and $SiMe_2Cl_2$ were major products, with rather more of the former. Mixtures of approximately equal amounts of $GeMe_3Cl$ and $GeMe_2Cl_2$, which, because of the low yield of $GeMeCl_3$, must have mainly been derived from $GeMe_3-$ groups,

TABLE 23

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B		
Parent Compound	$SiMe_3SiMe_2GeMe_3$			$SiMe_3SiMe_2SiMe_2GeMe_3$		
Gold Chloride Run	1	2	3	2	3	4
Column	702	702	702	702	702	702
Cell Temperatures	35°/35°C	35°/35°C	35°/35°C	35°/35°C	48°/35°C	47°/35°C
Evaporation Temperature	26°C	26°C	26°C	50°C	55°C	52°C
Evaporation Time (Min.)	3	3	3	5	6¼	6½
Sample Size (μM)	1.0	2.7	3.6	0.3	1.8	1.8
Sensitivity	0.250	0.250	0.250	0.400	0.400	0.250
Products (M.U.) -						
MeCl	2.2	3.9	6.4	0.8	14.1	9.5
$SiMe_3Cl$	7.1	18.6	25.2	5.0	21.4	12.7
$SiMe_2Cl_2$	5.2	14.0	19.4	5.2	31.2	20.3
$GeMe_3Cl$	2.3	7.6	11.2	1.3	3.5	1.8
$GeMe_2Cl_2$	3.9	8.5	10.1	1.7	12.9	8.5
$GeMeCl_3$	0.2	0.5	0.6	0.1	0.9	0.4
$GeCl_4$						
Empirical Ratios -						
Si	2	2	2	3	3	3
Ge	1.04	1.02	0.98	0.91	0.99	0.97
Me	7.95	7.86	7.87	9.38	10.16	10.09

were yielded, together making a similar amount. It was thus apparent that the parent had the structure $SiMe_3.SiMe_2.GeMe_3$ and, on account of the excess of $SiMe_3Cl$, was probably contaminated with about 10 to 15% of its isomer.

6.72 The Product Believed to be $SiMe_3.SiMe_2.SiMe_2.GeMe_3$

This product was produced in preparation 3 as the larger, and chromatographically more retarded, component of a double 'peak' corresponding to a molecular formula: Si_3GeMe_{10}. In preparation 3 its yield was about 1.2% and it was also apparently a product of the second reaction (0.4%). In the first gold chloride run there was some evidence of the high boiling products observed in the gold chloride runs on Si_4Me_{10} (see Section 5.42) and accordingly the cell temperature was raised for the succeeding runs (Table 23B). The results of the second and third runs were consistent with the empirical formula Si_3GeMe_{10}. The major products, $SiMe_3Cl$ and $SiMe_2Cl_2$ were present in ratios of around 1 : 1.5. The germanium products, although mainly $GeMe_2Cl_2$, were assumed to have largely come from $GeMe_3$ groups on account of the low $GeMeCl_3$ analysis. The yield of MeCl supported this assumption. Thus it was deduced that the parent compound was $SiMe_3.SiMe_2.SiMe_2.GeMe_3$, which was contaminated with about 10 to 15% of its isomer.

6.73 The Product Believed to be $SiMe_3.SiMe_2.GeMe_2.SiMe_3$

This product was produced in a yield of only 0.6% in the third preparation, as the less retarded of the two products presumed to be Si_3GeMe_{10} isomers. It was also possibly a trace product of the first

TABLE 24

Gold Chloride Reaction on Permethyl Silico-Germanes

	A			B	
Parent Compound	$SiMe_3SiMe_2GeMe_2SiMe_3$			Asymmetric $Si_2Ge_2Me_{10}$	
Gold Chloride Run	1	2	3	2	3
Column	702	702	702	702	702
Cell Temperature	46°/35°C	46°/35°C	46°/35°C	46°/35°C	46°/35°C
Evaporation Temperature	52°C	51°C	52°C	57°C	56°C
Evaporation Time (Min.)	6½	7½	7½	6½	6½
Sample Size (μM)	1.0	1.5	0.5	0.9	0.5
Sensitivity	0.500	0.250	1.000	0.500	0.500
Products (M.U.) -					
MeCl	3.3	2.8	9.5	6.8	6.2
$SiMe_3Cl$	25.7	18.1	20.8	12.7	6.1
$SiMe_2Cl_2$	12.6	10.0	13.1	10.6	5.3
$GeMe_3Cl$	0.7	0.6	0.3	5.6	1.1
$GeMe_2Cl_2$	9.1	6.8	6.7	14.0	8.5
$GeMeCl_3$	1.7	1.7	5.7	1.9	2.2
$GeCl_4$	0.1	0.1	0.1	0.2	0.1
Empirical Ratios -					
Si	3	3	3	1	1
Ge	0.91	0.98	1.13	0.93	1.04
Me	10.00	10.07	10.45	4.85	5.05

preparation. It was separated only with considerable difficulty from its suspected isomer. Successive gold chloride runs on the small amount of the compound available, showed a progressive increment in the germanium analysis (Table 24A). The average of the three runs, however, indicated clearly an empirical formula, Si_3GeMe_{10}. Examination of the ratio of $SiMe_3Cl$ to $SiMe_2Cl_2$ showed a progressive fall from 2 : 1 to 1.6 : 1. When this is considered, together with the presence of some $GeMe_3Cl$ in mixtures of methyl germanium chlorides which were obviously derived to a large extent from $-GeMe_2-$ groups, it would seem to indicate a progressively increasing amount of $SiMe_3.SiMe_2.SiMe_2.GeMe_3$ in a parent largely consisting of $SiMe_3.SiMe_2.GeMe_2.SiMe_3$. The increasing amount of the isomer is possibly explained by the fact that the sample was clearly exhausted by the end of the third run, and that the isomer was presumably less volatile, and therefore traces of it would tend to concentrate at the end of the evaporation. The total degree of contamination was probably in the range 5 to 10%.

6.74 The Product Believed to be a Mixture of $SiMe_3.SiMe_2.GeMe_2.GeMe_3$ and $SiMe_3.GeMe_2.SiMe_2.GeMe_3$

This product was prepared in a yield of approximately 1.2% in the third preparation and was a possible contaminant of the two $Si_2Ge_2Me_{10}$ isomers described already. Its chromatographic behaviour was almost exactly that expected for a compound with the formula $n\text{-}Si_2Ge_2Me_{10}$. In accordance with the hypothesis of retention values based on methyl groups (Section 6.3) this product would be expected to have five methyl groups attached to silicon and five attached to germanium. There were

two possible chain structures that would satisfy this condition; O-O-●-● and O-●-O-●.

This product was the most difficult of all to purify as it was flanked on both sides on the chromatograms by its suspected positional isomers. Nevertheless a fairly pure product, that gave a sharp chromatographic peak and was therefore not predominantly a mixture of O-●-●-O and ●-O-O-●, was ultimately obtained, unfortunately in only a small yield. Doubly unfortunate was the electrical power cut that occurred in the middle of the first gold chloride run, as there was barely enough of the sample left for two more analytical runs, and the results of the first run could not be used. On the basis of the two successful runs, (see Table 24B) the empirical formula was deduced to be $SiGeMe_5$. Examination of the products showed that after allowance had been made for demethylation at germanium, the parent must have contained approximately equal amounts of $SiMe_3$-, -$SiMe_2$-, $GeMe_3$- and -$GeMe_2$- groups (with a slight excess of $SiMe_3$- and, probably, -$GeMe_2$- groups). This would indicate that the parent consisted of either or both of the suggested compounds and was contaminated with an excess of O-●-●-O over any ●-O-O-● present.

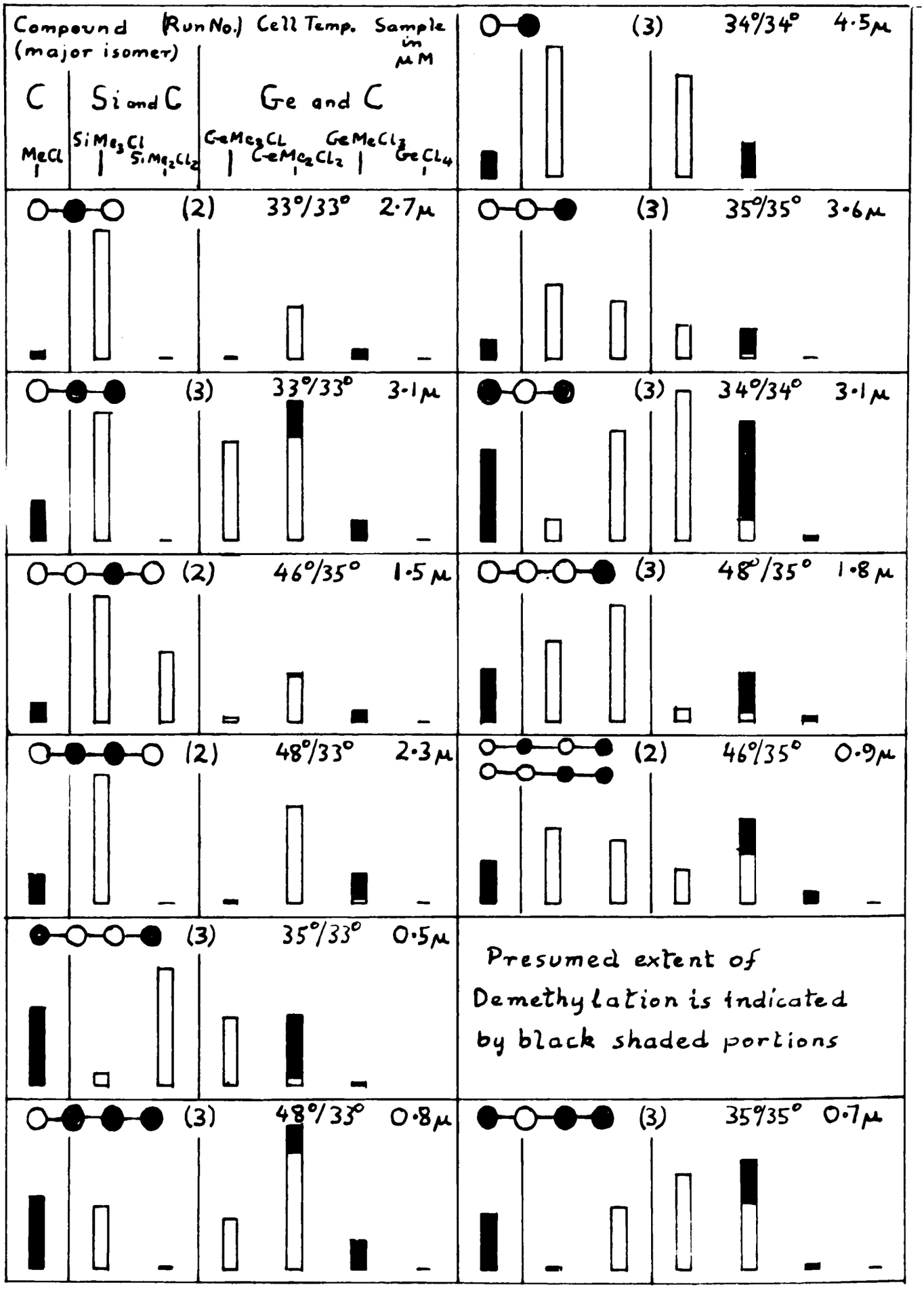
As every other permethyl silico-germane was prepared in the third reaction, it is extremely unlikely that either of the compounds, O-O-●-● and O-●-O-●, was not prepared to a certain extent. In addition to the chromatographic hypothesis developed in Section 6.3, it would seem that in all respects these two compounds would (together with $SiGeMe_6$) come closest of the permethyl silico-germanes to being exactly intermediate between the permethyl silanes and permethyl germanes, and would be expected

to have nearly identical properties. It is concluded, therefore, that both compounds were probably present and were chromatographically identical. The tentative explanation of the yields of the coupling reaction predicted an isomer ratio, O-O-●-● to O-●-O-●, of around 3 : 1 (see Section 6.21).

6.75 A Possible Branched-Chain Product

The only product that appeared to survive the 'washing' procedure in the third preparation, beside the permethyl silico-germanes (as identified in the previous Sections) and the permethyl silanes and germanes, was the product marked with a question mark in Fig. 40. This appeared just after the Ge_3Me_8 on chromatograms of runs using the tritolyl phosphate column. The compound was found to have a heat of solution on this column of 9.93 Kcal, which was only just lower than that of n-Si_4Me_{10}, and was therefore a little high for its position on the chromatogram if it was a branched chain permethyl silico-germane as might be expected. This product was separated as much as possible from the Ge_3Me_8 and run on the gold chloride system. Apart from traces of the methyl silicon chlorides and methyl germanium chlorides, as would be expected from residues of the previous experiments, the only product that appeared on the chromatogram up to and including the expected position of the parent, was MeCl, which was prepared in a reasonable yield. It would therefore be expected that the compound did not have fissile bonds apart from those to methyl groups, and that the other product, or products, were more retarded than the parent. It must be concluded that this was not a branched-chain silico-germane, but must have been a particularly inert siloxane or similar compound that was relatively

FIG. 45 Molar Ratios of the Products of the Gold Chloride Reaction on the Permethyl Silicogermanes



unaffected by sulphuric acid.

There was no other evidence of branched-chain compounds in the products of the permethyl silico-germane preparations.

6.8 Summary of the Analyses

Fig. 45 is a diagrammatic summary of the product ratios obtained from the gold chloride reaction on the permethyl silico-germanes. This clearly shows the chemical differences between the isomeric compounds, even when contaminated to a certain extent with their isomers.

It is concluded that the following permethyl silico-germanes have been prepared and identified:

$SiMe_3.GeMe_3$

$SiMe_3.GeMe_2.SiMe_3$

$SiMe_3.SiMe_2.GeMe_3$

$GeMe_3.GeMe_2.SiMe_3$

$GeMe_3.SiMe_2.GeMe_3$

$SiMe_3.SiMe_2.GeMe_2.SiMe_3$

$SiMe_3.SiMe_2.SiMe_2.GeMe_3$

$SiMe_3.GeMe_2.GeMe_2.SiMe_3$

$GeMe_3.SiMe_2.SiMe_2.GeMe_3$

$GeMe_3.GeMe_2.GeMe_2.SiMe_3$

$GeMe_3.GeMe_2.SiMe_2.GeMe_3$

and at least one, but more probably both, of the following:

$SiMe_3.SiMe_2.GeMe_2.GeMe_3$

$SiMe_3.GeMe_2.SiMe_2.GeMe_3$

FIG. 46 Sketch of the Band appearing after Ge_4Me_{10} in the Preparative Chromatograms of the "Washed" Products from the third Permethyl Silicogermane Preparation, indicating a possible explanation – Tritolyl Phosphate, Heat up from 90°C to 150°C.

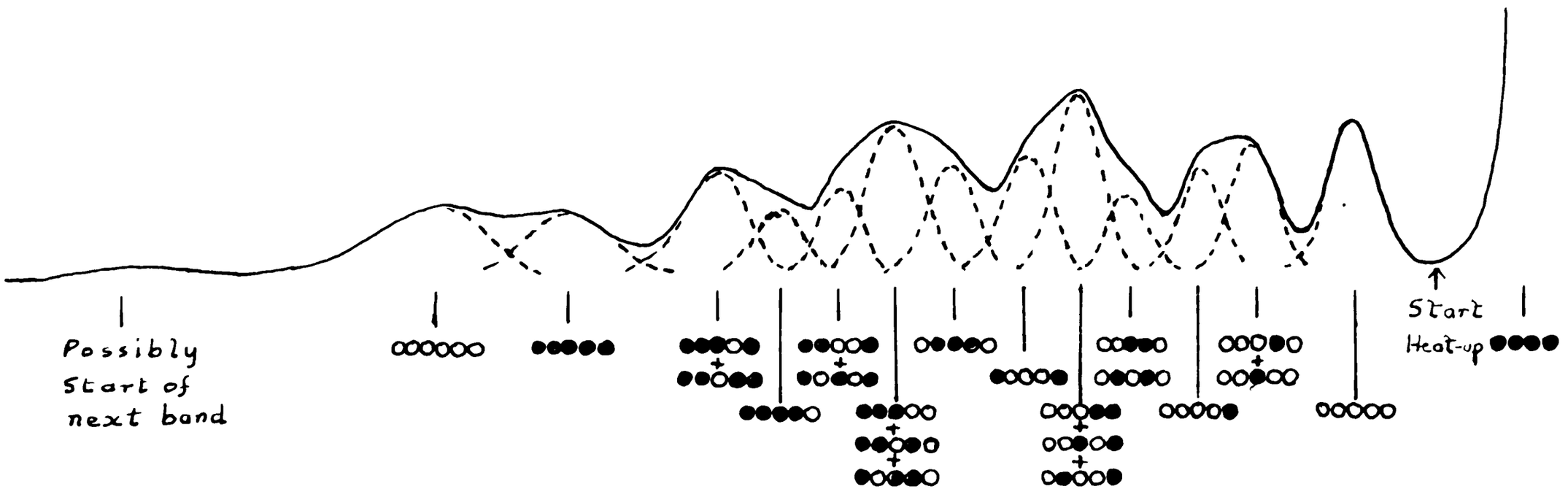
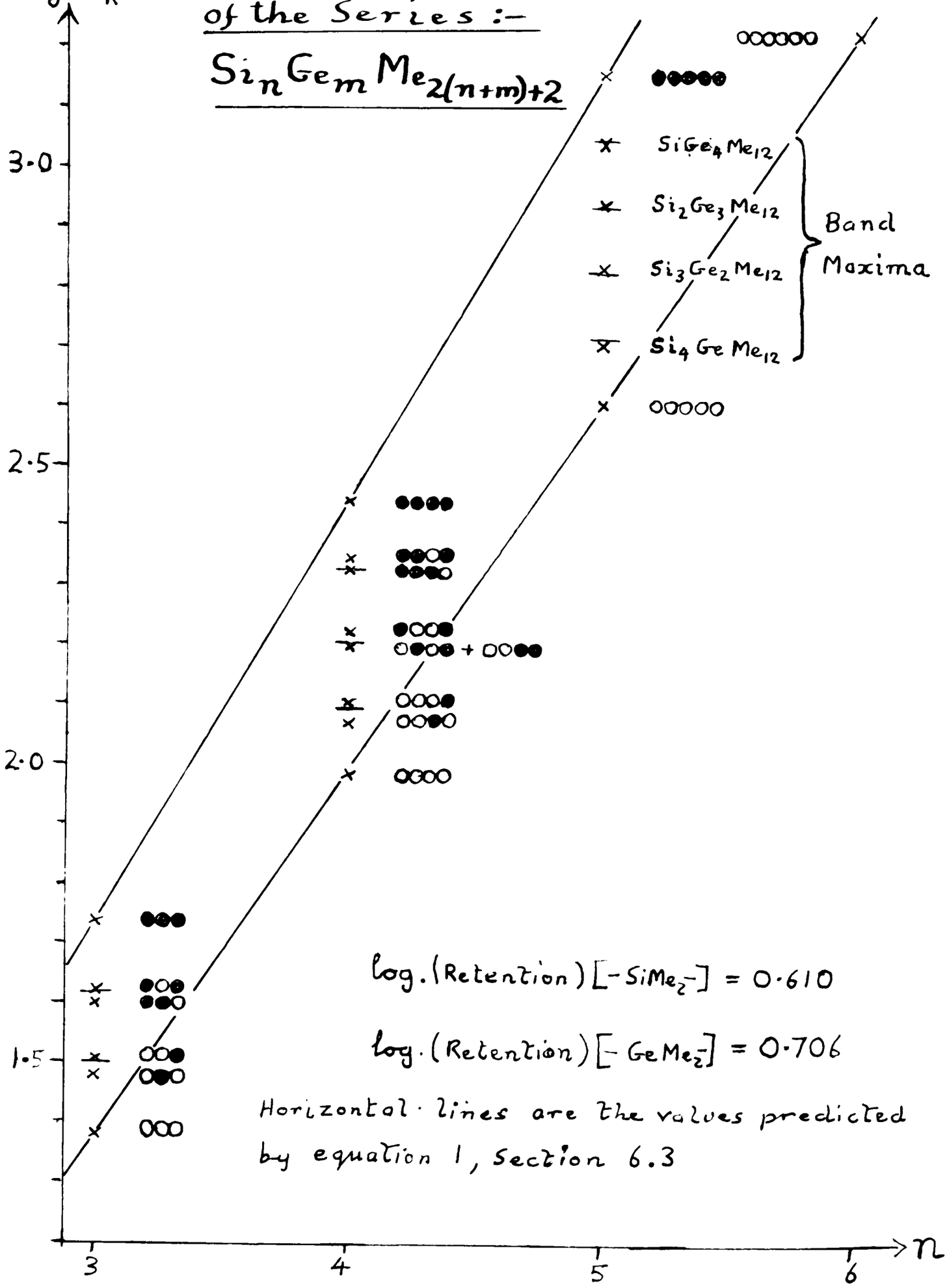


FIG. 47 Tritolyl Phosphate 120°C,

Retention of the Higher Members of the Series :-

$Si_nGe_mMe_{2(n+m)+2}$



$\log.(\text{Retention})[-SiMe_2-] = 0.610$

$\log.(\text{Retention})[-GeMe_2-] = 0.706$

Horizontal lines are the values predicted by equation 1, Section 6.3

6.9 Evidence of Higher Members in the Permethyl Silico-Germane Series

In the preparative chromatography of the products of the third reaction, there was evidence of the presence of compounds more strongly retarded than n-Ge_4Me_{10}. To investigate these, two of the preparative chromatograms were run, for longer than required for the products already described, at maximum sensitivity, and a band of peaks was observed. As the runs were, in any case, not conducted under isothermal conditions the best presentation was achieved by commencing a heat-up just before the emergence of the band. A sketch of the bands obtained from two similar runs is shown in Fig. 46. On the basis of the retention hypothesis developed in Section 6.3, a possible explanation and a tentative peak assignation have been carried out on this diagram. In an attempted confirmation of this, an isothermal chromatogram was carried out in the analytical system at 120°C on the tritolyl phosphate column. In order to be able to measure the earlier peaks, a fairly small sample was required. As a result, the best that could be measured of these higher boiling compounds were the band maxima and their approximate areas. Fig. 47 shows the logarithmic plot obtained from this run, which gives strong evidence for the existence of the five membered chains. On this basis the approximate yields in preparation 3, number of peaks probably seen and number of possible isomers were as follows:

n-Si_5Me_{12}		0.08%	
n-Si_4GeMe_{12}	2 peaks seen	0.09%	(3 isomers)
n-$Si_3Ge_2Me_{12}$	up to 3 peaks seen	0.12%	(6 isomers)
n-$Si_2Ge_3Me_{12}$	up to 3 peaks seen	0.12%	(6 isomers)
n-$SiGe_4Me_{12}$	at least one peak seen	0.06%	(3 isomers)
n-Ge_5Me_{12}		0.04%	

PART THREE

GAS - SOLID CHROMATOGRAPHY

AT SUB - AMBIENT TEMPERATURES

CHAPTER SEVEN

THE DESIGN, CONSTRUCTION, AND OPERATION OF A SUB-AMBIENT GAS CHROMATOGRAPH.

7.1 Introduction

This chapter is concerned with the design and operation of a chromatograph to investigate the interactions of certain solid phases with permanent gases and other low boiling compounds. In particular it was hoped that investigations into the 'fixation' of nitrogen as a ligand on transition-metal ions could be effected chromatographically, and work in this field is now proceeding.

The work described here was carried out by the Author in conjunction with S.S. Blume and M.M. Norgett (D.Phil. students): The Author designing, assembling, calibrating and testing the chromatograph, and the others constructing many of the components and operating the completed apparatus. M.M. Norgett is carrying out the current research.

The desired operating temperature range was approximately -190° to -70°C, and it was felt by the Author that the apparatus described by Merritt et al.[135] was unnecessarily complicated and that of Altenau et al.[136] (manual addition of liquid nitrogen to the oven of a commercial instrument) rather crude. In both cases, the temperatures obtained were only accurate to $\pm 2 - 3$°C which was felt to be insufficient for the purposes mentioned above.

The method of obtaining the variable sub-ambient temperature selected by the Author was to immerse a simple air oven in liquid nitrogen and suspend

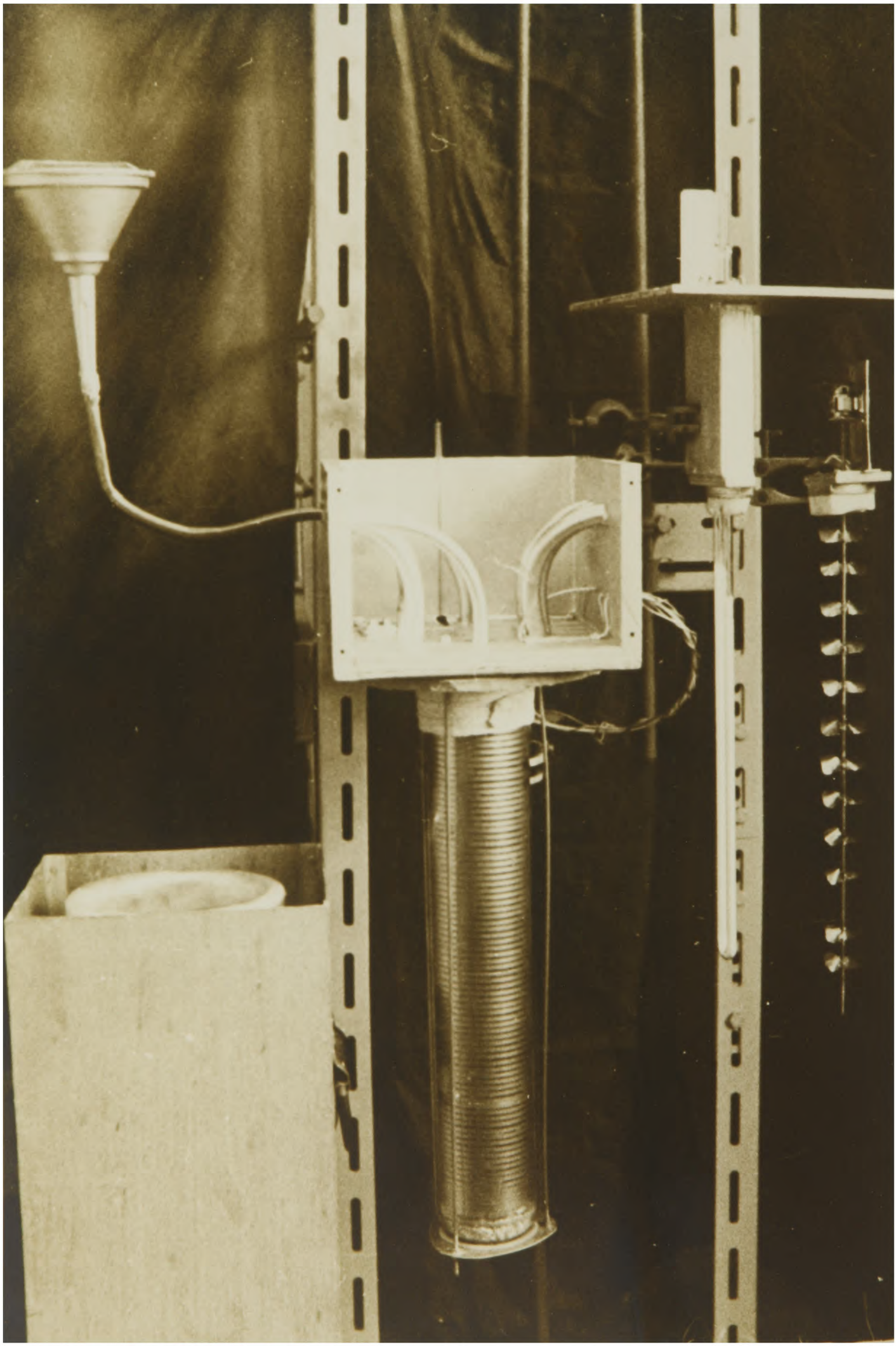
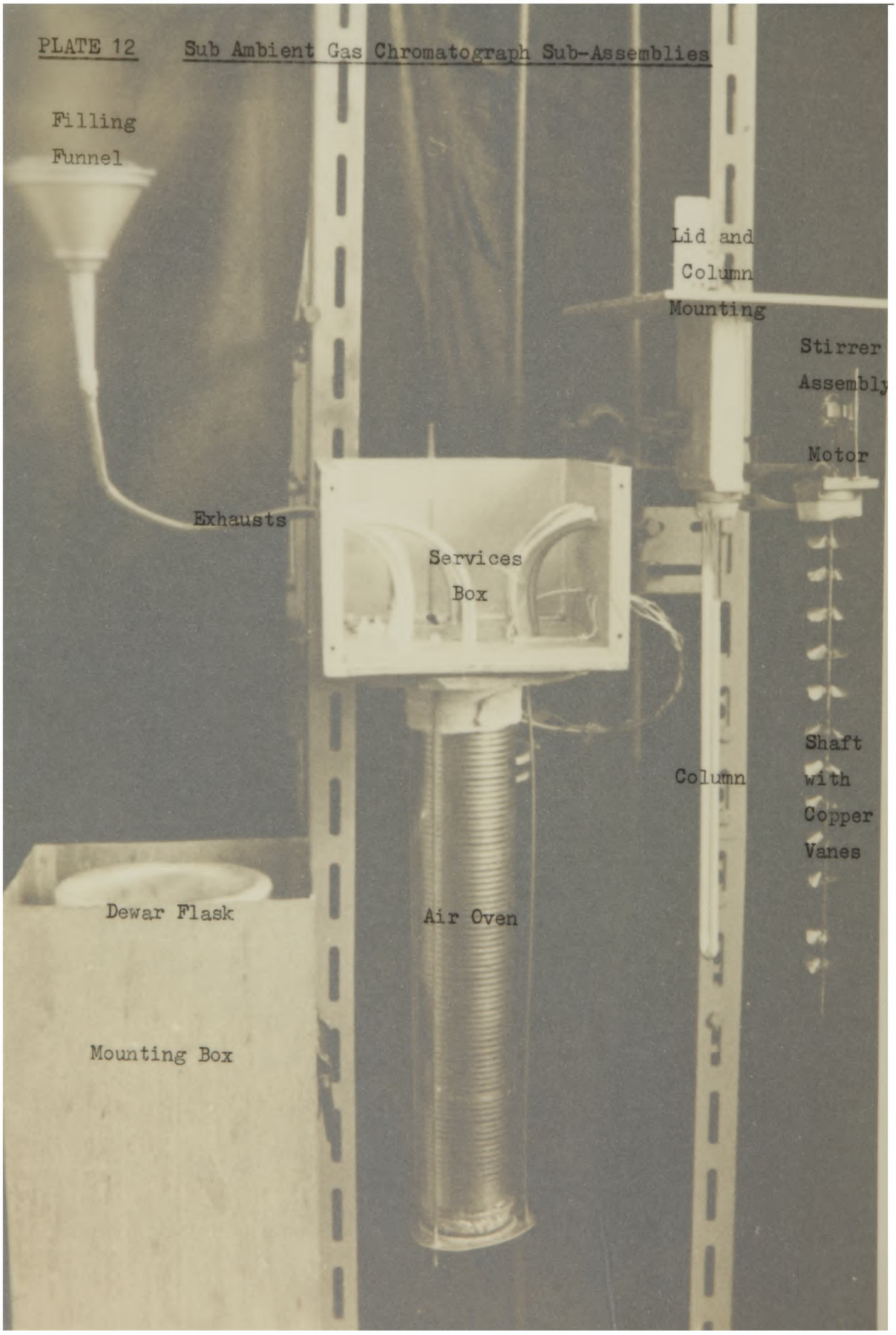


PLATE 12 Sub Ambient Gas Chromatograph Sub-Assemblies



the chromatographic column inside it. Since considerations of the size and shape of the available Dewar vessels dictated an oven comparatively narrow in proportion to its length, the principle of constantly spaced heating tape around a cylindrical former (see Section 2.41) was employed. The oven consequently had to be mounted vertically and considerable end effects were anticipated, thus some system of stirring the atmosphere of the oven had to be devised.

7.2 Design and Construction of the Oven and its Ancilliary Equipment (Fig. 48 and Plate 12)

7.21 The Oven

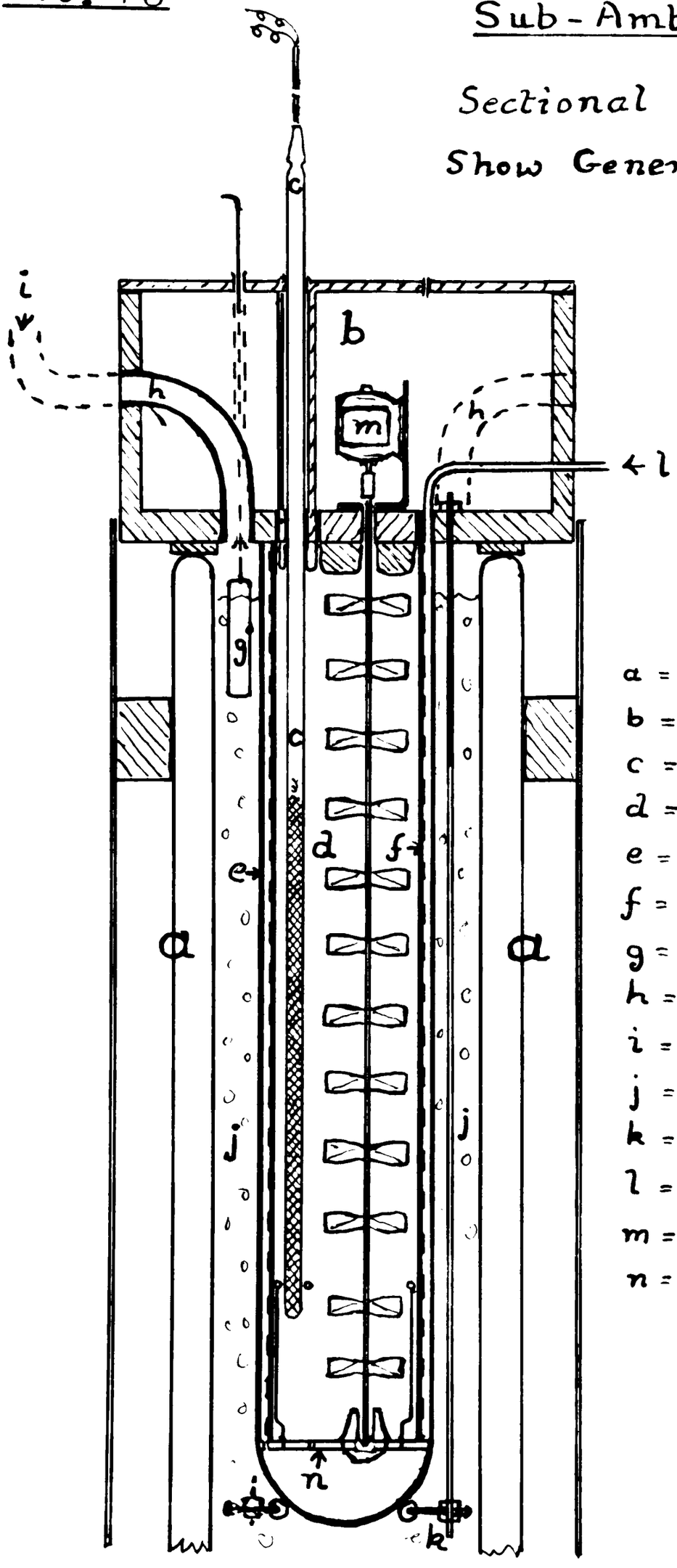
It was felt that with an oven immersed in liquid nitrogen with its ancilliary equipment at the top, there would be a considerable end effect at the top at low oven temperatures, and a lesser effect at the bottom at high oven temperatures. As it was intended to operate 'U' shaped chromatographic columns with a total packed length of about 50cm., an oven length of about 45cm. was selected. A maximum outer working diameter of 9.5cm. was dictated by the inner diameter (12.7cm.) of the available Dewar flask of suitable length.

The oven was built inside a glass tube with the lower end rounded off, an overall length of 47.5cm. and an outside diameter of 8.4cm.. Inside this tube, flush with the open top, was mounted a glass tube of length 44cm. and inner diameter 7.0cm. with the heater wound on it. There was an air gap of about 1.5mm. between the two tubes. At the bottom of

FIG. 48

Sub-Ambient Oven

Sectional Diagram to Show General Arrangement



a = Dewar Vessel and Box
b = Services Box
c = Column
d = Oven
e = Oven Outer Tube
f = Oven Inner Tube with Heater
g = Float
h = Nitrogen Exhausts
i = Liquid Nitrogen Filler
j = Liquid Nitrogen
k = Oven Support
l = Oven Gas Supply
m = Stirrer Motor
n = Bulkhead and Bearing

the heater tube was a bulkhead of 'Hardboard' carrying and spacing the heater inside the outer tube and fitted with a glass bearing for the stirrer shaft, a wire framework for locating the bottom of the column so that it would not encounter the stirrer fans, and holes so that gas coming down the air gap could pass into the bottom of the oven space. The space between the bulkhead and the rounded bottom was filled with 'Vermiculite'. The complete oven was suspended from the base of the services box described below by means of three brass rods with a duralumin plate padded with rubber at the bottom to support the rounded end of the oven.

The furnace was wound with 0.125" x 0.0031" Nichrome V tape (British Driver Harris Ltd.) of resistance 4.22 ohm/yd.. The turns were spaced at 5mm. between centres with the exception of about 4cm. at the bottom and top where spacings of 4 and 6mm. were respectively employed to reduce the expected end effects. The turns were stuck down by 'Araldite' adhesive (Ciba A.R.L.) which was also used for sticking and sealing the tops of the two tubes separately to the services box, and all other joints in the oven assembly. The return wire from the furnace was led up the inside of the furnace tube. The resistance of the heater at room temperature was about 92 ohms.

The top of the oven tube was wrapped for about 5cm. of its length with asbestos tape to a depth of about $\frac{1}{2}$ cm. to act as a wick to minimise the effect of a drop in level of the surrounding liquid nitrogen.

The oven power was obtained from a 'Volstat' constant voltage transformer and controlled by a 'Variac' transformer (see Section 2.41).

7.22 The Stirrer

To minimise heat conduction out of the oven, the thinnest practical stirrer shaft was desirable. 0.125" dia. steel welding rod was chosen and this carried 12 small copper sheet vanes, with an effective diameter 3.8cm., at approximately 3cm. intervals. The bottom end of the shaft was ground down to a fine rounded point to fit inside the glass bearings. In view of the operating temperatures, no liquid lubricant was used, but the end of the shaft was polished with graphite. The shaft was mounted offset in the oven so that the column and thermocouple could be mounted opposite and the maximum possible fan diameter could be used. The top of the shaft was machined so that a 'bush', subsequently replaced with a piece of silicone rubber tubing, could couple it coaxially to the motor. The vanes were made of 0.009" copper sheet, originally soldered, but subsequently stuck to the shaft with 'Araldite', and given a propeller-type twist so that they would produce a downdraught when rotated.

The shaft was driven by a small D.C. motor (Mabuchi, Japan) of 28-40 gm.cm. torque which was mounted on a removable trap door, through which the shaft passed, fitting into the base of the services box.

7.23 The Services Box

The services box was designed as the central piece of the apparatus, to accomodate all the individual units and their supplies. It was constructed, without a top or front, out of 'Gabon' resin-bonded plywood of various thicknesses. The box fitted into the top of the box in which the Dewar flask was mounted, and had a thin polyurethane foam washer stuck on its bottom to act as a seating onto the top of the Dewar flask.

The oven was attached to the centre of the base, and trap doors were cut in the latter to carry the stirrer and column assemblies. A series of 10 holes were cut in the base around the oven with corresponding holes in the two sides for taking 15mm. o.d. PVC tubing to act as exhausts for the evaporated nitrogen and to permit filling of the Dewar flask. The tube used for filling was subsequently replaced by copper tubing since the PVC tubing, when carrying liquid nitrogen, tended to crack. These tubes also assisted with the cooling of the atmosphere in the services box. A vertical glass tube was fitted in an additional hole in the base and projected through the top of the box, which was removable. A stiff wire with a sealed cork float at the bottom passed through this tube to act as a liquid nitrogen level indicator.

A small hole was drilled in the base so that a supply of dried nitrogen could be introduced between the oven tube and heater tube, entering the oven at the bottom, to act as the oven atmosphere, and to provide a constant thermal environment for the heater. The nitrogen (helium would have been preferable) was supplied at about 100 ml/minute.

The base was constructed with two accurately fitting trap doors, one carrying the motor and top of the stirrer shaft and the other firmly attached by means of a box construction to the removable top of the services box. This latter assembly was drilled to take the two arms of the column, with the thermocouple in between, and hold them vertical, whilst leaving them free to be moved up and down, so that contact with the stirrer would be avoided.

The electrical supplies for oven and stirrer and the nitrogen supply for the oven were led in through one of the sides and a removable perspex

front completed the box. Both the top and front were attached by screws.

It was intended that the box should be hermetically sealed with PVC adhesive tape over the joints of front and top, and 'Plasticine' where columns and thermocouple emerged. A small outlet was provided in the top of the box for the oven nitrogen. In fact this was found to be unnecessary as only a minute flow could be detected through this hole despite sealing all permanent joints with a solution of 'Perspex'. in chloroform as a paint. As a result it proved impossible to totally exclude moisture from the services box and some trouble was encountered with condensation of ice at the top of the stirrer shaft.

The overall dimensions of the box were approximately 21.5cm. wide and deep and 12.5cm. high.

7.24 The Thermocouple

A copper (32 gauge) Constantan (28 gauge) thermocouple was made up with the wires threaded down thin glass tubes and the junctions projecting about 2.5cm. from the ends. The junctions were coated with Araldite as insulation and to give additional mechanical strength. The standard probe was immersed in liquid oxygen in a small Dewar flask and the sensor probe was inserted in the column support assembly so that it could be moved down the centre line of the 'U' of the column. The output of the thermocouple was fed directly onto a Honeywell 10 mV potentiometric recorder so that a continuous monitor of the temperature could be taken.

The thermocouple was calibrated in melting ice ($0^{\circ}C$), slowly freezing mercury ($-38.9^{\circ}C$), solid/gas CO_2 ($-78.5^{\circ}C$), slowly melting dry ether ($-116.3^{\circ}C$), liquid oxygen/gas ($-183.0^{\circ}C$) and fresh liquid nitrogen/gas

(-195.8°C). A graph was drawn of the values obtained, using the difference values obtained from the literature[137] for the interpolations. Since the absolute values quoted differed only slightly from the experimental values, it was felt that the thermocouple was accurate and reproducible within the limits of the recorder which were estimated to correspond to about $\pm$0.2 to $\pm$0.3°C. ($\pm 5\mu V$) and the interpolation was sufficiently accurate to be within these limits.

7.25 The Columns

The columns were packed in glass tubes with an outside diameter of about 7mm., the separation of the limbs of the 'U' was about 9mm. and the tube made to project down into the oven about 35-40 cm.. It was anticipated that no major end effect would be encountered more than about 5 cm. from the bottom of the oven and more than about 10 cm. from the top. This allowed about 2 x 25 cm. of packed column at the lower end of the 'U'. The glass tubing continued about the top of the services box for 5-8 cm. and B7 Quickfit cones were blown onto the ends. To these were fitted the column gas supply, injection port and detector fittings, which were retained by springs.

For the oven trials the column projected 38 cm. into the oven (6 cm. from the bottom) allowing the thermocouple to probe down to the 37 cm. level.

7.3 Operation and Performance of the Oven and its Ancilliary Equipment

7.31 Preliminary Running

A preliminary run was carried out to see if any modifications were required.

Nitrogen, dried by molecular sieve, was passed through the oven to purge it of all condensible matter (H_2O, CO_2, O_2) for 30 minutes at 200 ml/min., prior to filling the Dewar flask with liquid nitrogen. When this had been done and the oven was cooled right down, the purge flow was cut to about 100 ml/min., and the oven was then run up.

It had already been found that with such a long and comparatively flexible stirrer shaft, vibration occurred at low shaft speeds and the motor laboured somewhat. However, if the current was increased, a 'vibration barrier' was suddenly passed and the shaft vibration stopped allowing the motor to speed up; the motor current could then be considerably reduced and the shaft would still rotate smoothly at 1000 - 2000 r.p.m. (estimated by strobe effect).

It was now found that under conditions where there was a rapid ebullition of liquid nitrogen, i.e. at high operating temperatures ($-100^{\circ}C$ to $-70^{\circ}C$), with the consequent greater cooling of the services box, the stirrer motor laboured even under high applied currents. This was found to be caused by the oil in its bearings freezing. As the motor did not run well without oil, a modification was carried out. This consisted of heating the end plates of the motor with cotton covered Manganin wire connected in series with the motor, and then boxing in the motor with asbestos paper. At the same time the motor oil was replaced

with an oil containing molybdenum di-sulphide normally used for clocks (Standard Oil Co.). These measures proved to be adequate.

The bottom glass bearing was rather easily worn away with consequent damage to the tip of the stirrer shaft and reduction of shaft speed. Eventually this was replaced with a bearing made of stainless steel lubricated with graphite.

It was also found that the oven nitrogen flow was insufficent to keep moisture out of the services box although none was detected in the oven itself. An attempt was made to improve the sealing and a bag of silica gel was introduced into the services box.

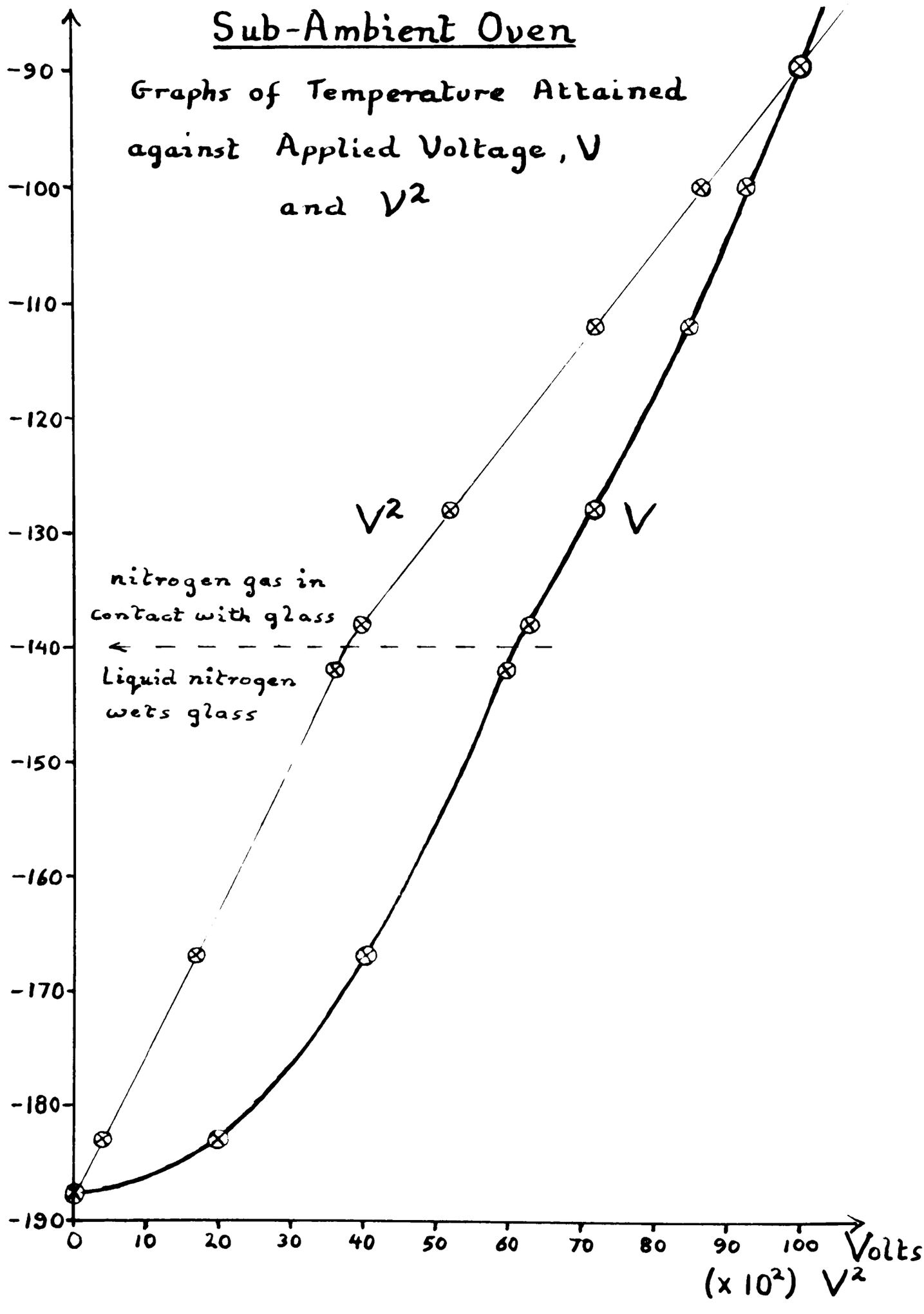
A series of calibration runs was carried out to discover the characteristics of the oven. In particular the applied voltage/oven temperature curve, with the probe near the centre of the packed column, was required together with the temperature profile down the length of the oven at various temperature settings. Also it was required to know the oven response time to change of temperature setting, and the effect of drop in liquid nitrogen level.

Temperatures were read to the nearest half-degree, corresponding to twice the detectable change.

7.32 Oven Response Time

On examination of the temperature/time curves obtained directly from the thermocouple recorder, it was found that, as expected, on a step change of applied voltage, the response was approximately first order with a time constant of approximately $4\frac{1}{2}$ minutes. This time compared favourably with the response of tubes heated on the outside described in

FIG. 49


T°C
Sub-Ambient Oven
Graphs of Temperature Attained against Applied Voltage, V and V²
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
V²
V
nitrogen gas in contact with glass
Liquid nitrogen wets glass
0
10
20
30
40
50
60
70
80
90
100
Volts
(x 10²) V²

Section 2.41. From this it can be seen that for a temperature change of 60° it would take about 25 minutes to settle within 0.5° of its equilibrium value. In fact, the usual technique chosen was to over-compensate initially and adjust the voltage to the desired value when the temperature reached about 2° short of the desired temperature, which, because of the response lag, was very rapidly reached.

7.33 Relation of Temperature to Applied Voltage

A series of values of temperature against applied voltage was taken and plots of V against T and V^2 against T were drawn (Fig. 49). For Newton's law of cooling the latter plot should have been approximately linear, but proved not to be so. The general curvature of the plot may be partly due to the change of heater resistance with temperature, but it is seen that there was a change of slope at about $-140^{\circ}C$. This may be explained by the fact that at low temperatures the wall of the furnace would be effectively in contact with liquid nitrogen, whereas at the higher temperatures the wall would be effectively in contact with a thin layer of nitrogen gas, which appeared to be a more effective remover of heat, accounting for the reduced slope.

The temperatures, once attained, were held within $\pm 0.5^{\circ}$ provided the liquid nitrogen was topped up as described in the next Section.

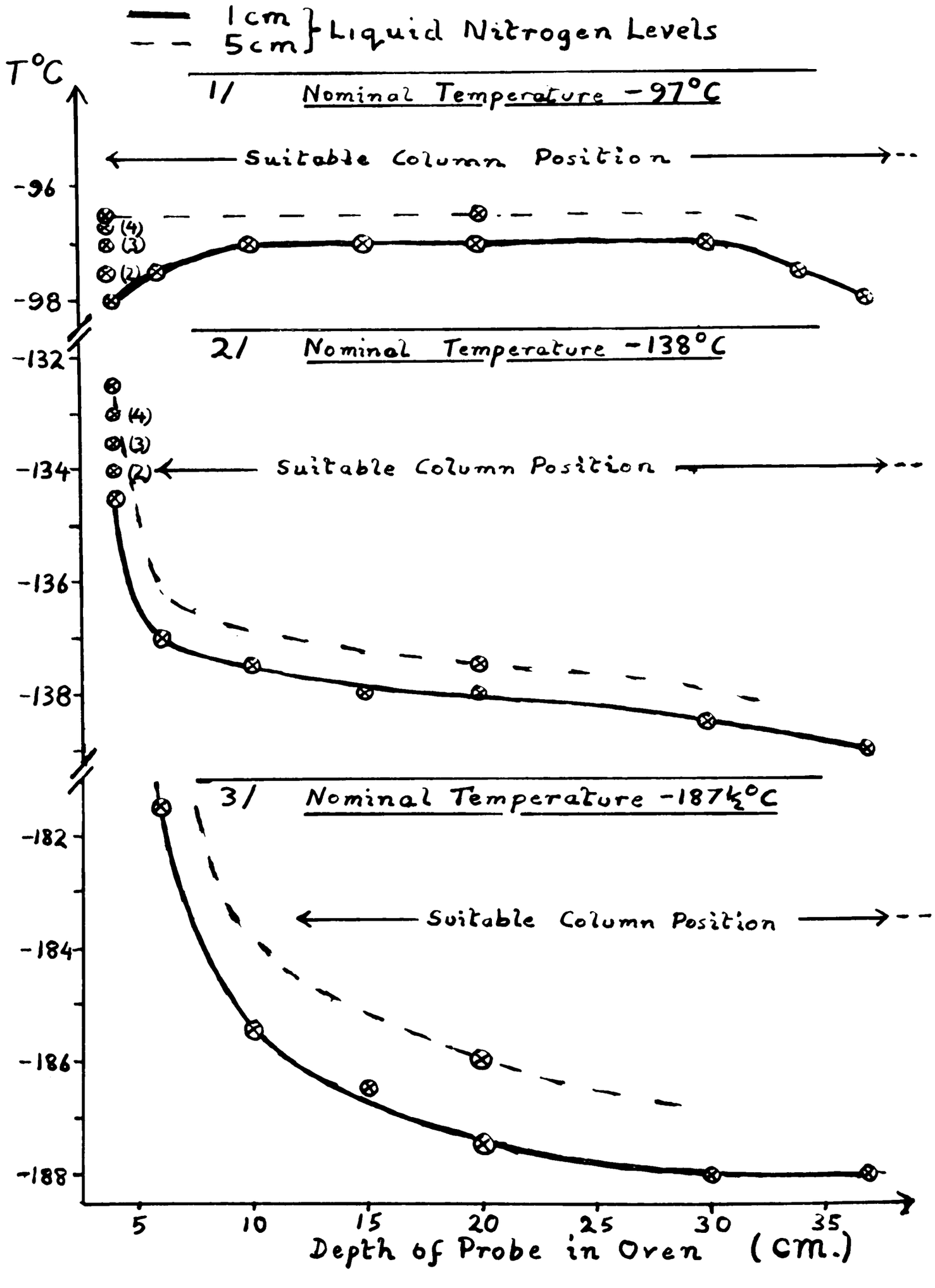
7.34 Oven Temperature Profile and Effect of Liquid Nitrogen Level

A series of thermocouple readings at three separate nominal oven temperatures was taken, varying the depth of the probe and the liquid nitrogen level. In each set, the readings were first taken with the

FIG. 50

Sub-Ambient Oven

Temperature Profiles



liquid nitrogen kept 1 cm. $\pm$ 0.5 from the top of the Dewar vessel and the thermocouple probe at different levels in the oven. At least 3 minutes were allowed for the thermocouple to equilibrate for each reading. Then with the thermocouple near the top of the oven, where the maximum effect of change in nitrogen level was expected, the level was allowed to fall and the temperatures at different levels down to 5 cm., were noted. Finally the probe was replaced at the centre of the oven and the temperature with the nitrogen level 5 cm., from the top was noted. As a check, the Dewar flask was again filled to the 1 cm. level and the temperature checked for drift. The time taken for the nitrogen level to fall was also noted. These results are shown in Fig. 50 and Table 25.

From these experiments, if a temperature range along the column of $\pm 2^{\circ}$ is acceptable, the following approximate conclusions are obtained:

TABLE 25

Voltage Applied	Temp.	Usable Levels in Oven	Temp. Change for Liq. N_2 from 1cm. to 5cm.		Time Taken for Liq. N_2 to drop 1cm. to 5cm.
			At Centre	4cm. from Top	
0	$-187\frac{1}{2}^{\circ}$	12cm.-37+cm.	$+1\frac{1}{2}^{\circ}$	$+2\frac{1}{2}^{\circ}$	35 mins.
$63\frac{1}{2}$	-138°	6cm.-37+cm.	$+\frac{1}{2}^{\circ}$	$+2^{\circ}$	15 mins.
95	-97°	4cm.-37cm.	$+\frac{1}{2}^{\circ}$	$+1\frac{1}{2}^{\circ}$	8 mins.

The temperature profiles show that the top end profile improved with rise of oven temperature, and was almost negligible (and even negative) at the highest temperature shown. As expected, the lower end profile was best at the lower temperatures and only really became noticeable at the highest temperature. As this temperature was sufficiently near the design maximum, it was not deemed necessary to modify the lower end,

the column being merely raised in the oven somewhat when operated at higher temperatures. A possible modification would have been to mount a small additional heater of 2 - 3 ohms on the bottom bulkhead.

A similar test with the stirrer turned off was carried out. The results were not so reproducible and tended to gradually drift with time. It was concluded that the oven temperature profile was improved by a factor of 2 to 2½ by having the motor running. The effect of varying the speed of the motor was not very great, presumably because at high shaft speeds the stirrer blades were 'stalled' aerodynamically and therefore not very efficient.

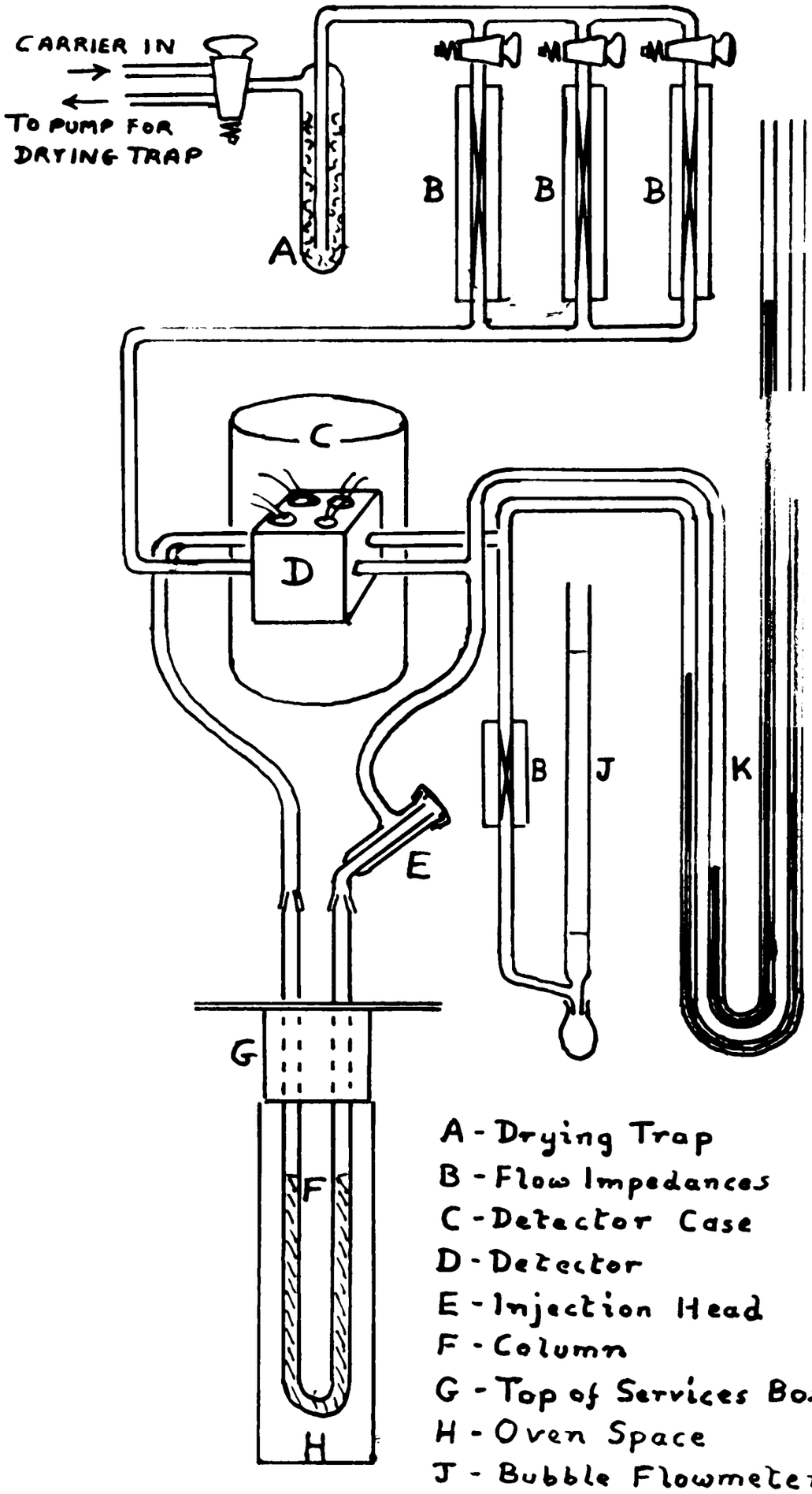
7.4 Conclusions on the Oven Design

It may be concluded from the above that the oven design was suitable for obtaining temperatures in the range -188°C to -90°C or possibly higher, with a precision of $\pm\frac{1}{2}^{\circ}$ at the centre and a temperature gradient, down a 25 cm. range of less than $\pm 1^{\circ}$, provided that the apparatus was refilled with liquid nitrogen at least every 8 minutes at the higher temperatures and 15 minutes at the lower.

At temperatures between -140°C and -100°C, longer columns could be used (30 cm.) without altering the temperature range along them. At higher temperatures than -100°C it was suggested that, without modification to the bottom of the oven, the columns be raised 2 to 4 cm. in the oven.

These characteristics were considerably more favourable than those previously mentioned in the literature[135, 136].

FIG. 51 Sub-Ambient Chromatograph
Schematic Diagram



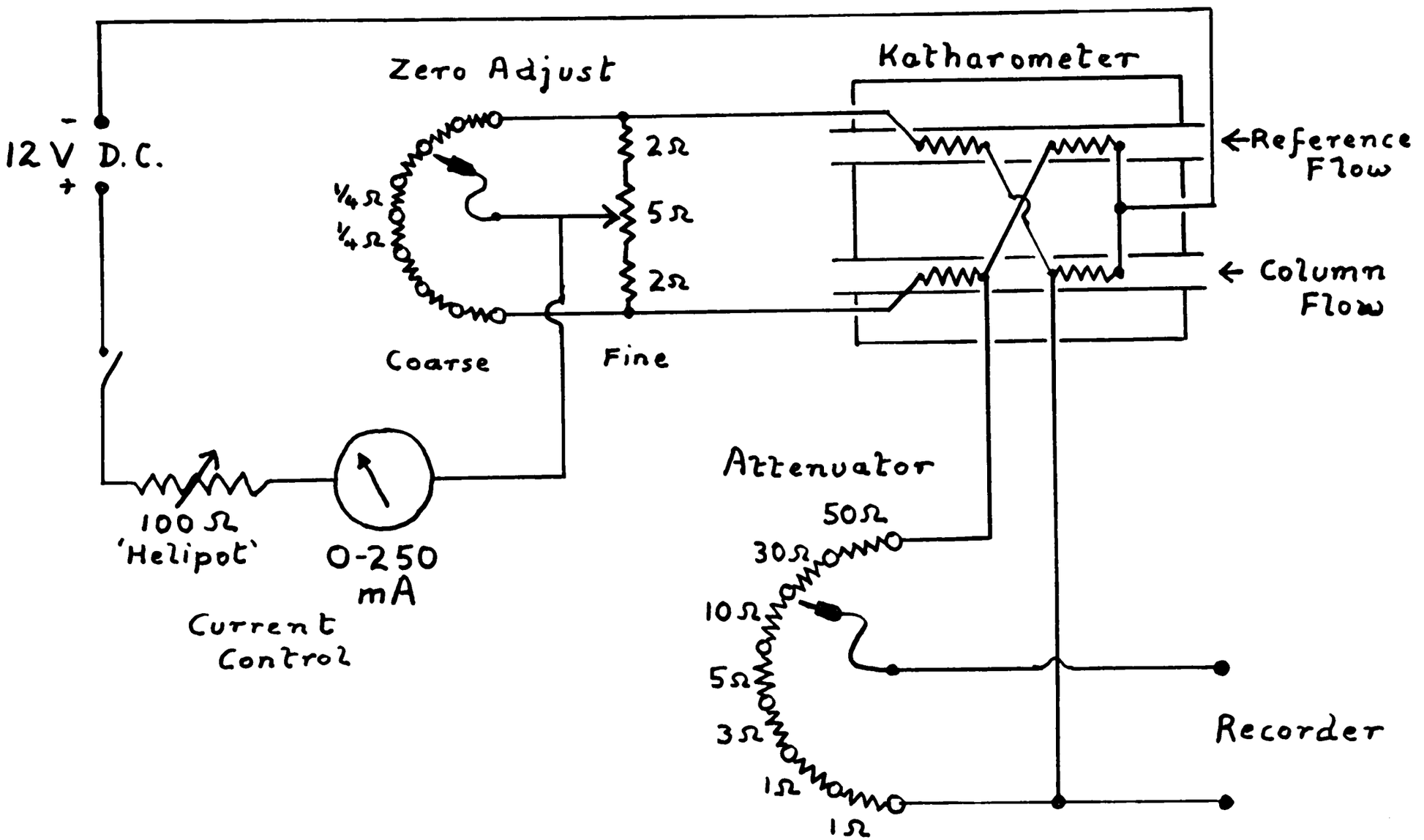
7.5 The Chromatograph (see Fig. 51)

7.51 Apparatus

Hydrogen or helium carrier gas was dried by passage through a trap containing molecular sieve (B.D.H., type 5A), and cooled with liquid nitrogen. As considerable differences in column impedance to gas flow on account of differing types of phase and temperature variations were anticipated, three flow restrictors were arranged in parallel so that a range of control could be obtained with the supply in the pressure range 10 to 20 psig. These were constructed as described in Section 2.42., and were lagged for short term temperature stability. The gas was then passed through the reference side of a Gow-Mac katharometer (see Section 2.45) and thence to the injection head. This was constructed in the same way as that described in Section 2.43, Fig. 12A, but was unheated. The injection head was fitted with a B7 quickfit socket for fitting to the column. The outlet of the column was fitted to a similar socket and both joints were maintained by springs mounted on the top of the services box. The effluent was passed through the detection side of the karharometer and thence via a low flow impedance to a bubble flowmeter. The pressures at both sides of the column were compared with atmospheric pressure by two mercury manometers permanently attached to the system. Most of the connections between components of the gas chromatograph were made with 1/8" o.d. nylon tubing which was joined internally to glass by sleeve joints sealed by Araldite adhesive. Taps and cone and socket fittings were lubricated with Apiezon L grease.

The katharometer was mounted in a vertical brass tube, diameter 4"

FIG. 52 Katharometer - Circuit Diagram



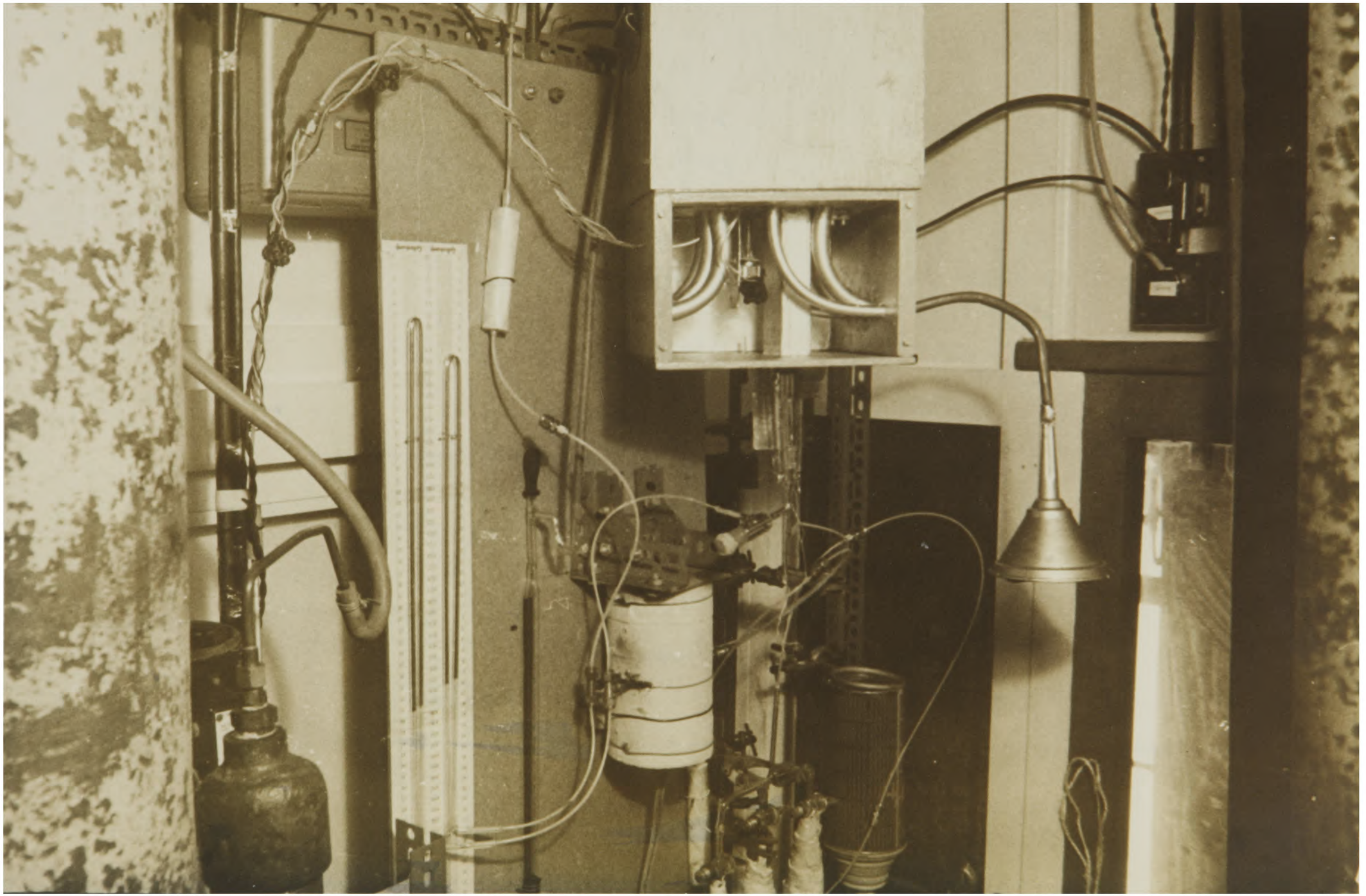
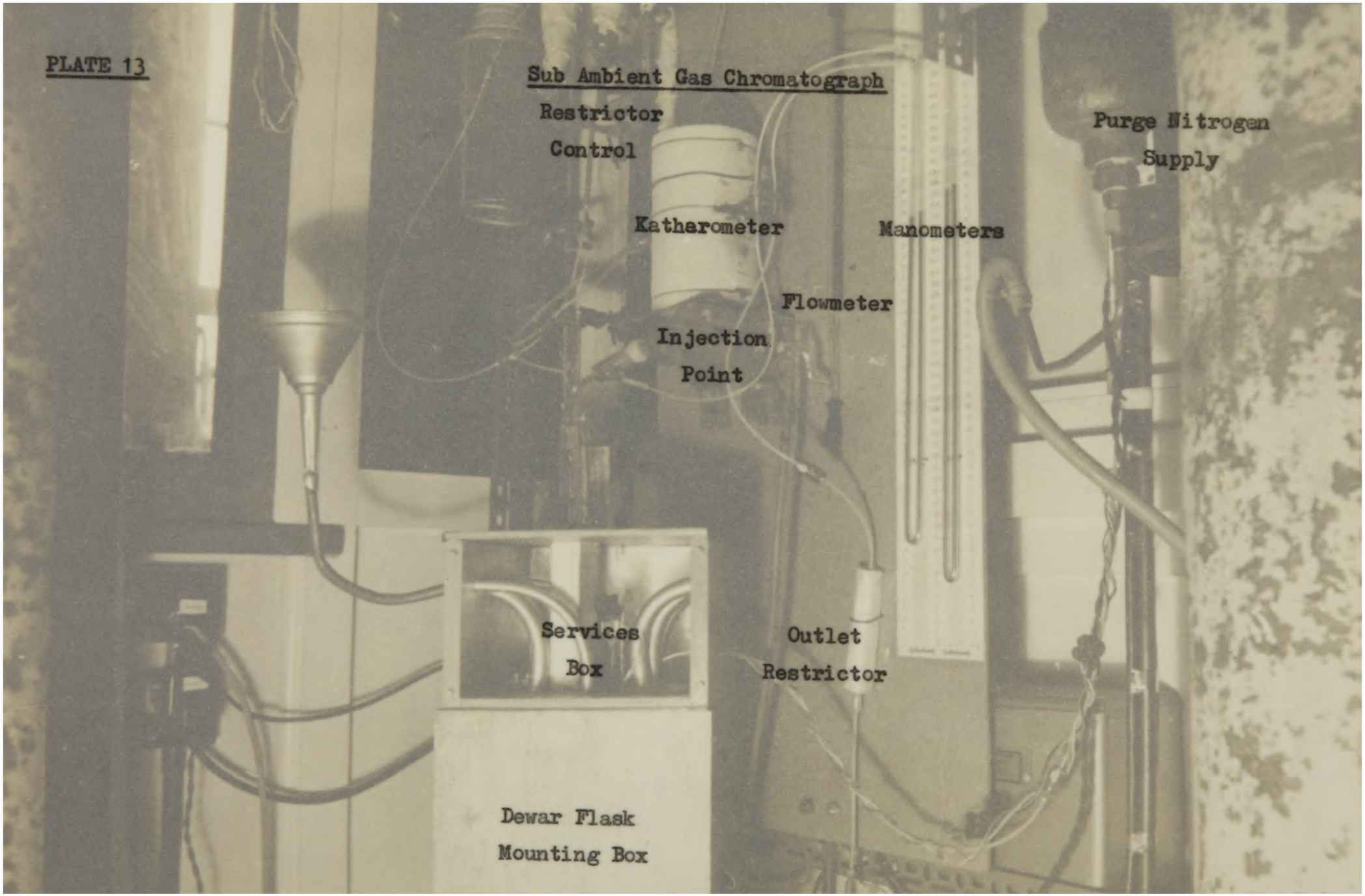


PLATE 13


Sub Ambient Gas Chromatograph
Restrictor Control
Purge Nitrogen Supply
Katherometer
Manometers
Flowmeter
Injection Point
Services Box
Outlet Restrictor
Dewar Flask Mounting Box

and height 8", closed at the bottom and filled with brass turnings. No heating or temperature control was provided. A simple bridge circuit, running off the same 12 volt stabilised power pack as the detectors in Section 2.45, with a modified zero adjustment, was used and this is shown in Fig. 52. The output was fed into a Honeywell Brown 1mV potentiometric recorder.

Most of the completed installation is shown in Plate 13.

7.52 Performance and Operation

The gas flow impedances allowed stable flow rates to be obtained in the range 25 to 250 ml/min.. Such flows gave a stable base line on the recorder chart with minimum attentuation of the signal. The sensitivity was such that the minimum detectable concentration of argon in hydrogen carrier was about 1×10^{-8} gm./ml., (5 ppm.). Despite lack of thermostatting of all but the column, drift was generally low.

Samples were injected with small medical syringes, 0.25 or 1.0 ml. capacity. As injection caused instantaneous pressure surges which were detected, no marker was necessary.

On all columns so far investigated using hydrogen as carrier, the 'dead volumes' calculated from the helium peak were the same at low temperatures as at room temperature. In such cases the helium peak may be used as an 'air peak' marker and all results were worked out on this basis.

7.6 Calculation of Heats of Adsorption

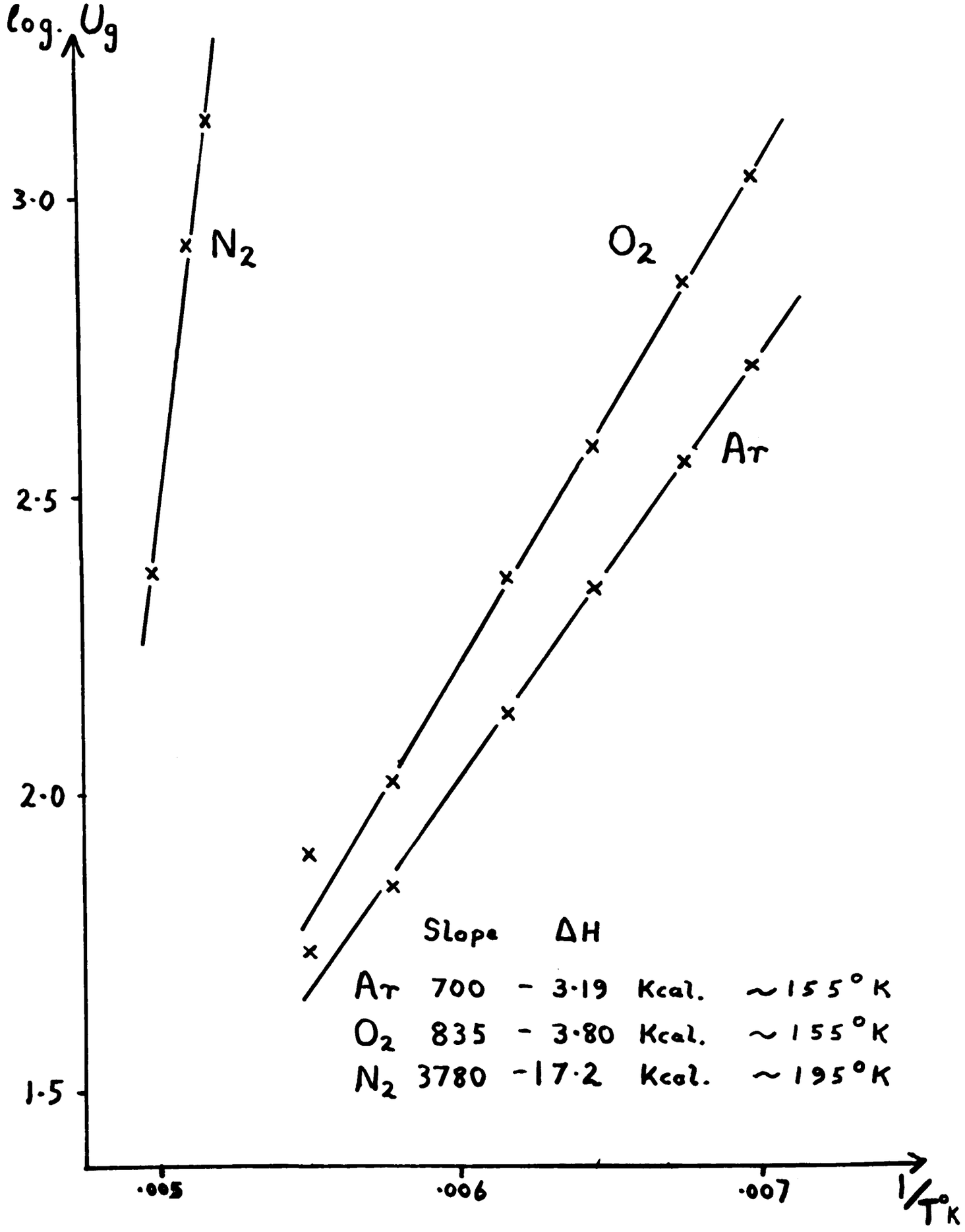
It has been shown in Section 2.72 that the quantity Vg in G.L.C. is defined as the retention volume for an ideal column containing 1 gm. of the stationary phase. Attempting to apply a similar concept to G.S.C. some difficulties are encountered.

In G.S.C. a chromatographic process is essentially equilibration between the gas phase and surface adsorption on a solid. For obtaining a similar function to Vg therefore, the pressure and other corrections to retention volumes will still be applicable, but the adsorption is due to an area of surface rather than a weight of solvent. In most cases, the surface area per gram of an adsorbent will vary from sample to sample and in a given sample will vary according to the treatment of that sample. This has been the principal objection to the use of G.S.C. for routine chromatography since the work of Scott[19], as retention values will tend to vary considerably with adsorption of water vapour from the carrier, phase changes etc..

However, for a given sample of adsorbent, provided the carrier gas is well 'dried', there is no phase change in the temperature range of the experiment, and no compound in any quantity is irreversibly adsorbed, it may be considered that the surface area is effectively unchanged and is therefore proportional to the weight of adsorbent.

In Section 2.73 it is noticed that the value for ΔH is obtained by subtracting log.Vg values. The same ΔH value would be obtained if no correction for column weight had been made, as there was no change in the weight between experiments. Similarly it is possible in this case to calculate ΔH values from either the corrected retention volumes, or from

FIG. 53 Graphical Evaluation of ΔH ads. of Gases on 5A Molecular Sieve



the corrected retention volumes divided by the weight of stationary phase, provided that the surface area does not change. The corrected 'retention volume per gram of adsorbent' is termed Ug after Janak[138]. Thus the ΔH value may be calculated from the following expression:

$$\frac{\Delta \log.Ug}{\Delta\, 1/T} = \frac{-\Delta H}{2.303\ R}$$

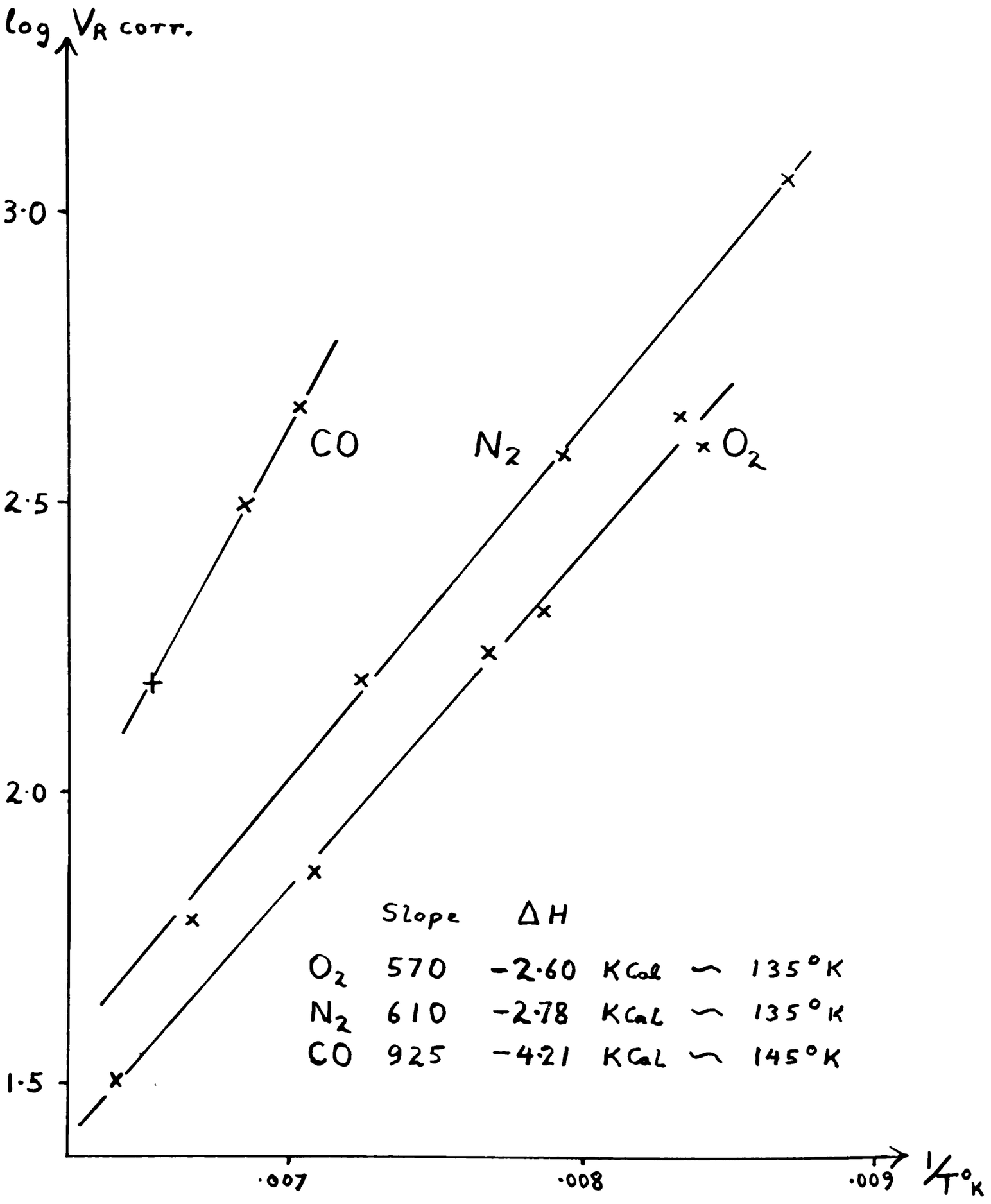
It will be appreciated that Ug is not as useful as Vg, as it cannot be used to predict retention volumes of columns unless a separate determination of surface area is done on different samples of adsorbent.

7.7 Results Obtained with the Sub-Ambient Chromatograph

Retention values were measured for Ar, O_2 and N_2 on a column of powdered 5A molecular sieve (B.D.H.), admixed with 'Embacel' (M. & B.) to reduce its effective weight, over a range of temperatures so that ΔH values could be calculated graphically, see Fig. 53. This experiment was carried out to test the Sub-Ambient Chromatograph. As the results were satisfactory, preliminary experiments in the investigation of the interaction of solid phases, containing different anions, but otherwise substantially the same, with Ar, O_2, N_2 and CO were carried out. The phases chosen were alumina, modified in turn with approximately 20% of NaCl, KCl and $BaCl_2$ by evaporation of slurries followed by drying at approximately 250°C.

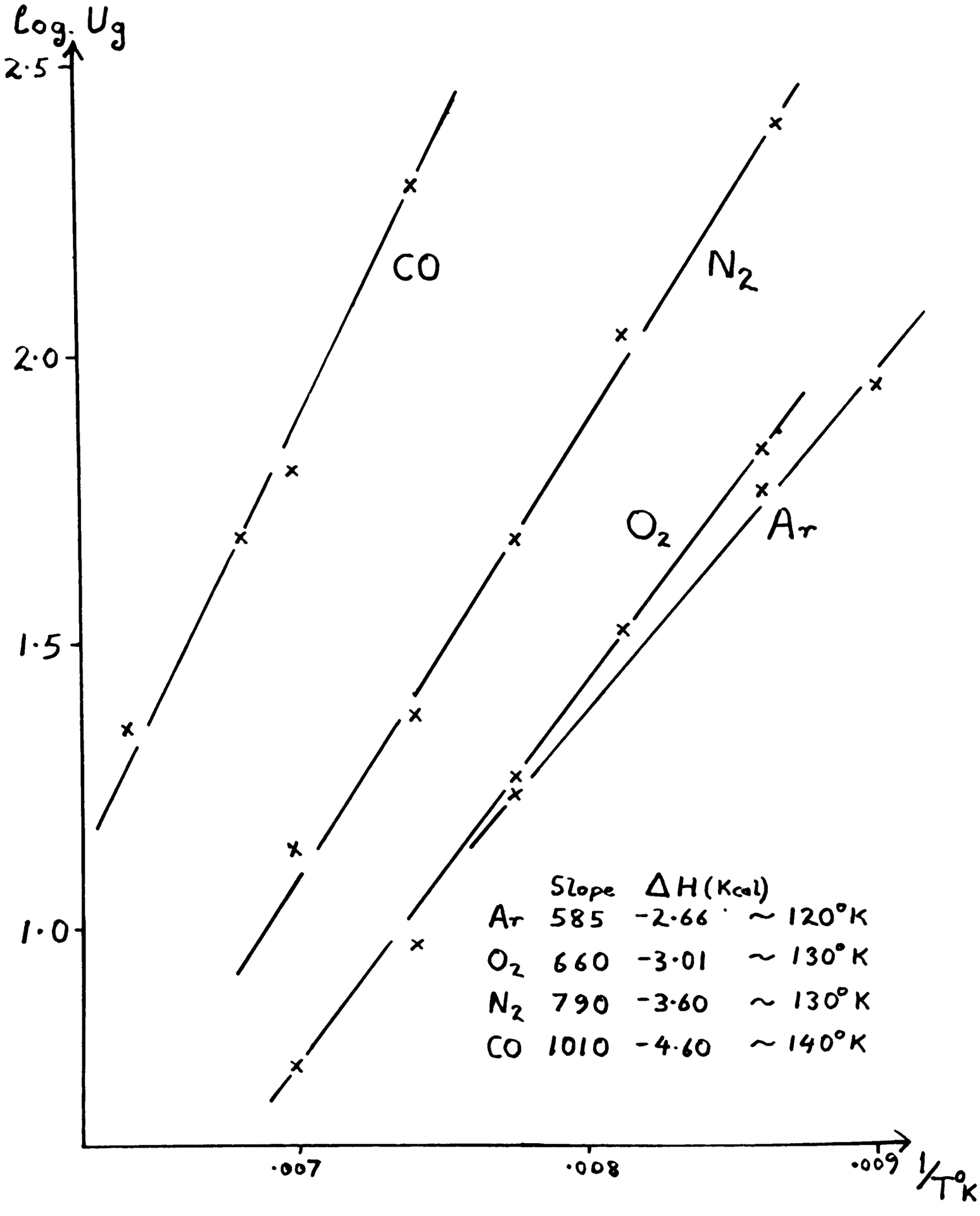
The graphical evaluation of the heats of adsorption is shown in Figs. 54, 55 and 56. The ΔH values obtained have a probable maximum error of $\pm$6%. These values are tabulated below and are compared with the values

FIG. 54 Graphical Evaluation of ΔH ads. of Gases on Alumina / NaCl



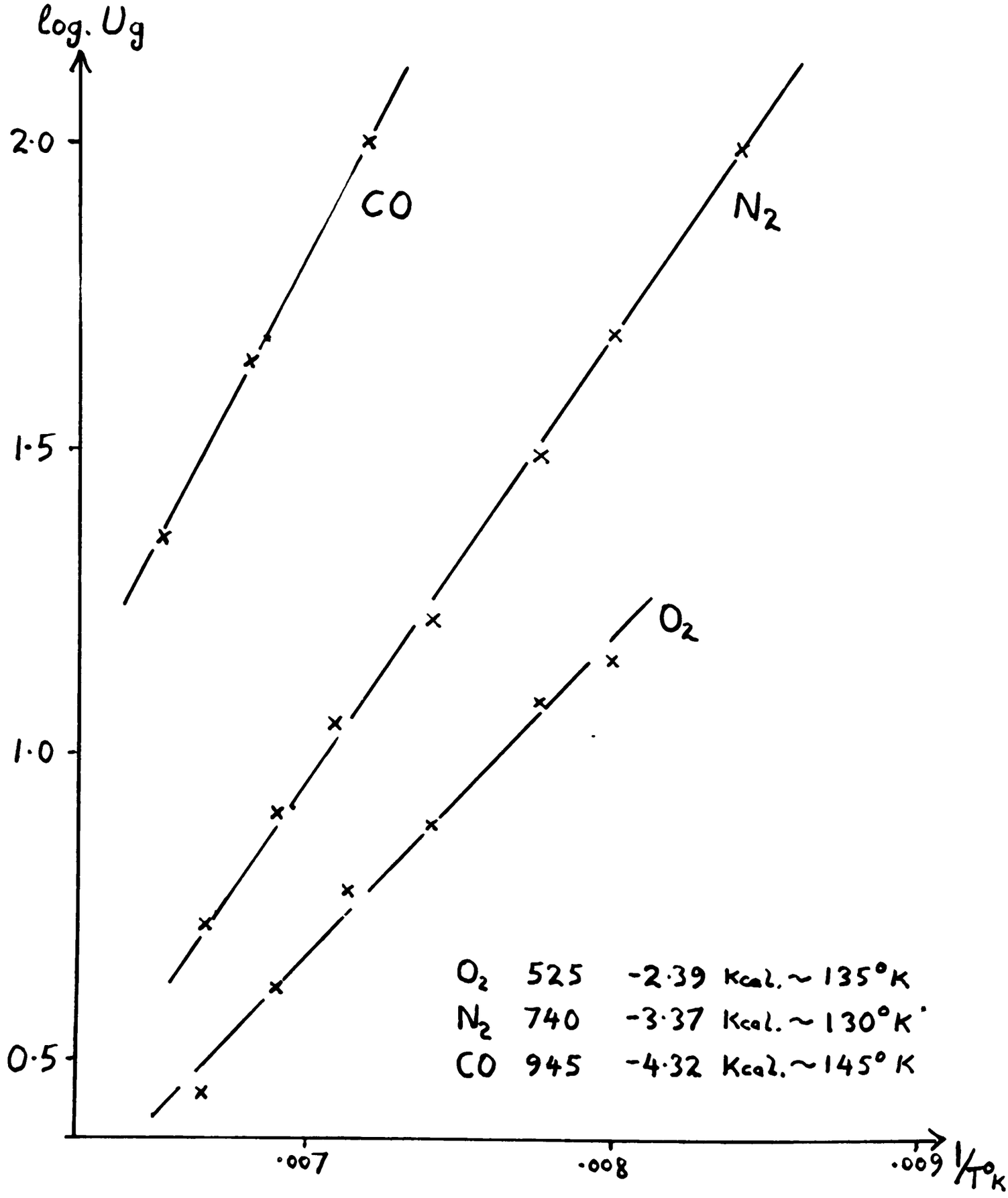
	Slope	ΔH	
O_2	570	−2·60 KCal	~ 135°K
N_2	610	−2·78 KCal	~ 135°K
CO	925	−4·21 KCal	~ 145°K

FIG. 55 Graphical Evaluation of $\Delta H_{ads.}$ of Gases on Alumina / KCl



	Slope	ΔH (Kcal)	
Ar	585	-2·66	~ 120°K
O_2	660	-3·01	~ 130°K
N_2	790	-3·60	~ 130°K
CO	1010	-4·60	~ 140°K

FIG. 56 Graphical Evaluation of ΔH ads. of Gases on Alumina / $BaCl_2$



obtained by Blume, on pure alumina, and with the molar heats of evaporation of the gases concerned.

TABLE 25

ΔH values in Kcal/mole.

Phase	Ar	O_2	N_2	CO
5A Molecular Sieve	-3.19	-3.80	-17.2	-
Alumina/NaCl	-	-2.60	-2.78	-4.21
Alumina/KCl	-2.66	-3.01	-3.60	-4.60
Alumina/$BaCl_2$	-	-2.39	-3.37	-4.32
Alumina	-2.93	-3.20	-3.47	-3.65
Approx. Temperature	120°K	135°K	130°K	145°K
(The temperatures on 5A sieve were 20°-40° higher)				
Heat of Evaporation	-1.50	-1.63	-1.33	-1.41

7.3 Conclusions and Discussion

Since the latent heat of evaporation represents the heat of interaction of the gas molecules in the liquid phase, the latent heat at the boiling point should prove a useful function for assisting in the assessment of the effects of the gas molecules with the solid phases. Accordingly the results have been retabulated in two ways: The first, Table 26, compares the heats of adsorption of the other gases with those of oxygen so that the relative effects of the gases may be noted, the second, Table 27, compares the heats of adsorption with the latent heats so that the effect of the phases may be seen.

TABLE 26

Heats of adsorption compared with oxygen.

Phase etc.	Ar	O_2	N_2	CO
Evaporation	0.92	1	0.82	0.87
Alumina	0.92	1	1.08	1.14
Alumina/NaCl	-	1	1.07	1.62
Alumina/KCl	0.88	1	1.15	1.53
Alumina/$BaCl_2$	-	1	1.41	1.81

This table shows that there is little relative effect between Ar and O_2, and since the nature of the interactions with Ar would be expected to be limited to simple effects like Van der Waals' attractions, it may be deduced that the adsorption of O_2 on these phases is similar in nature. However, both N_2 and CO show a relatively greater interaction on all the phases when compared with their evaporation, this effect in general increasing down the series, and being greater with CO.

TABLE 27

Heats of adsorption compared with latent heat of evaporation = 1

Phase	Ar	O_2	N_2	CO
Alumina	1.95	1.96	2.61	2.59
Alumina/NaCl	-	1.60	2.09	2.99
Alumina/KCl	1.77	1.85	2.71	3.26
Alumina/$BaCl_2$	-	1.47	2.53	3.06

This table shows deactivation of the phase by the various modifiers with respect to O_2 and Ar, being greatest with $BaCl_2$. With nitrogen there is an apparent deactivation on NaCl and a slight effect on $BaCl_2$, whereas CO has increased activity on all three modified phases.

The apparent partial contradiction of these two tables may be resolved if the effects are related to Ar (and hence O_2) by regarding the deactivations to the gases as due to a reduction in polarising power of the phases. Thus the first table may be regarded to give a more realistic picture of the selective effect of the modifier and hence as a measure of the 'extra energy' of adsorption of N_2 and CO on the modifiers themselves. This is best shown by taking the last two columns of Table 27 and normalising them to Alumina.

TABLE 28

Phase etc.	Normalised Values		% Extra Energy		Extra Energy Kcal.	
	N_2	CO	N_2	CO	N_2	CO
Evaporation	0.76	0.76	-24%	-24%	-	-
Alumina	1.0	1.0	0	0	0	0
Alumina/NaCl	0.99	1.42	- 1%	+42%	+0.03	-1.25
Alumina/KCl	1.06	1.34	+ 6%	+34%	-0.20	-1.17
Alumina/$BaCl_2$	1.30	1.59	+30%	+59%	-0.78	-1.60

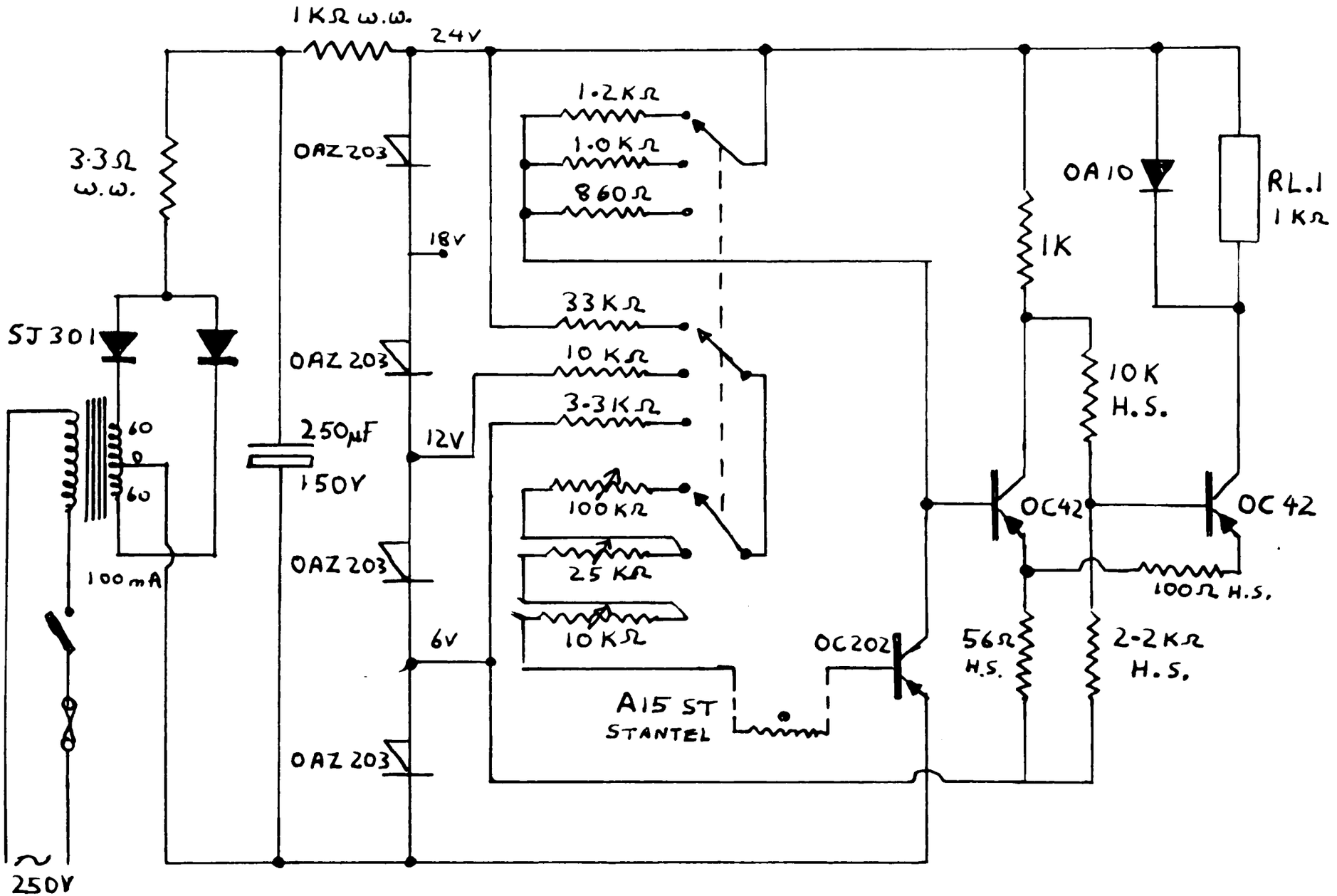
With the existing technique it is seen that quite small relative changes in heats of adsorption on different phases may be detected. When the quality of the results is improved by improved experimental technique, as familiarity with the equipment increases, some good values of ligand interactions should be obtained, and the method should be widely applicable.

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FIG. 57 Temperature Controller



APPENDIX 1

Direct Column Heating Using a Temperature Controller

A thermistor inserted in the temperature sensing tube of the chromatographic column heating arrangement described in Section 2.41 was used as sensor for the temperature controller shown in Fig. 57. Power for the column heating was provided by the Volstat/Variac transformer combination (described in Section 2.41) which was ultimately used directly for column heating. Since other equipment was also powered by these transformers, constant current conditions were desirable. Accordingly the circuitry was designed so that series and parallel resistors were brought into circuit with the column heater when the relay (Rl 1) was actuated. There was a choice of eight different series/parallel combinations, so that a suitable set could be chosen that, when in circuit, the equilibrium temperature would be about 3 to 5°C below the desired operating temperature, and when out of circuit from 3 to 5°C above the operating temperature, thus allowing for ambient changes of $\pm$ 2°C.

The performance of this system was observed using the thermometer in the sensing tube. It was found that there was a considerable lag in response to switching which resulted in a temperature variation, of period 3 minutes, in a range of the order of $\pm$ 1°C about the mean temperature. The amplitude of this variation was not particularly constant. If the series/parallel resistors and power setting were varied to give equilibrium temperatures 10°C either side of the temperature

setting the frequency of the variations was reduced to about 1½ minutes, but the amplitude was increased to around $\pm$ 1½°C..

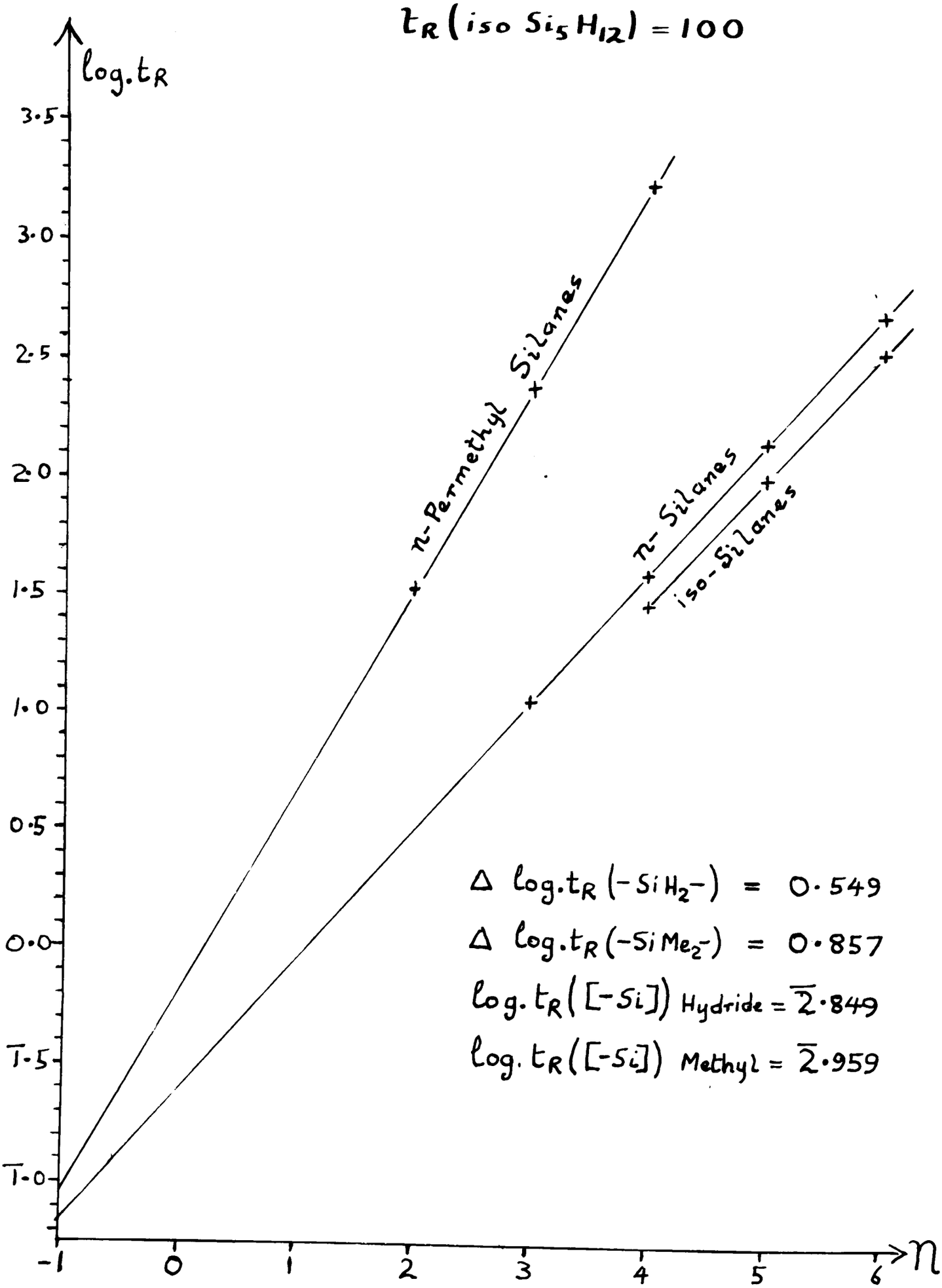
Under operational conditions, if the Variac setting was reduced, corresponding to a fall in ambient temperature, then the mean temperature also fell to a reduced extent. The mean temperature also drifted with time: This was possibly due to ambient changes affecting the control unit itself, since a similar unit had been employed to control the temperature of a room with the controller internally mounted, and this proved satisfactory.

In the event, it was felt that even with the amplitude of the temperature oscillation reduced, the advantages would be minimal over the control achieved by the direct method described in Section 2.41, and that development of the temperature control method described here would consume an inordinate amount of time. Accordingly the direct method of heating was selected and this method was abandoned.

In retrospect, it is obvious that even using the slowly responding sensor already described, proportional temperature control, run directly off mains, would have been more satisfactory than either of the methods mentioned above. The Author was, however, unaware of this technique at the time.

FIG. 58 Tritolyl Phosphate 64·5°C

t_R (iso Si_5H_{12}) = 100



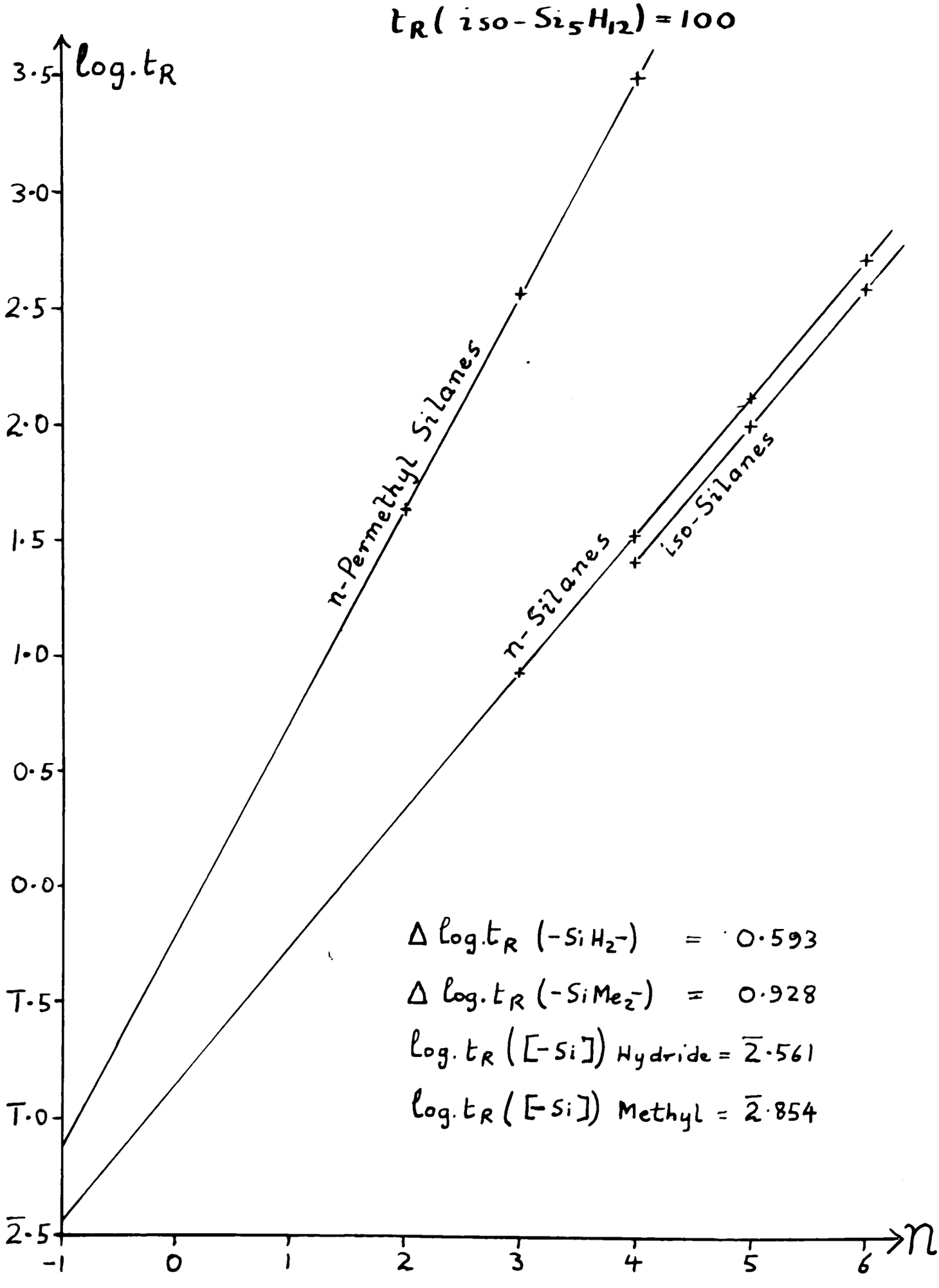
$\Delta \log.t_R(-SiH_2-) = 0.549$

$\Delta \log.t_R(-SiMe_2-) = 0.857$

$\log. t_R([-Si])$ Hydride = $\bar{2}$·849

$\log. t_R([-Si])$ Methyl = $\bar{2}$·959

FIG. 59 Silicone 702 64·5°C



APPENDIX 2

Chromatography of Silanes and Permethyl Silanes

In view of the almost perfectly additive chromatographic properties of the silanes, germanes and silico-germanes[29-31] (see Section 6.3) based on a common 'theoretical hydrogen point', it was wondered if the silanes and permethyl silanes would form a similar series. If this was the case, descending the series in $-SiH_2-$ and $-SiMe_2-$ units respectively, a common 'theoretical minus-silicon point' would be reached.

A sample of silanes was prepared in the First Apparatus (see Section 2.52), and selected compounds were separated and 'chopped' to suitably sized samples using the preparative system. A sample of the permethyl silanes, prepared by the method described in Section 5.3, was similarly treated. The two samples were first run separately for identification purposes on both of the columns, and then combined for the precision runs, which were carried out on both columns. The results, expressed as $\log.t_R$ (t_R of iso-Si_5H_{12} = 100) on both columns are shown below and are plotted in Figs. 58 and 59.

It can be clearly seen that the 'theoretical minus-silicon points' of both series fail to coincide on the plots obtained with either column. The difference is less with the polar tritolyl phosphate column.

Tritolyl Phosphate 64.5°C

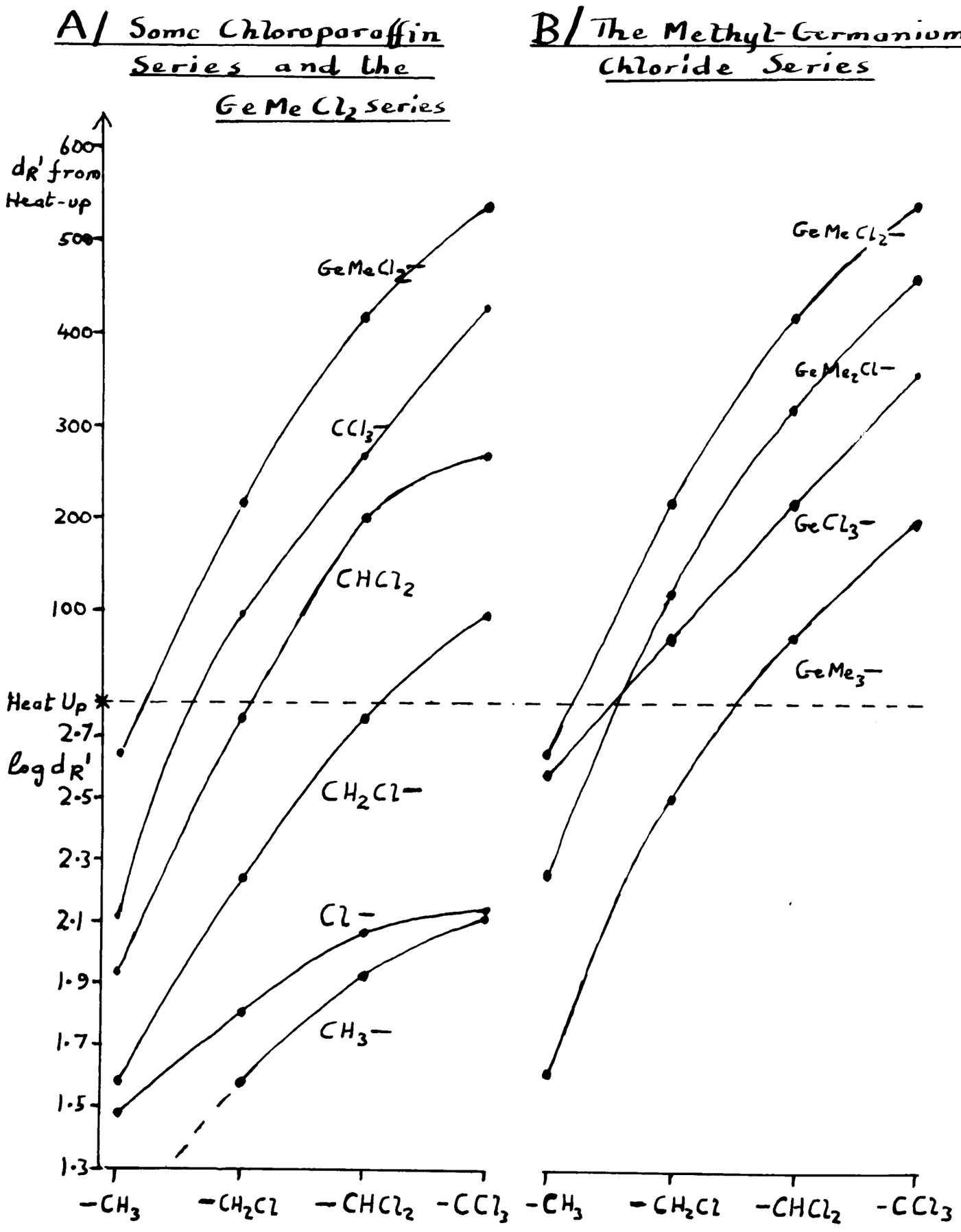
Si_3H_8	1.051	(- Si)	$\bar{2}$.849
iso-Si_4H_{10}	1.464		
n-Si_4H_{10}	1.589	-SiH_2-	0.549
iso-Si_5H_{12}	2.000		
n-Si_5H_{12}	2.147		
iso-Si_6H_{14}	2.540		
n-Si_6H_{14}	2.692		
Si_2Me_6	1.532	(- Si)	$\bar{2}$.959
Si_3Me_8	2.382		
n-Si_4Me_{10}	3.244	-$SiMe_2$-	0.857

Silicone 702 64.5°C

Si_3H_8	0.932	(- Si)	$\bar{2}$.560
iso-Si_4H_{10}	1.406		
n-Si_4H_{10}	1.524	-SiH_2-	0.593
iso-Si_5H_{12}	2.000		
n-Si_5H_{12}	2.121		
iso-Si_6H_{14}	2.593		
n-Si_6H_{14}	2.712		
Si_2Me_6	1.638	(- Si)	$\bar{2}$.854
Si_3Me_8	2.571		
n-Si_4Me_{10}	3.493	-$SiMe_2$-	0.928

FIG. 60 Silicone 702. Gold Chloride Technique:

Chromatography of Chloromethyl Series



APPENDIX 3

The Chloromethyl Methyl Germanium Chlorides

3.1 Chromatographic Identification (see Section 4.21)

In general, compounds in the same chemical series have chromatographic retention times (distances) in order of their molecular weights. This can however be modified by the presence of specific interactions of the compounds with the stationary phase.

The chromatographic technique finally adopted for the products of the gold chloride reaction consisted of an isothermal period at 30°C followed by an exponential heat-up stage with an equilibrium temperature of 90°C. Thus no single method of presentation of chromatographic results could be meaningfully used. It was found that a plot of $\log.d_R$, (the apparent retention distance) up to the heat-up point followed by a linear plot of retention distance from this point, with scales suitably adjusted, gave reasonable patterns for various series of compounds with different radicals attached to $-CH_3$, $-CH_2Cl$, $CHCl_2$ and $-Cl_3$ groups, see Figs. 59A and 60A.

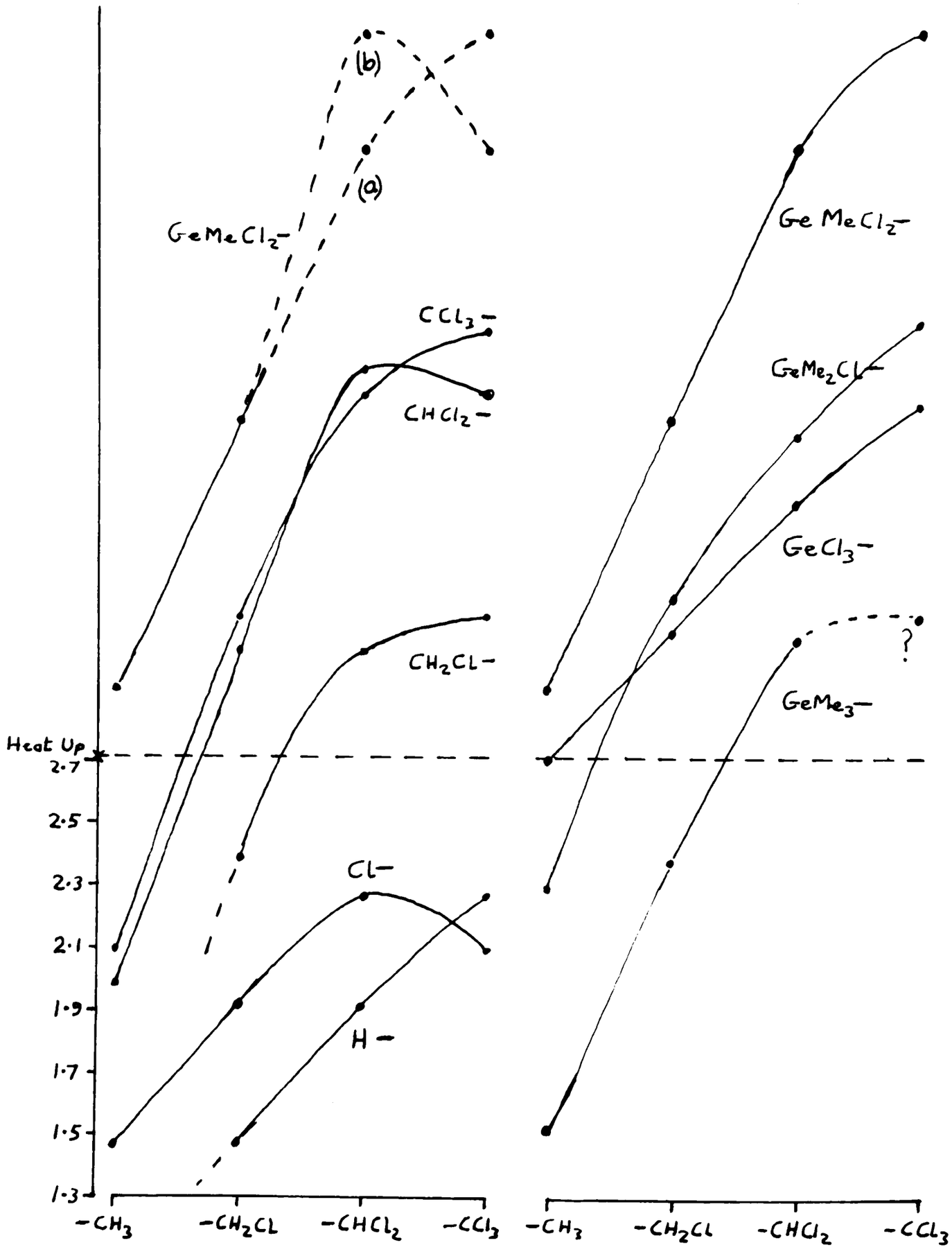
On the Silicone 702 column it was found that the successive compounds in a variety of chlorinated hydrocarbon series showed an increment in retention with successive members of the series, which, on the scales described above, got progressively less, so that the plots (Fig. 60A) were more or less curved. A trial plot of the series with a $GeMeCl_2$- radical showed a similar curved line if the order of the three chromatographic

FIG. 61 **Tritolyl Phosphate - Gold Chloride Technique**

Chromatography of Chloromethyl Series

A/ Some Chloroparaffin Series and the $GeMeCl_2-$ Series

B/ The Methyl Germanium Chloride Series



peaks were assigned in order of increasing molecular weight. Plots of the other suspected chloromethyl (methyl) germanium chlorides formed similar curves (Fig. 60B). The plot of the $GeCl_3$- series was straightest and the suspected $GeMe_3$- series was most curved. The chromatographic evidence on Silicone 702 therefore pointed to a straightforward solution with the assignation of the members of the different series in the order of their molecular weights.

On the tritolyl phosphate column, however, the interaction of $-CH_3$, $-CH_2Cl$, $-CHCl_2$ and $-CCl_3$ groups can lead to chromatographic anomalies (see Fig. 61A). Thus, although the series with a H- radical forms a similar plot to those on the Silicone 702 phase, the series with a Cl- radical shows a maximum retention at $CHCl_3$. This is due to the action between the stationary polar phase with the somewhat protonic hydrogen of the chloromethanes, which is non-existent in CCl_4. Other groups modify the behaviour of the chloromethyl groups between these extremes depending on their interaction with the stationary phase: The series with a $CHCl_2$- radical retains the anomaly in a slightly reduced form, but the series with CH_2Cl- and CCl_3- although forming highly curved plots, retain their chromatographic order with molecular weight.

What little chemical evidence there was as to the retention order of the chloromethyl (methyl) germanium chlorides, indicated that an anomalous order occurred on tritolyl phosphate. This quantitative evidence was not strong as the relative amounts of the three members of each of the series appeared to vary from run to run, carried out under similar conditions, using the same column. A trial plot of the

series believed to be $GeMeCl_2.CCl_nH_{3-n}$ (n = 0 - 3) is shown on Fig. 61A (a) based on no anomaly and (b) based on an anomaly. If plot (b) was correct, it would require a progressive increase in the differences between adjacent retention values (measured in these scale units) for the first three members, followed by the negative interval to the fourth. A similar plot of the $GeCl_3$- series would show this in an even more exaggerated way. This is contrary to the plots of all the other series, where the curvature in the plot is always in the same direction; moreover the anomaly would be greatest with the $GeCl_3$- series and least with the $GeMe_3$ series on this column which is contrary to the order of curvature of these series observed using the Silicone 702 column, which must be due to an incipient anomaly of the retentions on this column. Thus it is considered to be more likely for plots type (a), without the anomaly, to be correct on tritolylphosphate, and in this case the curvatures of the plots are similar, but more marked, than those obtained on the other column (see Fig. 61B).

It is considered that the chromatographic evidence outweighs the limited and unreliable chemical evidence, and the assignations of peaks in Appendices 3.2 and 3.3 are consequently based on the former.

APPENDIX 3.2

Retention Values of the Products of the Gold Chloride Reaction on $GeMeCl_3$, $GeMe_2Cl_2$, $GeMe_3Cl$, and $GeMe_4$ (see Section 4.21)

The results are expressed as log.Vg values for the isothermal parts of the chromatograms (30°C), and as relative distances on the recorder chart from the heat-up points ($d_{R'}$) for the column operation to the final equilibrium temperature of approximately 90°C.

Underlined values indicate the reference values for the individual runs. The log.Vg values are ultimately referred to the values for $GeMeCl_3$ (which gave rise to the most symmetrical peaks in the methyl germanium chloride series). These reference values were determined in a series of precision runs, carried out on the last set of columns employed in this work, and were found to be:

1.846 ± 0.005 on Silicone 702

and 1.980 ± 0.005 on tritolyl phosphate.

The $d_{R'}$ values are referred to arbitrarily chosen values for the compound believed to be $CCl_3.GeCl_3$ which were:

357 mm. (relative) on Silicone 702

and 376 mm. (relative) on tritolyl phosphate.

The letter 'p' indicates the compounds presumed to be present in particular runs (e.g. by comparison with similar runs carried out on the other columns), but which gave rise to immeasurable peaks either because of practical chromatographic coincidence with larger peaks, or because of short retention times.

Results that could only be obtained approximately are indicated by log.Vg values quoted to two places of decimals only, and by d_R, values in brackets.

Retention values on Silicone 702:

Parent Compound	$GeMeCl_3$				$GeMe_2Cl_2$		
Run No.	1	3	4	6	2	5	7
Products							
HCl	p	p	p	p	p	p	p
CH_3Cl +	?						
CH_2Cl_2	0.890	0.890	p		0.892	0.892	0.89
$CHCl_3$ x	p	p	p	p	p	p	p
CCl_4	1.331	1.329	1.330	1.330	1.322	1.330	1.327
$CCl_2:CH_2$							
$CCl_2:CHCl$							
$GeMe_4$							
$GeMe_3Cl$							
$GeMe_2Cl_2$					1.921	1.922	
$GeMeCl_3$	1.846	1.846	1.846	1.846	1.846	1.846	1.846
$GeCl_4$	1.234	1.234	1.235	1.235	1.230	1.235	1.232
(Tentative)							
$CH_2Cl.GeMe_3$							
$CHCl_2.GeMe_3$							
$CCl_3.GeMe_3$							
$CH_2Cl.GeMe_2Cl$							
$CHCl_2.GeMe_2Cl$							
$CCl_3.GeMe_2Cl$							
$(CH_2Cl)_2GeMeCl$							
$CH_2Cl.GeMeCl_2$					(220)	(220)	(220)
$CHCl_2.GeMeCl_2$					420	416	425
$CCl_3.GeMeCl_2$						536	545
$CH_2Cl.GeCl_3$	75	76	76	75	76	75	74
$CHCl_2.GeCl_3$	216	217	217	216	(216)	(216)	(216)
$CCl_3.GeCl_3$	357	357	357	357		357	357

+ CH_3Cl was not resolved from Cl_2 on either column. Except under mild conditions its absence or presence had to be inferred.

x $CHCl_3$ was not resolved from $GeCl_4$ on Silicone 702.

APPENDIX 3.2 (contd.)

Retention values on Silicone 702:

Parent Compound	$GeMe_2Cl_2$		$GeMe_3Cl$				
Run No.	9	11	2	4	5	7	10
Products							
HCl	p	p	p	p	p	p	p
CH_3Cl			p	p	p	p	p
CH_2Cl_2	0.882	0.902	0.892	0.89	0.882	0.890	0.871
$CHCl_3$	p	p	p	p	p	p	p
CCl_4	1.323	1.326	1.330	1.326	1.324	1.325	1.324
$CCl_2:CH_2$							0.700
$CCl_2:CHCl$							1.538
$GeMe_4$							
$GeMe_3Cl$			1.488	1.486	1.484	1.481	1.478
$GeMe_2Cl_2$	1.921	1.922	1.921	1.921	1.919	1.922	1.923
$GeMeCl_3$	1.846	1.846	1.846	1.85	1.846	1.846	1.846
$GeCl_4$	1.227	1.230	1.235	1.23	1.236	1.239	1.231
(Tentative)							
$CH_2Cl.GeMe_3$							
$CHCl_2.GeMe_3$							
$CCl_3.GeMe_3$							
$CH_2Cl.GeMe_2Cl$			118	118	118	118	118
$CHCl_2.GeMe_2Cl$					317	318	316
$CCl_3.GeMe_2Cl$					462		
$(CH_2Cl)_2GeMeCl$					617	620	617
$CH_2Cl.GeMeCl_2$	221	220	220	218	220	220	(218)
$CHCl_2.GeMeCl_2$	417	415			417	419	415
$CCl_3.GeMeCl_2$	538	535			536	540	536
$CH_2Cl.GeCl_3$	73					75	75
$CHCl_2.GeCl_3$	(216)	(217)					(212)
$CCl_3.GeCl_3$	357	357					357

APPENDIX 3.2 (contd.)

Retention values on Silicone 702:

Parent compound	$GeMe_3Cl$	$GeMe_4$				
Run No.	11	1	2	3	4	5
Products						
HCl	p					
CH_3Cl	p	0.00	0.00	0.00	1.90	0.00
CH_2Cl_2	0.892					
$CHCl_3$	p					
CCl_4	1.330					
$CCl_2:CH_2$						
$CCl_2:CHCl$						
$GeMe_4$		0.506	0.507	0.533	0.505	0.507
$GeMe_3Cl$	1.485	1.484	1.484	1.494	1.482	1.485
$GeMe_2Cl_2$	1.922			1.921	1.921	1.921
$GeMeCl_3$	1.846					
$GeCl_4$	1.244					
(Tentative)						
$CH_2Cl.GeMe_3$						1.777
$CHCl_2.GeMe_3$						75
$CCl_3.GeMe_3$						193
$CH_2Cl.GeMe_2Cl$	118					
$CHCl_2.GeMe_2Cl$	315					
$CCl_3.GeMe_2Cl$	460					
$(CH_2Cl)_2GeMeCl$	617					
$CH_2Cl.GeMeCl_2$	(220)					
$CHCl_2.GeMeCl_2$	414					
$CCl_3.GeMeCl_2$	535					
$CH_2Cl.GeCl_3$	75					
$CHCl_2.GeCl_3$	(215)					
$CCl_3.GeCl_3$	357					

APPENDIX 3.2 (contd.)

Retention values on Silicone 702:

Parent compound	$GeMe_4$			
Run No.	6	7	8	Averages
Products				
HCl		p	p	
CH_3Cl	$\bar{1}.90$	$\bar{1}.90$	$\bar{1}.99$	$\bar{1}.96$
CH_2Cl_2	0.89	0.872	0.888	0.887
$CHCl_3$		1.25	1.25	1.25
CCl_4		1.320	1.327	1.327
$CCl_2:CH_2$				0.700
$CCl_2:CHCl$				1.538
$GeMe_4$	0.500	0.498		0.508
$GeMe_3Cl$	1.482	1.482	1.484	1.484
$GeMe_2Cl_2$	1.921	1.921	1.921	1.921
$GeMeCl_3$		1.86	1.85	1.846
$GeCl_4$		1.25	1.25	1.235
(Tentative)				
$CH_2Cl.GeMe_3$	1.768	1.772	1.774	1.773
$CHCl_2.GeMe_3$	74	75	76	75
$CCl_3.GeMe_3$	193	193	194	193
$CH_2Cl.GeMe_2Cl$	118	118	118	118
$CHCl_2.GeMe_2Cl$	320		318	317
$CCl_3.GeMe_2Cl$				461
$(CH_2Cl)_2GeMeCl$				618
$CH_2Cl.GeMeCl_2$		219	217	220
$CHCl_2.GeMeCl_2$	418	425	427	420
$CCl_3.GeMeCl_2$				538
$CH_2Cl.GeCl_3$				75
$CHCl_2.GeCl_3$				216
$CCl_3.GeCl_3$				357

Retention values on Tritolyl Phosphate:

Parent Compound	$GeMeCl_3$		$GeMe_2Cl_2$				
Run No.	2	5	1	3	6	8	10
Products							
HCl +	0.73	0.72	p	0.73	0.65	0.73	0.79
CH_3Cl	?						
CH_2Cl_2 x	1.04		1.04	1.05	1.05	1.04	1.04
$CHCl_3$	1.488		1.484	1.493	1.488	1.486	1.489
CCl_4	1.290	1.291	1.290	1.292	1.296	1.293	1.287
CCl_2:CHCl							
$GeMe_4$							
$GeMe_3Cl$							
$GeMe_2Cl_2$			72	74		72	72
$GeMeCl_3$	1.980	1.980	1.980	1.980	1.980	1.980	1.980
$GeCl_4$	1.074	1.076	1.073	1.079	1.081	1.068	1.070
(Tentative)							
$CH_2Cl.GeMe_3$							
$CHCl_2.GeMe_3$							
$CCl_3.GeMe_3$							
$CH_2Cl.GeMe_2Cl$							
$CHCl_2.GeMe_2Cl$							
$CCl_3.GeMe_2Cl$							
$(CH_2Cl)_2GeMeCl$							
$CH_2Cl.GeMeCl_2$			359	359	359	359	359
$CHCl_2.GeMeCl_2$				640	648	647	650
$CCl_3.GeMeCl_2$			770	767		778	772
$CH_2Cl.GeCl_3$	131	133	133	134	131	131	134
$CHCl_2.GeCl_3$	268	270		272	270	265	
$CCl_3.GeCl_3$	376	376	(380)	376	(380)	377	375

\+ HCl produced badly 'tailing' peaks on tritolyl phosphate.

x CH_2Cl_2 was only partly resolved from $GeCl_4$ on tritolyl phosphate.

APPENDIX 3.2 (contd.)

Retention values on Tritolyl Phosphate:

Parent Compound	$GeMe_3Cl$				
Run No.	1	3	6	8	9
Products					
HCl	p	p	p	p	0.69
CH_3Cl	p	p	p	p	p
CH_2Cl_2	1.03	1.04	1.036	1.032	1.028
$CHCl_3$	1.48	1.48	1.474	1.479	1.478
CCl_4	1.289	1.292	1.286	1.287	1.290
CCl_2:CHCl					1.613
$GeMe_4$					
$GeMe_3Cl$	1.529	1.530	1.525	1.524	1.531
$GeMe_2Cl_2$	72	71	72	71	73
$GeMeCl_3$		1.980	1.980	1.980	1.980
$GeCl_4$	1.064	1.079	1.074	1.067	1.071
(Tentative)					
$CH_2Cl.GeMe_3$					
$CHCl_2.GeMe_3$					
$CCl_3.GeMe_3$					
$CH_2Cl.GeMe_2Cl$	172	172	171	172	172
$CHCl_2.GeMe_2Cl$	340				343
$CCl_3.GeMe_2Cl$			463	464	464
$(CH_2Cl)_2GeMeCl$			1090	1100	1110
$CH_2Cl.GeMeCl_2$	359	359	359	359	359
$CHCl_2.GeMeCl_2$				653	655
$CCl_3.GeMeCl_2$			770	774	773
$CH_2Cl.GeCl_3$				131	132
$CHCl_2.GeCl_3$					271
$CCl_3.GeCl_3$					380

APPENDIX 3.2 (contd.)

Retention values on Tritolyl Phosphate:

Parent Compound	$GeMe_4$ +			
Run No.	12	13	14	Averages
Products				
HCl	0.65	p	p	0.71
CH_3Cl	p	$\bar{1}.91$	p	$\bar{1}.91$
CH_2Cl_2	1.03			1.032
$CHCl_3$				1.484
CCl_4				1.290
CCl_2:CHCl				1.613
$GeMe_4$	0.15	0.15	0.15	0.15
$GeMe_3Cl$	1.533	1.529	1.531	1.529
$GeMe_2Cl_2$	74	74	74	73
$GeMeCl_3$	1.980		1.980	1.980
$GeCl_4$ (Tentative)				1.073
$CH_2Cl.GeMe_3$	1.625		1.626	1.626
$CHCl_2.GeMe_3$	126		126	126
$CCl_3.GeMe_3$	152		155	154
$CH_2Cl.GeMe_2Cl$	172		172	172
$CHCl_2.GeMe_2Cl$				342
$CCl_3.GeMe_2Cl$				464
$(CH_2Cl)_2GeMeCl$				1100
$CH_2Cl.GeMeCl_2$				359
$CGCl_2.GeMeCl_2$				649
$CCl_3.GeMeCl_2$				772
$CH_2Cl.GeCl_3$				132
$CGCl_2.GeCl_3$				269
$CCl_3.GeCl_3$				376

+ These runs were carried out under similar conditions to runs between 4 and 6 on Silicone 702.

APPENDIX 3.3

Quantitative Analyses of the Products of the Gold Chloride Reaction on $GeMeCl_3$, $GeMe_2Cl_2$, $GeMe_3Cl$ and $GeMe_4$ (see Section 4.21)

The quantities of the individual germanium-containing products, or certain sets of products, are expressed as percentages of the total molar amount of germanium compounds.

The quantities of the individual chloromethanes are expressed as percentages of the total molar amount of carbon-containing compounds produced by Ge-C bond fission. These are not very accurate as the quantities of MeCl had, in most cases, to be indirectly estimated (see text).

These results are plotted in the graphs, Figs. 29 to 32.

APPENDIX 3.3 (contd.)

Products of the Gold Chloride Reaction on $GeMeCl_3$

Run No.	1	2	3	4	5	6
Column	702	TTP	702	702	TTP	702
$AuCl_3$ Cell Temp.	177	173	173	181	181	192
Gas Reactor Temp.	375	375	375	425	425	425
Products						
CH_3Cl						
CH_2Cl_2	tr.	tr.	tr.			
$CHCl_3$	5	15	15	tr.		
CCl_4	95	85	85	100	100	100
$GeMeCl_3$ remaining	82.3	78.9	84.5	29.8	34.6	27.2
$GeCl_4$	7.6	12.5	8.9	61.2	56.9	65.1
$GeCl_3.CH_2Cl$	7.6	2.7	1.6	4.1	3.1	4.5
$GeCl_3.CHCl_2$	2.4	3.3	5.0	2.6	2.7	1.6
$GeCl_3.CCl_3$	tr.	2.6	tr.	2.3	2.7	1.6

APPENDIX 3.3 (contd.)

Products of the Gold Chloride Reaction on $GeMe_2Cl_2$

Run No.	1	2	3	5	6	7	8	9	10	11
Column	TTP	702	TTP	702	TTP	702	TTP	702	TTP	702
$AuCl_3$ Cell Temp.	161	161	174	174	191	192	182	183	163	163
Gas Reactor Temp.	308	304	366	365	408	408	385	383	387	388
Products										
CH_3Cl	?	?	?	?	?	?	?	?	?	?
CH_2Cl_2	tr.	1	2	5	1	1	2	4	tr.	tr.
$CHCl_3$	10	9	3	3	4	4	2	2	3	3
CCl_4	90	90	95	92	95	95	96	94	97	97
$GeMe_2Cl_2$ remaining	85.0	88.1	14.7	25.2	0	0	7.4	14.5	64.0	74.6
$GeMeCl_3$	4.0	3.2	28.7	21.5	23.7	33.1	44.2	35.5	5.3	4.4
$GeCl_4$	tr.	0.1	7.8	6.4	67.7	52.8	13.7	10.1	3.8	1.7
$GeMeCl_2.CCl_nH_{3-n}$	10.6	8.1	45.5	42.1	1.6	4.4	32.2	35.6	26.3	19.9
$GeCl_3.CCl_nH_{3-n}$	0.6	0.5	3.3	4.8	7.0	9.7	2.8	4.3	0.6	0.4

APPENDIX 3.3 (contd.)

Products of the Gold Chloride Reaction on $GeMe_3Cl$

Run No.	1	2	3	4	5	6	7	8	9	10	11
Column	TTP	702	TTP	702	702	TTP	702	TTP	TTP	702	702
$AuCl_3$ Cell Temp.	148	148	161	161	171	171	180	183	193	195	174
Gas Reactor Temp.	252	252	305	305	360	358	396	400	414	415	368
Products											
CH_3Cl	76	72	62	66	60	61	39	37	22	26	54
CH_2Cl_2	12	12	12	10	11	8	15	14	13	10	10
$CHCl_3$	4	4	7	9	5	8	8	9	11	15	7
CCl_4	8	12	19	15	24	23	38	40	45	46	29
$CCl_2{:}CH_2$ & $CCl_2{:}CHCl$									9	3	
$GeMe_3Cl$ remaining	92.8	90.4	83.8	87.7	48.5	51.8	26.4	16.8	5.6	7.0	52.7
$GeMe_2Cl_2$	6.8	7.2	10.1	8.5	13.0	12.7	17.1	18.9	20.2	22.1	13.3
$GeMeCl_3$		0.3	0.3	tr.	0.9	1.1	2.8	5.5	9.0	9.8	1.2
$GeCl_4$	tr.	0.8	0.2	tr.	0.5	1.0	3.5	13.1	18.6	10.8	0.6
$GeMe_2Cl.CCl_nH_{3-n}$	0.4	0.7	5.5	3.7	29.7	28.9	36.5	30.0	19.8	23.1	26.3
$(CH_2Cl)_2GeMeCl$					4.1	1.5	5.3	5.2	5.8	4.6	2.9
$GeMeCl_2.CCl_nH_{3-n}$	tr.	0.6	tr.	tr.	3.3	3.0	7.8	9.9	18.2	18.0	2.7
$GeCl_3.CCl_nH_{3-n}$							0.6	0.6	1.8	1.5	0.3

APPENDIX 3.3 (contd.)

Products of the Gold Chloride Reaction on $GeMe_4$

Run No.	1	2	3	4	5	6	7	8
Column	702	702	702	702	702	702	702	702
$AuCl_3$ Cell Temp.	49	70	90	109	129	150	169	187
Gas Reactor Temp.	49	70	90	109	129	150	169	187
Products								
CH_3Cl	100	100	100	100	100	100	99	94
CH_2Cl_2						tr.	1	4
$CHCl_3$							tr.	1
CCl_4							tr.	1
$GeMe_4$ remaining	99.1	97.7	93.0	83.6	59.8	22.7	0.6	0
$GeMe_3Cl$	0.9	2.3	6.9	16.1	35.5	63.1	52.7	20.0
$GeMe_2Cl_2$			tr.	0.3	3.4	8.8	31.6	54.7
$GeMeCl_3$					tr.	1.0	1.0	1.8
$GeCl_4$							tr.	tr.
$GeMe_3.CCl_nH_{3-n}$					2.1	3.7	12.2	19.4
$GeMe_2Cl.CCl_nH_{3-n}$						0.7	1.6	4.1
$GeMeCl_2.CCl_nH_{3-n}$						tr.	0.3	tr.
$GeCl_3CCl_nH_{3-n}$								tr.?

APPENDIX 4

The Permethyl Silanes, Permethyl Germanes and Permethyl Silico-Germanes

This appendix summarises the more significant chromatographic retention data obtained in the work described in Chapter 6.

APPENDIX 4.1

Retention Values of the Products of the Preparative Reactions (see Section 6.2)

In most cases, the products of a particular preparative reaction were not all observed on any one chromatogram. This was due to the large variations in quantity of the products, lack of resolution of isomers (particularly if one isomer was present in a small amount relative to the other) and to the difficulty of detecting trace products with long retention times (particularly on the low efficiency column; Silicone 702). Comparison between different chromatograms of the same mixture, however, established the presence and relative amounts of the components as shown in Table 17.

Preliminary chromatography was carried out using a similar technique to that employed for the gold chloride analyses, and these results are presented in the same manner as those in Appendix 3.2..

In these Tables the starting materials for the preparations are denoted

by s, and the 'washed' products by w.

The reference compounds for the chromatograms at 30°C are $GeMeCl_3$ (see Appendix 3.2) and Ge_2Me_6, with Ge_3Me_8 or Ge_4Me_{10} as reference after the heat-up points. The reference for the other chromatograms is Ge_3Me_8.

Retention Values, Tritolyl Phosphate 30°C with heat-up to 90°C

	Permethyl Silico-Germane Preparations								
Compound	1.s	1	1.w	2.s	2	3.s	3	3.w	Average
$SiMe_3Cl$	0.72	0.74				0.72	0.74		0.73
$SiMe_2Cl_2$				1.042		1.051			1.047
$GeMe_3Cl$	1.530	1.530		1.534	1.530	1.530	1.530		1.531
$GeMe_2Cl_2$	79	79		82		79			80
$GeMeCl_3$	1.980			1.980		1.980			1.980
O		$\bar{1}.85$	$\bar{1}.85$		$\bar{1}.87$		p	$\bar{1}.99$	$\bar{1}.89$ +
●	0.15	0.14	0.16	0.14	0.22	0.18	p	0.20	0.17
O–O		0.90	0.92		0.88		0.896	0.894	0.895
O–●		1.14	1.10		1.12		1.128	1.127	1.128 x
●–●		1.362	1.362		1.362		1.362	1.362	1.362
O–O–O		p	p		1.904		1.910	1.904	1.906
O–●–O		51	49				53	52	51
O–O–●					62		68	70	67
O–●–●		110	111				110	111	111
●–O–●					120		120	121	120
●–●–●		161	159		162		165	168	163
(6.75)							207	209	208
O–O–O–O		p	p		p		315	319	317
O–O–●–O		392	390				392	390	391
O–O–O–●					410		422	426	419
O–●–●–O		499	500				503	493	499
O–O–●–●							526	530	528
O–●–O–●									
●–O–O–●					564		573	568	568
●–●–●–O			652				661	658	657
●–●–O–●					715		708	710	711
●–●–●–●			930		930		930	930	930

+ The predicted value for $SiMe_4$ based on Si_2Me_6 and Si_3Me_8 is $\bar{1}.894$

x The predicted value for $SiMe_3.GeMe_3$ (see Section 6.3) is 1.128

APPENDIX 4.1 (contd.)

Log.Vg Values: Tritolyl Phosphate 60°C

Permethyl Silico-Germane Preparations

Compound	Vg. Calibration	1.w	2.w	3.w	Average
0-0	0.51	0.52	0.50	0.49	0.51
0-●		0.73	0.70	0.70	0.71
●-●	0.894	0.902	0.903	0.896	0.899
0-0-0	1.346	1.32	1.338	1.343	1.337
0-●-0		1.476	1.45	1.47	1.465
0-0-●		1.54	1.526	1.521	1.529
●-●-0		1.652		1.652	1.652
●-0-●			1.704	1.693	1.699
●-●-●	1.842	1.842	1.842	1.842	1.842
(6.75)				1.959	1.959
0-0-0-0		p	p	2.199	2.199
0-0-●-0		p		2.327	2.327
0-0-0-●			2.385	2.372	2.379
0-●-●-0		2.470		p	2.470
0-0-●-●)		?	?	2.494	2.494
0-●-0-●)					
●-0-0-●			2.574	2.536	2.555
●-●-●-0		2.619		2.616	2.618
●-●-0-●			2.670	2.656	2.663
●-0-●-●		2.789	2.792	2.789	2.790

APPENDIX 4.1 (contd.)

Log.Vg Values: Tritolyl Phosphate 90°C

Compound	Vg.Calibration	Permethyl Silico-Germane Preparations							
		1	1.w	2	2.w	3	3.w	1w+3w	Average
0–0	0.21	p	p	p	p	p	0.195	0.215	0.207
0–●		0.35	p	0.35	0.38	p	0.364	0.355	0.360
●–●	0.535	p	p	0.54	p	p	0.529	0.532	0.534
0–0–0	0.914	0.913	p	0.910	0.909	0.916	0.913	0.914	0.913
0–●–0		1.032	1.046			p	p	1.05	1.043
0–0–●			?	1.066	1.065	1.070	1.066	1.067	1.067
●–●–0		1.186	1.197			1.19	1.18	1.18	1.187
●–0–●				1.211	1.220	1.212	1.209	1.210	1.212
●–●–●	1.340	1.340	1.340	1.340	1.340	1.340	1.340	1.340	1.340
(6.75)		1.428	p	p	1.429	1.428	1.419	1.423	1.425
0–0–0–0	1.655	1.657	1.668	1.661	1.661	1.654	1.646	1.648	1.656
0–0–●–0		p	p			1.754	1.754	1.753	1.754
0–0–0–●				1.791	1.791	1.796	1.792	1.793	1.793
0–●–●–0		1.870	1.875			p	p	1.869	1.871
0–0–●–●)		?	?	?	?	1.903	1.901	1.900	1.901
0–●–0–●)									
●–0–0–●				1.945	1.948	1.940	1.935	1.937	1.941
●–●–●–0		2.008	2.012			2.013	2.004	2.010	2.009
●–●–0–●				2.051	2.051	2.048	2.041	2.049	2.048
●–●–●–●	2.18	2.163	2.17	2.165	2.162	2.167	2.158	2.166	2.166

APPENDIX 4.1 (contd.)

Retention Values: Silicone 702, 30°C with heat-up to 90°C

Permethyl Silico-Germane Preparations

Compound	1.s	1	1.w	2.s	2	3.s	3	Averages
$SiMe_3Cl$	0.850	0.843				0.861	0.842	0.849
$SiMe_2Cl_2$				1.106		1.101		1.104
$GeMe_3Cl$	1.479	1.485		1.490	1.492	1.492	1.475	1.486
$GeMe_2Cl_2$	1.923			1.929		1.931		1.926
$GeMeCl_3$	1.846			1.846		1.846		1.846
O		0.22	0.21		0.19		0.32	0.24
●	0.530	0.531	0.511	0.532	0.536	0.534	0.57	0.535
O–O		1.415	1.415		1.378		1.384	1.398
O–●		1.647	1.647		1.614		1.624	1.633 +
●–●		1.865	1.865		1.865		1.865	1.865
O–O–O		p	p		146		142	144
O–●–O		197	199				p	198
O–O–●					210		208	209
●–●–O		279	278				p	279
●–O–●					300		291	296
●–●–●		381	381		381		381	381

The peaks of the compounds with four-membered chains were virtually immeasurable under these conditions.

+ The predicted value for $SiMe_3.GeMe_3$ (see Section 6.3) is 1.631

APPENDIX 4.1 (contd.)

Log.Vg Values: Silicone 702 , 90°C

Permethyl Silico-Germane Preparations

Compound	Vg. Calib.	1	1.w	2.w	3.w	Average	Predict. Equn.1
0–0	0.51	0.55	p	p	p	0.53	
0–●		0.71	p	0.67	p	0.69	0.69
●–●	0.846	0.841	p	0.858	p	0.848	
0–0–0	1.304	1.314	1.303	1.321	1.308	1.310	
0–●–0		1.425	1.433	1.43	p	1.429	1.457
0–0–●		1.483	p	1.463	1.463	1.470	
0–●–●		1.578	1.590		p	1.584	1.604
●–0–●				1.615	1.614	1.615	
●–●–●	1.750	1.750	1.750	1.750	1.750	1.750	
0–0–0–0	2.114	p	p	p	2.099	2.107	
0–0–●–0		p	p		p		2.234
0–0–0–●				p	2.25	2.25	
0–●–●–0		2.318	2.33		p	2.324	
0–0–●–●) 0–●–0–●)					2.36	2.36	2.360
●–0–0–●				2.406	2.41	2.408	
●–●–●–0		p	2.46		p	2.46	2.487
●–●–0–●				2.510	2.501	2.506	
●–●–●–●		p	2.61	2.62	2.610	2.613	

APPENDIX 4.2

Retention Values of the Products of the Gold Chloride Reaction on the Permethyl Silico-Germanes (see Sections 6.5 to 6.7)

These results are expressed as log.Vg values on the columns at 30°C. The reference compound is $GeMeCl_3$ (see Appendix 3.2).

APPENDIX 4.2 (contd.)

Log. Vg Values on Silicone 702, 30°C.

Parent	O–●		O–●–O		O–●–●		
Run No.	2	3	2	3	1	2	3
Products							
MeCl	$\bar{1}$.98	0.03	$\bar{1}$.98	$\bar{1}$.98	0.02	0.00	0.01
$SiMe_3Cl$	0.840	0.855	0.850	0.860	0.849	0.847	0.847
$SiMe_2Cl_2$			1.084	1.086		1.086	1.077
$GeMe_3Cl$	1.484	1.484	1.474	1.473	1.492	1.494	1.484
$GeMe_2Cl_2$	1.920	1.920	1.930	1.931	1.932	1.934	1.939
$GeMeCl_3$		1.85	1.846	1.846	1.846	1.846	1.846
$GeCl_4$			1.237	1.232		1.239	1.226

Parent	O–●–●–O			●–●–●–O			●–O–●		
Run No.	1	2	3	1	2	3	1	2	3
Products									
MeCl	$\bar{1}$.98	0.00	0.00	$\bar{1}$.99	0.01	0.00	0.02	0.01	0.02
$SiMe_3Cl$	0.840	0.852	0.845	0.837	0.839	0.836	0.842	0.837	0.842
$SiMe_2Cl_2$	1.077	1.077	1.072	p	p	p	1.093	1.093	1.097
$GeMe_3Cl$	1.475	1.472	1.469	1.477	1.476	1.474	1.484	1.483	1.488
$GeMe_2Cl_2$	1.927	1.930	1.929	1.925	1.926	1.928	1.937	1.938	1.934
$GeMeCl_3$	1.846	1.846	1.846	1.846	1.846	1.846	1.846	1.846	1.846
$GeCl_4$	1.227	1.222	1.220	1.233	1.221	1.226			

APPENDIX 4.2 (contd.)

Log.Vg Values on Silicone 702, 30°C

Parent	●-O-O-●				●-O-O-●		
Run No.	1	2	3	4	1	2	3
Product							
MeCl	0.03	0.01	0.03	0.03	0.01	0.02	0.03
$SiMe_3Cl$	0.842	0.832	0.839	0.839	0.835	0.825	0.844
$SiMe_2Cl_2$	1.089	1.083	1.093	1.090	1.089	1.082	1.091
$GeMe_3Cl$	1.481	1.477	1.484	1.479	1.482	1.481	1.486
$GeMe_2Cl_2$	1.926	1.928	1.932	1.923	1.928	1.927	1.931
$GeMeCl_3$	1.846	1.846	1.846	1.846	1.846	1.846	1.846
$GeCl_4$		1.223	1.238			p	

Parent	O-O-●			(6.75)	O-O-O-●		
Run No.	1	2	3	1	2	3	4
Product							
MeCl	0.03	0.00	0.01	0.03	0.02	0.01	0.03
$SiMe_3Cl$	0.830	0.839	0.860	0.844	0.840	0.845	0.850
$SiMe_2Cl_2$	1.084	1.080	1.100	1.090	1.098	1.098	1.099
$GeMe_3Cl$	1.476	1.472	1.496	1.484	1.484	1.484	1.485
$GeMe_2Cl_2$	1.923	1.919	1.938	1.926	1.926	1.924	1.934
$GeMeCl_3$	1.846	1.846	1.846		1.85	1.846	1.846
$GeCl_4$							

APPENDIX 4.2 (contd.)

Log.Vg Values on Silicone 702, 30°C

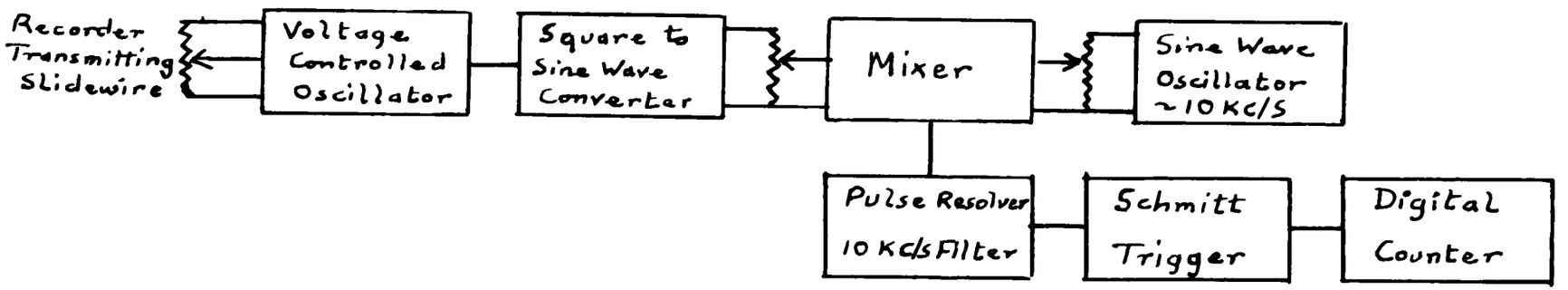
Parent	O-O-●-O			(O-O-●-●) (O-●-O-●)		Averages
Run No.	1	2	3	2	3	
Products						
MeCl	0.01	0.01	0.02	0.03	0.02	0.01
$SiMe_3Cl$	0.850	0.848	0.838	0.845	0.846	0.843
$SiMe_2Cl_2$	1.094	1.096	1.092	1.094	1.094	1.091
$GeMe_3Cl$	1.478	1.478	1.477	1.481	1.478	1.481
$GeMe_2Cl_2$	1.932	1.932	1.920	1.926	1.927	1.928
$GeMeCl_3$	1.846	1.846	1.846	1.846	1.846	1.846
$GeCl_4$	p	p	p	1.221	p	1.228

Log.Vg Values on Tritolyl Phosphate, 30°C

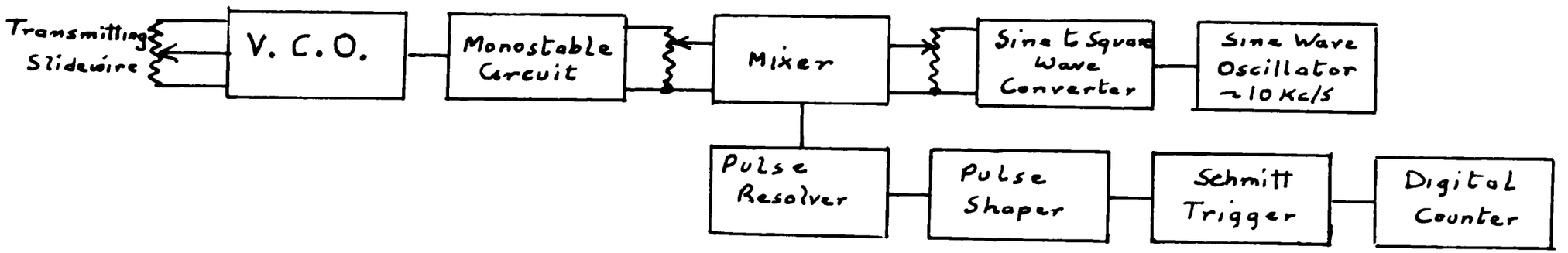
Parent	O-●	O-●-O	Averages
Run No.	1	1	
Products			
MeCl	0.01	0.02	0.02
$SiMe_3Cl$	0.726	0.732	0.729
$GeMe_3Cl$	1.534	1.528	1.531
$GeMe_2Cl_2$	H74	H74	H74
$GeMeCl_3$	1.980	1.980	1.980

FIG. 62 DIGITAL INTEGRATOR – SCHEMATIC

A/ Original Suggestion



B/ Final Form



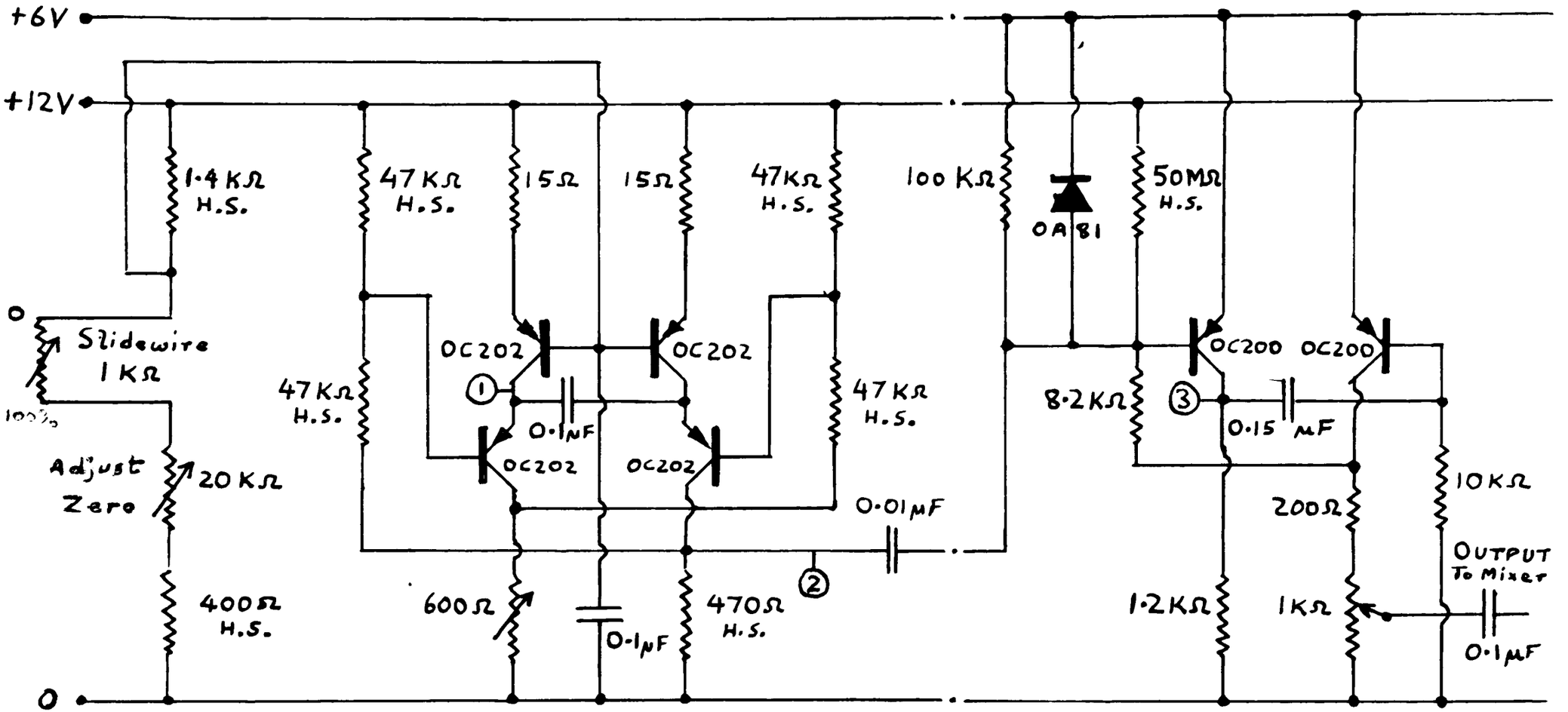
APPENDIX 5

A Digital Integrator

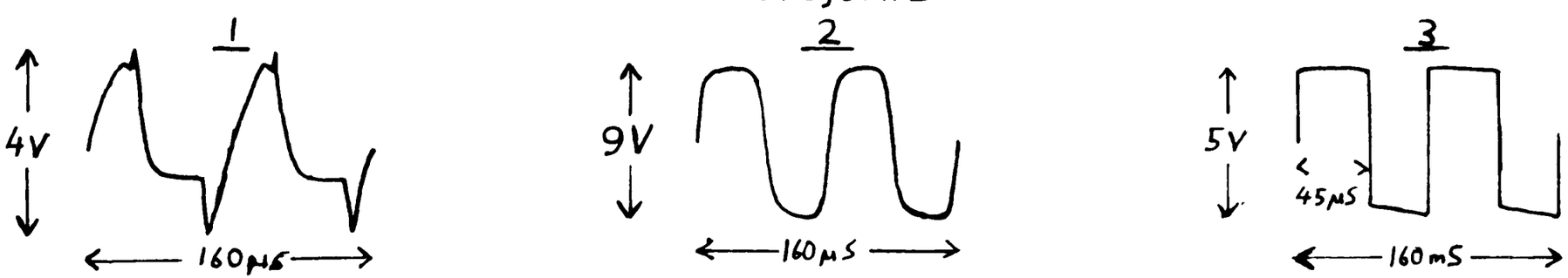
It was decided to attempt the design of a circuit that could be used in conjunction with the digital counter/timer described in Section 2.42, to act as a digital integrator. The input signal was to be provided using a transmitting slidewire attached to the recorder.

The Author suggested that integration could be effected by the use of a voltage controlled oscillator, the transmitting slidewire providing the control voltage by acting as a potential divider. The simple circuits described in the literature at the time used the control voltage to modulate the frequency of various types of square wave oscillators. It was therefore suggested by the Author that the output of such an oscillator should be converted to a sinusoidal waveform and then 'beat' with the output of a reference crystal oscillator, after suitable amplitude adjustment. The beat frequency obtained should then be proportional to the recorder signal. The component frequencies could then be filtered out, together with any high harmonics, leaving a reasonably pure sinusoidal output which would operate a Schmitt Trigger, in turn driving the digital counter. This suggestion (see Fig. 62A) was then passed to Mr. K. Mayo and Mr. G. Collins of the Electronic Workshop to see if it would work in practice. The Author's research terminated before much work could be done on the device and therefore all research and detail design was carried out by Mr. Mayo and Mr. Collins. As the integrator in its final state was successful, and bore a considerable

FIG. 63 A/ Voltage Controlled Oscillator B/ Monostable Circuit



Waveforms



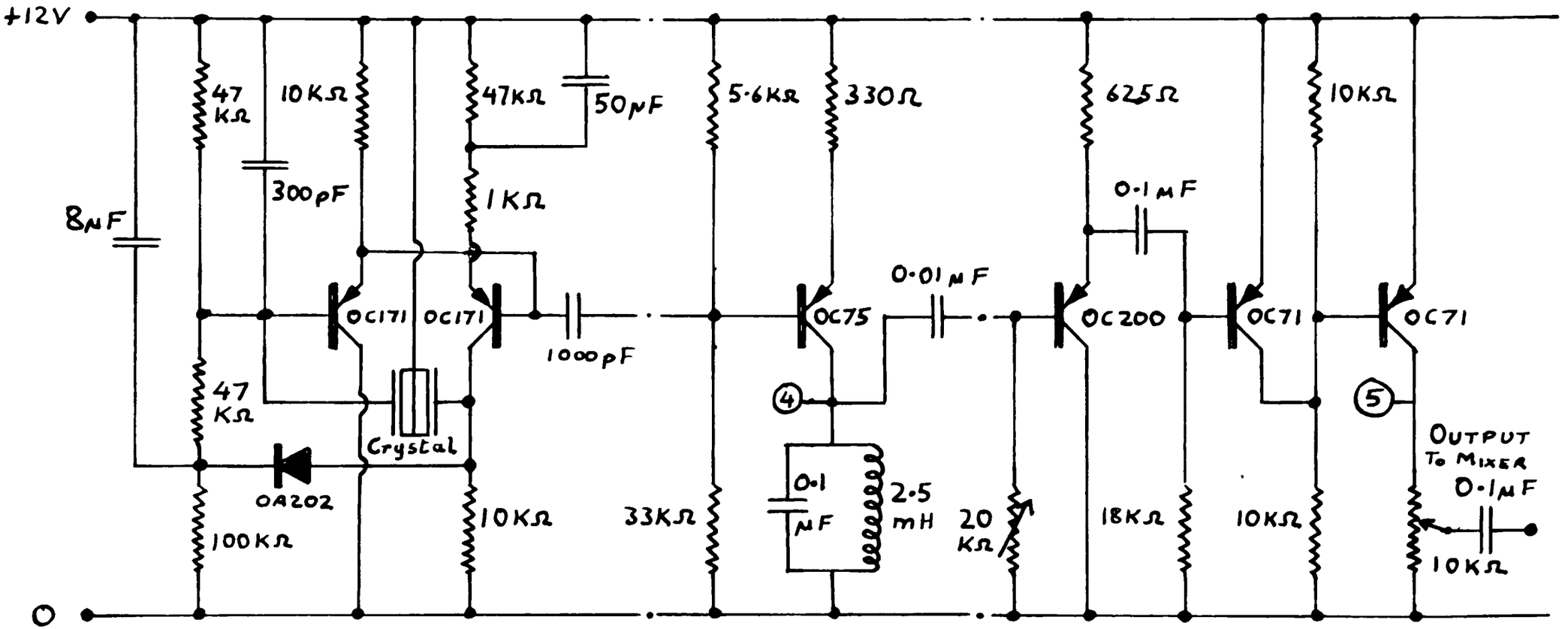
resemblance to the Author's original suggestion, a brief description is included here.

It was found that the original idea of sine wave mixing was not very practical. This was partly on account of the variations in amplitude with frequency in the output of any simple variable oscillator, and partly due to the difficulty of constructing an amplifier with a reasonably constant output amplitude over the range 0 - 500 cs., while at the same time completely rejecting the component frequencies of around 10 Kc/s. As it was considerably easier to obtain constant amplitude square waves, by operating transistors up to saturation currents, and to amplify square waves in a similar manner, Mr. Mayo and Mr. Collins decided to attempt a square wave mixing to obtain a wave form of square pulses of constant amplitude with durations varying approximately sinusoidally in accordance with the beat frequency. These pulses could then be integrated, using a capacitor, to obtain a beat wave of approximately sinusoidal form which could drive the Schmitt Trigger. A block diagram of the system is shown in Fig. 62B.

Figs. 63 to 66 show slightly simplified circuit diagrams of the units of the integrator, together with sketches of the waveforms obtained. The stages were coupled by capacitors which are shown in the output lines of each unit. A simple Zener diode power pack without feedback was used to provide supplies of 12 and 6 V.D.C.

The voltage-controlled oscillator [139] (Fig. 63A) produced an output, essentially of square wave form, with a frequency range of between 10 and 10.8 Kc/s. The 'on' time varied with frequency, and therefore the output was fed into a monostable circuit (Fig. 63B), which gave pulses of both

FIG.64 A/ Crystal Oscillator B/ Tuned Amplifier C/ Sine to Square Wave Converter



Waveforms

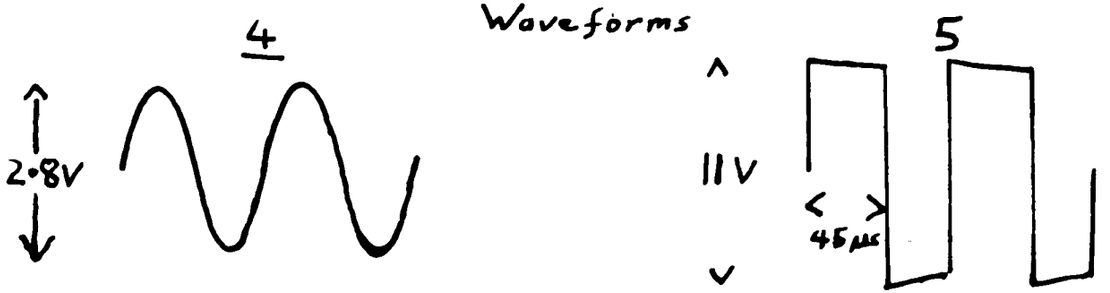
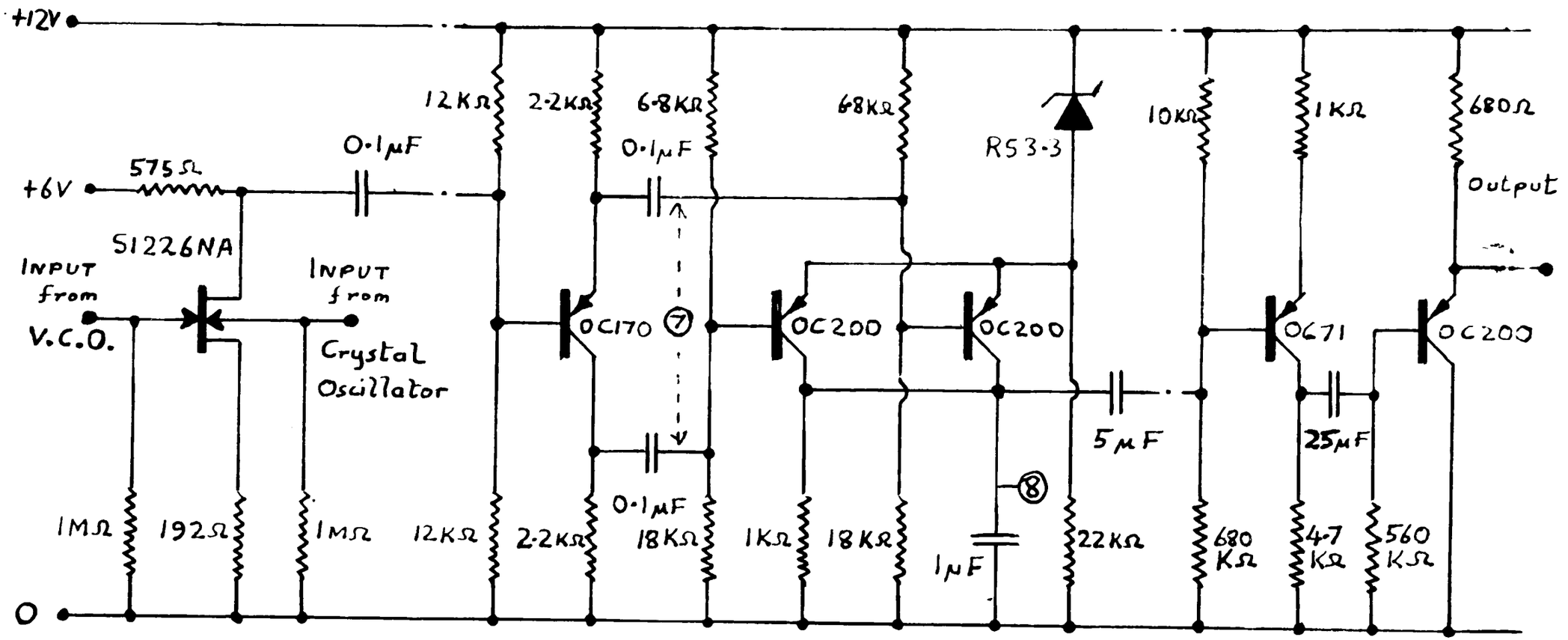
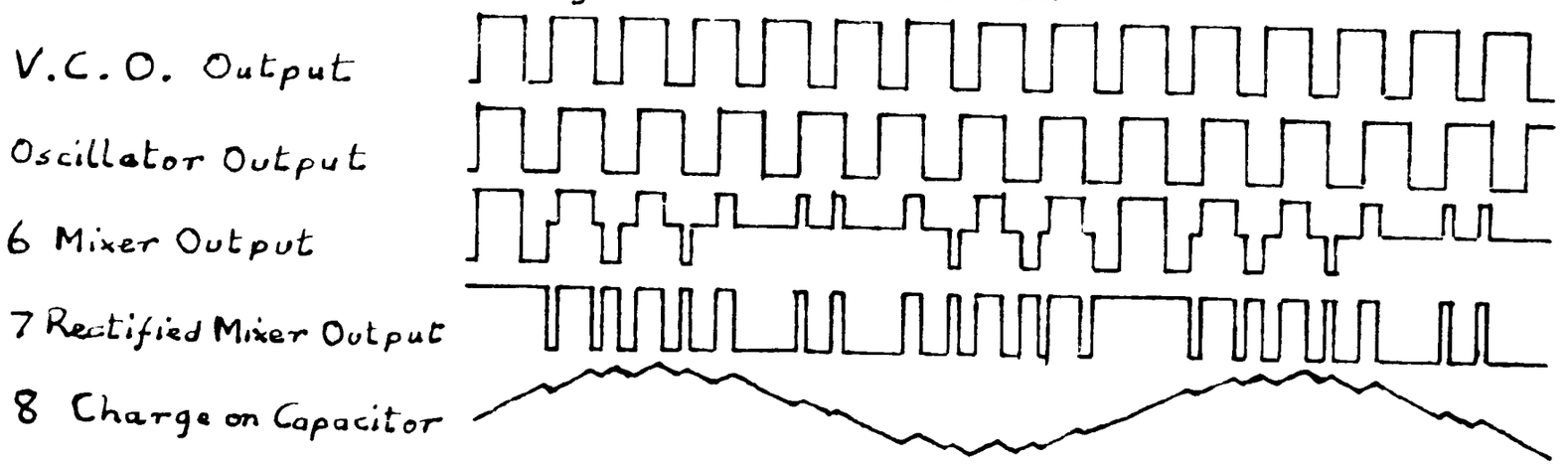


FIG.65 A/Mixer B/ Pulse Resolver C/ Amplifier



Waveforms - Schematic



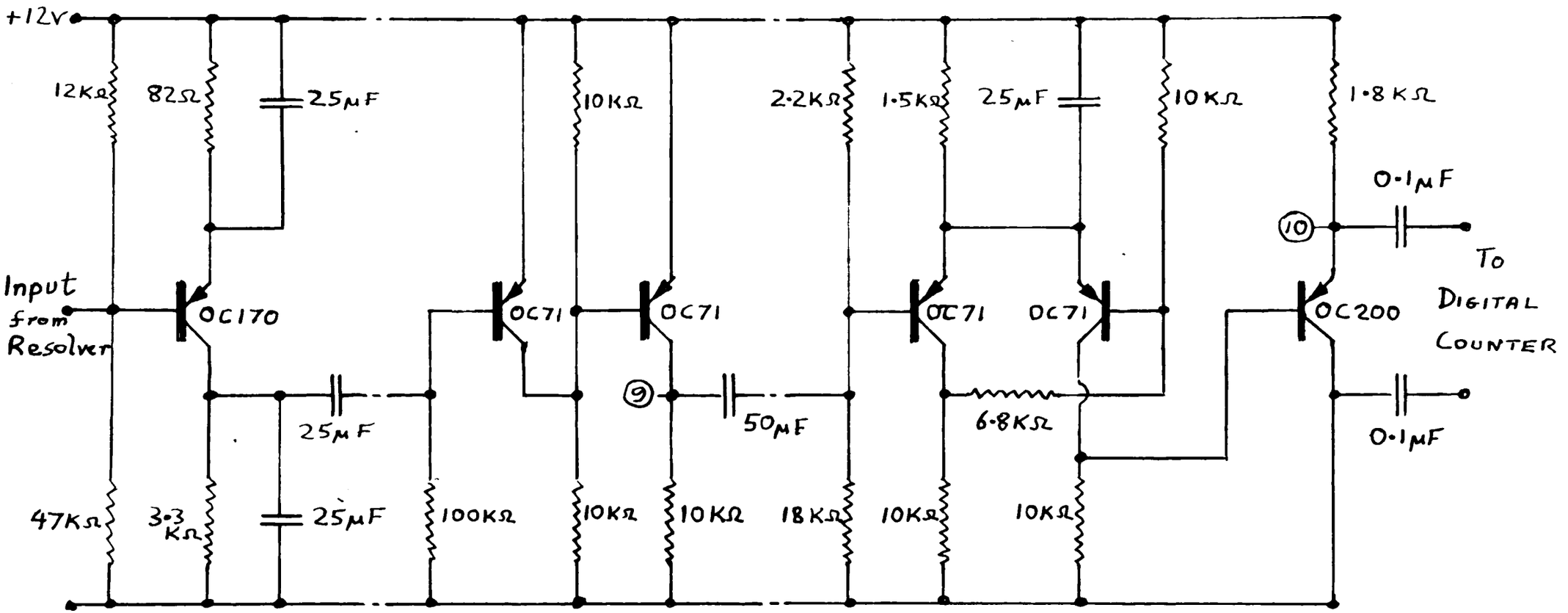
constant amplitude and 'on' time (about 45μS).

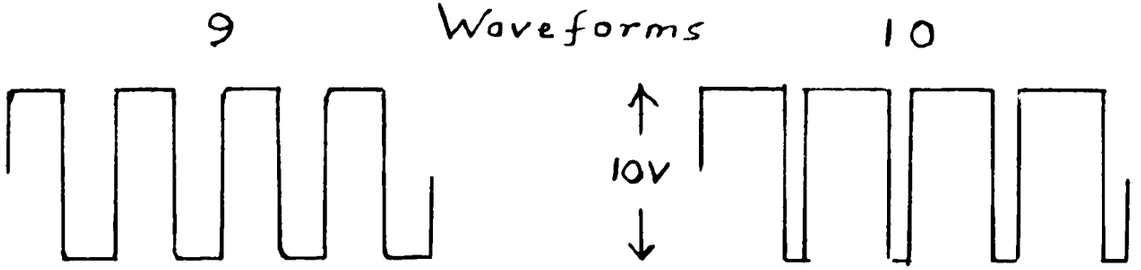
A crystal oscillator (Salford Electrical Instruments Ltd.) (Fig. 64A) was used to provide the reference frequency. The output of this oscillator was fed via a tuned amplifier (Fig. 64B) to an amplifier, the first stage of which could saturate, cutting off the second stage, thereby acting as a sine to square wave converter (Fig. 64C). The 'on' time of the output of this converter could be adjusted to the same value as that of the monostable circuit of the voltage controlled oscillator by means of the 20KΩ variable resistor.

The outputs of the two oscillator systems were then mixed using a double gated F.E.T. (Fig. 65A). This gave a very efficiency mixing, but it was found that the two gates had different characteristics and thus the amplitudes of the oscillator outputs had to be adjusted with some care. The resultant output from the drain of the F.E.T. was essentially a three level waveform (see Fig. 65). This was fed into a pulse resolver (Fig. 65B) which consisted of a phase splitter, in effect acting as a combination of a full wave rectifier and an amplifier. The problem of slight instability of the amplitudes of the input waveforms was overcome by biasing the OC200 transistors to start conducting at values between the mixer output levels and to reach saturation before the extreme levels were reached. The amplified and phase rectified current was used to charge a capacitor with a parallel leak resistance so that an approximately sinusoidal voltage was obtained across it. The frequency of this voltage corresponded to the beat frequency of the square wave inputs (see Fig. 65). The output was amplified by a two stage amplifier, the second stage being an emitter follower (Fig. 65C), and then

FIG. 66

A/ Sine Wave Shaper B/ Sine to Square Wave C/ Schmitt Trigger with Amplifier





had its high frequency components removed by a filter stage (Fig. 66A) so that a reasonably smooth sine waveform was obtained. This was used to trigger a bistable circuit (Fig. 66B), similar to that used with the crystal oscillator, to produce a square wave output, which in turn was used to fire the Schmitt Trigger (Fig. 66C). The output was then amplified by an emitter follower stage and was fed via isolating capacitors to the digital counter.

The integrator was used by R.G.L. Saul (Chemistry Part II student 1966-67) for some time towards the end of his research. He found that the count rate was effectively linear with respect to the slidewire deviation and that there was a 'negligible' drift once the integrator had warmed up, which took about ½ hour. His conclusion was that the integrator was probably more accurate than any of the other methods used for area measurement (see Section 2.74). It is suspected that the deviation from linearity of the integrator is probably less than the accuracy with which Mr. Saul could measure (approximately 0.4%).

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d 837 3197
e 1184 3853
f 1190 3853
g 1476 3853
h 48, 207 (1954) 6321
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