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DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM

A THESIS

entitled

THE ACTION OF CHLORINE TRIFLUORIDE ON BENZENE IN THE
VAPOUR PHASE

submitted by

RONALD ERIC BANKS, B.Sc., A.R.I.C..

(Bede College)

A candidate for the degree of Doctor of Philosophy

1956.



SUMMARY

Approved
M. Slaney 25/6th/1956

Chlorofluorination of Benzene

A controlled reaction between chlorine trifluoride and benzene in the vapour phase was achieved by allowing the reactants, suitably diluted with nitrogen, to mingle within the meshes of a copper packing which was contained in a reactor kept at 260°C. The product of the reaction was a complex, dense, somewhat lachrymatory, yellow liquid which proved both tedious and difficult to separate. Fractional distillation of the product through 60-plate concentric-tube columns resulted only in the isolation of azeotropic mixtures, some of which contained unchanged benzene. These were analysed by means of gas-liquid partition chromatography, and large-scale separations of some of the azeotropes carried out by this technique. Monochlorobenzene, a mixture of o-, m-, and p-chlorofluorobenzenes and cyclohexane derivatives with the following molecular formulae were isolated:- $C_6H_6ClF_5$, $C_6Cl_2F_{10}$, $C_6HCl_2F_9$, $C_6H_2Cl_2F_8$, $C_6H_3Cl_2F_7$ and $C_6Cl_3F_9$. Brominations, hydrogenations and reactions with iodine monochloride were carried out in an effort to identify double-bond structures in these compounds, but the results were not conclusive, and infra-red analysis had to be resorted to. The compounds containing hydrogen easily lose halogen hydracids at room temperature



and in the presence of alkali. It was not possible to deduce actual configurations, especially since some of the materials were isomeric mixtures, but possibilities have been suggested.

Analytical Section

Cation-exchange resins were applied to the analysis of solutions obtained by fusing organic compounds containing chlorine and fluorine with sodium, then leaching with water in an atmosphere of nitrogen. The total halogen was estimated by alkalimetry, and the chlorine either argentometrically or by a Vieböck procedure. The method thus represents a great step forward in the analysis of fluorine-containing organic compounds since it has none of the failings of a thorium nitrate estimation, and is shorter than a lead chlorofluoride procedure. The method was also extended to deal with nitrogen-containing halo-organic compounds.

A New Binary Test Mixture for Evaluating Distillation Columns at 50 mm. of Mercury

A test mixture consisting of methyl benzoate and methyl caprylate was developed in order to test the concentric-tube columns at reduced pressure. The efficiencies of the columns were found to decrease by 50% on reducing the pressure from 760 to 50 mm.

A Note on the Benzene-Fluorobenzene System

It was found that benzene and fluorobenzene do not form an azeotrope at atmospheric pressure, but an extremely efficient column (more than 70 theoretical plates) must be used to effect a separation of these compounds by fractional distillation. Analytical experiments indicated that gas-chromatographic separations should be achieved quite easily.

ACKNOWLEDGEMENTS

The work recorded in this thesis was carried out under the direction of Dr. W.K.R. Musgrave, and I wish to express my thanks to him for continual encouragement and co-operation. I am also indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to Professor M. Stacey, F.R.S., who arranged for me to spend a short time in the Chemistry Department at Birmingham University where infra-red analyses were carried out on some of my materials by Dr. H.W. Whiffen, Dr. H. Spedding and Mr. J. Burdon.

MEMORANDUM

The work reported here was carried out by the author at the University Science Laboratories, Durham, between September 1953 and July 1956. It is original, except where acknowledged by reference, and has not been presented for any other degree.

The main object was to investigate the action of chlorine trifluoride on benzene in the vapour phase, but before proceeding with this it was necessary to carry out analytical and distillation researches. Thus the thesis contains an Analytical Section and an Appendix.

Up to the present time the work has provided material for the following three publications:-

"The Semi-Micro Determination of Fluorine, Chlorine and Nitrogen in Organic Compounds. Part II. The Use of Cation Exchange Resins". (BANKS, CUTHBERTSON AND MUSGRAVE, Anal. Chim. Acta., 1955, 13, 442).

"The Use of Concentric-Tube Distillation Columns at Reduced Pressure". (BANKS AND MUSGRAVE, accepted but not yet published by J. Appl. Chem.)

"Vapour-Liquid Equilibrium Data for the Benzene-Fluorobenzene System". (BANKS AND MUSGRAVE - a note to be published in J.C.S.)

Signed: R. E. Banks

(R. E. BANKS)
9/7/56.

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Chlorofluorination of Benzene

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Chapter I

Introduction.

Chlorine trifluoride was discovered in 1930 by RUFF AND KRUG (Z. anorg. allgem. Chem., 1930, 190, 270), but for almost twenty years its use as a halogenating agent in organic chemistry amounted only to the observation that it reacted violently with organic substances. This lack of attention was not entirely due to its great reactivity, but also to the fact that elementary fluorine is needed for its synthesis, and in the early days of Fluorine Chemistry the production of this in quantity was a difficult and hazardous task. During the years of World War II, however, when certain fluorine-containing compounds were in great demand, tremendous advances were made in the means of preparation and the technology of elementary fluorine (Fluorine Symposium, Ind. Eng. Chem., 1947, 39, 236-434), which in turn rendered it possible for chlorine trifluoride to be made on a large scale (LEECH, Quart. Reviews, 1949, 3, 22; PORTER, Chem. Eng., 1948, 55, No. 4, 102). Thus only in comparatively recent years has it become readily available for study as a reagent in organic chemistry.

The first work to be reported which gave rise to a characterised product was carried out by HÜCKEL (Nachr. Akad. Wiss. Göttingen, Math-physik. Klasse, 1946, 36) who



obtained trifluoronitromethane (fluoropicrin) in small yield from the reaction of chlorine trifluoride with bromodifluoronitromethane. Apart from this, the only reports on the controlled reaction of chlorine trifluoride with organic compounds prior to 1950 either gave no details, or took the form of patent specifications. Thus, PORTER (loc. cit.) and also BURNETT AND BANKS (Chem. Soc. Symposium on Fluorine Chemistry, Nov. 1949) stated that such reactions result in the introduction of both chlorine and fluorine into the organic compounds, whilst LEECH (Brit. Pat. 633,678), and workers at The Pennsylvania Salt Manufacturing Company (Brit. Pat. 665,253) carried out liquid-phase chlorofluorinations of a variety of organic substances but made no attempt to isolate any definite products from the reaction mixtures they obtained. Leech moderated his reactions by diluting the organic reactants with carbon tetrachloride which is relatively inert to chlorine trifluoride at room temperature and in the presence of other organic material (ELLIS AND MUSGRAVE, J.C.S., 1953, 1063), and carried out analyses on the reaction products to show that they contained more combined chlorine than fluorine. The Americans moderated their reactions by using anhydrous hydrofluoric acid as a diluent.

for both the chlorine trifluoride and the organic substances.

In 1950 the first detailed report on the controlled reaction of chlorine trifluoride with an organic compound of the aromatic series was made from this laboratory by ELLIS AND MUSGRAVE (ibid., 1950, 3608). They passed chlorine trifluoride diluted with nitrogen into a solution of benzene in carbon tetrachloride and found chlorobenzene and fluorobenzene to be the chief products of the reaction which occurred. The main reaction was therefore one of substitution. Small amounts of products were isolated, however, which from their analyses and reactions appeared to be chlorofluoro- cyclohexanes, -cyclohexenes, -cyclohexadienes and -diphenyls. The effects of catalysts, which were chosen because they were either well-known halogen carriers or salts of transition metals which had been used in direct fluorinations of organic compounds, were also investigated. Their presence only affected the yields of products and not the mechanism of the reaction. Further work in which benzene derivatives and benzene homologues were used as starting materials gave parallel results (idem., ibid., 1953, 1063).

It seemed from the results obtained by Ellis and Musgrave that if the reaction between benzene and chlorine trifluoride

could be carried out in the vapour phase then the yields of chlorofluoro addition products would probably be much increased because the predominant reaction should be a free radical one. HASZELDINE in a private communication to SHARPE (Quart. Reviews, 1950, 4, 127) stated that he had evidence for the production of substitution and addition compounds in the vapour phase reactions of chlorine trifluoride with benzene and toluene but gave no details. Thus, in 1951, SOWLER AND MUSGRAVE (results unpublished) began investigations on the reaction between chlorine trifluoride and benzene in the vapour phase. They showed that it was possible to obtain quite good yields of addition products, but were never successful in isolating and characterising any definite compounds present in their reaction products. Sowler abandoned the work prematurely in 1952 and the subsequent work will be discussed in this thesis.

Before proceeding with this however, it is of interest to discuss briefly the methods already available for synthesising chlorofluoro- cyclohexanes, -cyclohexenes, and -cyclohexadienes so that they may be compared with the use of chlorine trifluoride in the preparation of the above types of compound. They will be split up into two

groups, the first being by far the largest and containing the two most important methods yet available. Full details of the compounds known, the methods by which they were prepared and the literature references are given in TABLE 1 .

A. THE FLUORINATION OF CHLOROBENZENES.

(i) Direct fluorination using elementary fluorine.

BIGELOW AND PEARSON (J.A.C.S., 1934, 56, 2773) claimed to be the first workers to carry out the direct fluorination of an aromatic halogen-containing compound successfully. They passed a current of fluorine through a dilute solution of hexachlorobenzene in carbon tetrachloride, and after removing the solvent completed the reaction by directly fluorinating the residual oil. From the final product they were able to isolate small amounts of hexachlorohexafluorocyclohexane and hexachlorotetrafluorocyclohexene. Elaborating further on this, FUKUHARA AND BIGELOW (ibid., 1938, 60, 427) progressively sublimed hexachlorobenzene into a glass chamber in which it came into contact with fluorine issuing through a roll of copper gauze. The resulting reaction yielded a complex, highly reactive, liquid product which was

stabilised by treatment with iron and acetic acid. From the final product were isolated ten liquid and two crystalline portions whose analyses showed them to be chlorofluoro compounds. No definite formulae were postulated.

Contrary to the belief of some authors, however, Bigelow and Pearson were not the first workers to carry out the fluorination of a chlorinated aromatic compound, and although it is not wholly relevant the work of BANCROFT AND WHEARTY (J. Phys. Chem., 1931, 35, 3121; Proc. Natl. Acad. Sci., 1931, 17, 183) will be mentioned here because it is of great historic interest and appears to have been neglected.

The aim of their work was to investigate certain theories of ring substitution in direct halogenations of the aromatic nucleus, and they attempted the direct fluorination of benzene, toluene, anisole, 1,3,5-trinitrobenzene, 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, and hexachlorobenzene. However, they only isolated products from two of these reactions. They passed fluorine into a solution of 1,3,5-trichlorobenzene in carbon tetrachloride and isolated a liquid product which was unstable when boiled at atmospheric pressure.

(b.pt. $150^{\circ}\text{C}.$), but distilled without decomposition at reduced pressure (b.pt. $75^{\circ}\text{C}./25\text{ mm.}$). It analysed to give a Cl:F ratio (atoms) of approximately 2:3, and without any proof of its aromatic character was stated to be dichlorotrifluorobenzene. From hexachlorobenzene, by passing elementary fluorine over it in a heated tube, they obtained a viscous, oily liquid which yielded two distinct fractions on distillation. The first (b.pt. $140\text{-}150^{\circ}\text{C}.$) they claimed to be tetrachlorodifluorobenzene, and the second (b.pt. $230\text{-}240^{\circ}\text{C}.$) trichlorotrifluorobenzene. Again no confirmation of the aromatic nature of these products was sought.

It is obvious from a consideration of the reports made by Bigelow and co-workers, and also a knowledge of the mechanisms of direct fluorination, that the products obtained by Bancroft and Whearty could not have been aromatics, and hence their analyses must have been highly inaccurate. This is not surprising because they were made using a modified DROGIN-ROSANOFF method (J.A.C.S., 1916, 38, 711) in which, after decomposing the sample being analysed by refluxing it with potassium-alcohol mixtures and then neutralising the solution, chlorine was determined by precipitating it as silver chloride with silver nitrate

and estimating excess of the latter reagent by a Volhard procedure, and Fluorine by precipitation as calcium fluoride.

(ii) Indirect fluorination using higher inorganic fluorides or inorganic perfluorides.

This method has been employed to fluorinate monochlorobenzene, o-dichlorobenzene, pentachloro-(trifluoromethyl)-benzene, and hexachlorobenzene by use of antimony pentafluoride, argentic fluoride, ceric fluoride, cobaltic fluoride, manganic fluoride and plumbic fluoride to give rise to fully halogenated cyclohexanes along with some cyclohexenes in the case of antimony pentafluoride. The fluorination of monochlorobenzene and o-dichlorobenzene produces chlorofluorocyclohexanes of known constitution, although in the latter case some chlorine is removed from the molecule and enters other products, so giving rise to trichlorononafluorocyclohexane together with chloroundecafluorocyclohexane, 1,2-dichlorodecafluorocyclohexane and perfluorocyclohexane.

TATLOW AND WORTHINGTON (J.C.S., 1952, 1251) suggest that chlorine fluorides may be responsible for this further chlorination.

Antimony pentafluoride results in more extensive replacement of chlorine by fluorine than does antimony trifluoride, and has been extensively used for this purpose (see McBEE et al, Ind. Eng. Chem., 1947, 39, 305, 378, 384, 391 and 415). The reactions are usually carried out in a metal vessel provided with a stirrer, the antimony pentafluoride being added as such to the starting materials, or being present as antimony pentachloride then converted to fluoride in situ by addition of hydrofluoric acid.

The use of inorganic perfluorides for fluorination purposes was introduced by FOWLER et al (ibid., 292) who showed that by passing hydrocarbon vapours over a heated bed (ca. 350°C.) of cobaltic or argentic fluoride hydrogen can be replaced by fluorine, which also adds to any double bonds present. Any chlorine present in the starting material is retained to a large extent (TATLOW AND WORTHINGTON, loc. cit.)

It may be noted that by employing all the perfluorides mentioned above to fluorinate chloro-(trifluoromethyl)-benzenes, LIGETT (U.S. Pat. 2,654,789; Am. C.A., 1954, 48, 12799a) has prepared a number of fully halogenated chlorofluoro-(trifluoromethyl)-cyclohexanes.

(iii) Indirect fluorination using bromine trifluoride.

During the course of investigations into the preparation of aromatic perfluoro compounds McBEE, LINDGREN AND LIGETT (Ind. Eng. Chem., 1947, 39, 378) showed that bromine trifluoride reacts quite smoothly with hexachlorobenzene at moderate temperatures giving rise to a mixture with the average composition $C_6Br_2Cl_4F_6$. They subsequently treated this with antimony pentafluoride to fluorinate it further, dehalogenated the product with zinc dust in alcohol, and obtained a very complex mixture of products. From this they isolated C_6F_6 , C_6F_8 , C_6ClF_7 , $C_6Cl_2F_8$, $C_6Cl_2F_6$, $C_6Cl_3F_7$ and $C_6Cl_3F_5$. A similar set of reactions was carried out using trifluoromethylbenzene as starting material. In such a reaction as this the structures of the products cannot be anticipated, and chemical investigations need to be carried out before a product can be fully characterised. This does not appear to have been done for the above compounds, although many American patents have been published dealing with the use of this method for their synthesis (see TABLE 1).

B. THE DIRECT CHLORINATION OF FLUOROBENZENES AND
OTHER FLUORO COMPOUNDS:

This type of reaction has received little attention, which is unfortunate because the known fluorobenzenes should give rise to chlorofluorocyclohexanes of known structure if exhaustively chlorinated.

(i) Chlorination of fluorobenzenes.

Only two compounds have been reported to give rise to chlorofluorocyclohexanes on chlorination, namely monofluorobenzene and 1,2,4,5-tetrafluorobenzene. The first reacted violently with chlorine in the presence of sunlight and at room temperature to give rise to 1-fluoro-1,2,3,4,4,5,6-heptachlorocyclohexane, a monofluorohexachlorocyclohexane and a high boiling, highly chlorinated oil which was not investigated (T. van der LINDEN, Rec. trav. Chim., 1936, 55, 282). The tetrafluorobenzene on treatment with chlorine yielded small amounts of tetrafluorohexachlorocyclohexane (FINGER et al, J.A.C.S., 1951, 73, 145).

(ii) Chlorination of other compounds.

During the course of a study of highly fluorinated organic compounds being carried out at Birmingham University

by TATLOW and co-workers, perfluorocyclohexene was chlorinated in ultra-violet light (J.C.S., 1952, 2351) and perfluorobicyclohexyl chlorinated at 600-650°C. (ibid., 4695) giving rise to 1,2-dichlorodecafluorocyclohexane, and chloroundecafluorocyclohexane respectively. The first reaction was originally reported by BRICE AND SIMONS (J.A.C.S., 1951, 73, 4017). Obviously reactions of this type are limited in number.

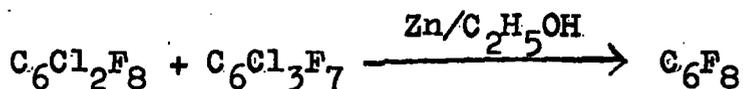
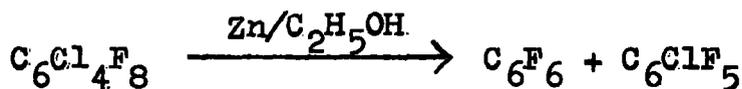
It can be seen that a great deal of work remains to be done on the synthesis of chlorofluoro-cyclohexanes, -cyclohexenes and -cyclohexadienes, new methods being required which can not only be applied to the syntheses of fully halogenated compounds of known structure, but also to those containing hydrogen. Thus, apart from the investigation into the use of chlorine trifluoride as a means for producing compounds of unknown structure, a complementary programme of work was begun in this laboratory by CUTHBERTSON AND MUSGRAVE which was planned to produce simple chlorofluoro compounds of the above types by unambiguous routes, and so of known structure. Briefly, the methods which they chose were:- the replacement of other halogens in known cyclohexanes and cyclohexenes by treatment with (a) hydrofluoric acid under

different conditions (b) anhydrous potassium fluoride in solvents such as glycerol or glycol (c) inorganic perfluorides, and the hydrolysis of tosyl esters of alcohols derived from cyclohexane by heating them with aqueous potassium fluoride in sealed tubes. So far only 1-chloro-1-fluorocyclohexane has been synthesised. This was done by means of reaction (a) above, 1-chlorocyclohexene being treated with anhydrous hydrogen fluoride both in the presence of, and without catalysts (aluminium trichloride, boron trifluoride and stannic chloride). For details see CUTHBERTSON, Ph.D. Thesis, Durham, 1956, and CUTHBERTSON AND MUSGRAVE, J. Appl. Chem., to be published.

There is not a great deal of information regarding the reactions of chlorofluoro-cyclohexanes, -cyclohexenes, and -cyclohexadienes and, through the work of Cuthbertson and experiments designed to discover the structures of the compounds produced by the vapour-phase chlorofluorination of benzene, it was hoped to fill some of the gaps in the literature. These experiments were based on four types of reaction namely, de-halogenation, de-hydrohalogenation, oxidation and reduction.

De-halogenations of chlorofluoro compounds of the

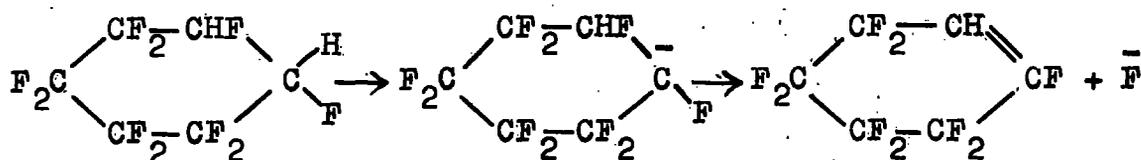
type under discussion can be carried out by means of zinc dust in acetamide, zinc dust and acetic acid, and zinc dust in alcohol. The use of the first and last of these reagents is well known from the work of McBEE et al (loc. cit.) on the indirect fluorination of hexachlorobenzene with bromine trifluoride, which produces intermediates in the synthesis of perfluorobenzene, chlorofluoro-cyclohexenes, and -cyclohexadienes (see p. 11). These workers have also reported the following reactions (U.S. Pat., 2,586, 364; Am. C.A., 1952, 46, 8675e):-



It appears that chlorine can be more easily removed than fluorine, and thus should be so preferentially if present on two adjacent carbon atoms in a molecule. This type of reaction has been much used for the preparation of fluorocarbon olefines, zinc being employed to remove bromine or chlorine from adjacent carbon atoms of fluorine-containing halo-alkanes.

Likewise, the removal of hydrogen bromide or chloride by bases has been used to prepare fluorocarbon olefines, but the use of this type of reaction in the formation of chlorofluorocyclohexenes, or perfluorocyclohexenes from chlorofluorocyclohexanes has received scant attention because of the scarcity of compounds of the latter type which contain hydrogen. Van der LINDEN (loc. cit.) has reported the removal of half the available chlorine from $C_6H_5Cl_6F$ by treating it with methyl alcoholic potassium hydroxide, whilst TOMPSON, TARRANT AND BIGELOW (J.A.C.S., 1946, 68, 2187) found that both chlorine and fluorine can be removed from $(CF_3)_2C_6H_3ClF_4$ and $(CF_3)_2C_6H_3ClF_2$ by means of alcoholic potassium hydroxide (10%). The acid and alkali catalysed hydrolyses of 1-chloro-1-fluorocyclohexane result in removal of both chlorine and fluorine to the extent of 50% of total halogen present in the molecule. (CUTHBERTSON AND MUSGRAVE, loc. cit.). Chloroundecafluorocyclohexane, however, does not undergo any exchange reactions with either aqueous or alcoholic alkali, but on reduction by lithium aluminium hydride in ethereal solution it is converted to undecafluorocyclohexane which easily undergoes de-hydrofluorination with aqueous potassium hydroxide to

yield perfluorocyclohexene (TATLOW AND WORTHINGTON, loc. cit.). It would appear, therefore, that hydrogen present in the molecule facilitates de-hydrohalogenations. ROYLANCE, TATLOW AND WORTHINGTON, (J.C.S., 1954, 4426) suggest that the elimination of hydrogen fluoride from a fluorohydrocarbon, with the formation of an unsaturated compound, proceeds through an intermediate fluorocarbonium ion, so:-



This type of mechanism can also be applied to removal of other halogens, for example 1,2-dibromo-1H-nonafluorocyclohexane on treatment with aqueous alkali loses both bromine and fluorine from the same carbon atom giving rise to unsaturated compounds.

Valuable information regarding structure can be obtained through the oxidation of chlorofluorocyclohexenes and -cyclohexadienes, especially if the reactions give rise to known dibasic acids. For example, McBEE, WISEMAN AND BACHMAN (Ind. Eng. Chem., 1947, 39, 415) obtained a dichlorooctafluorocyclohexene by fluorinating hexachlorobenzene with antimony pentafluoride. This they proved

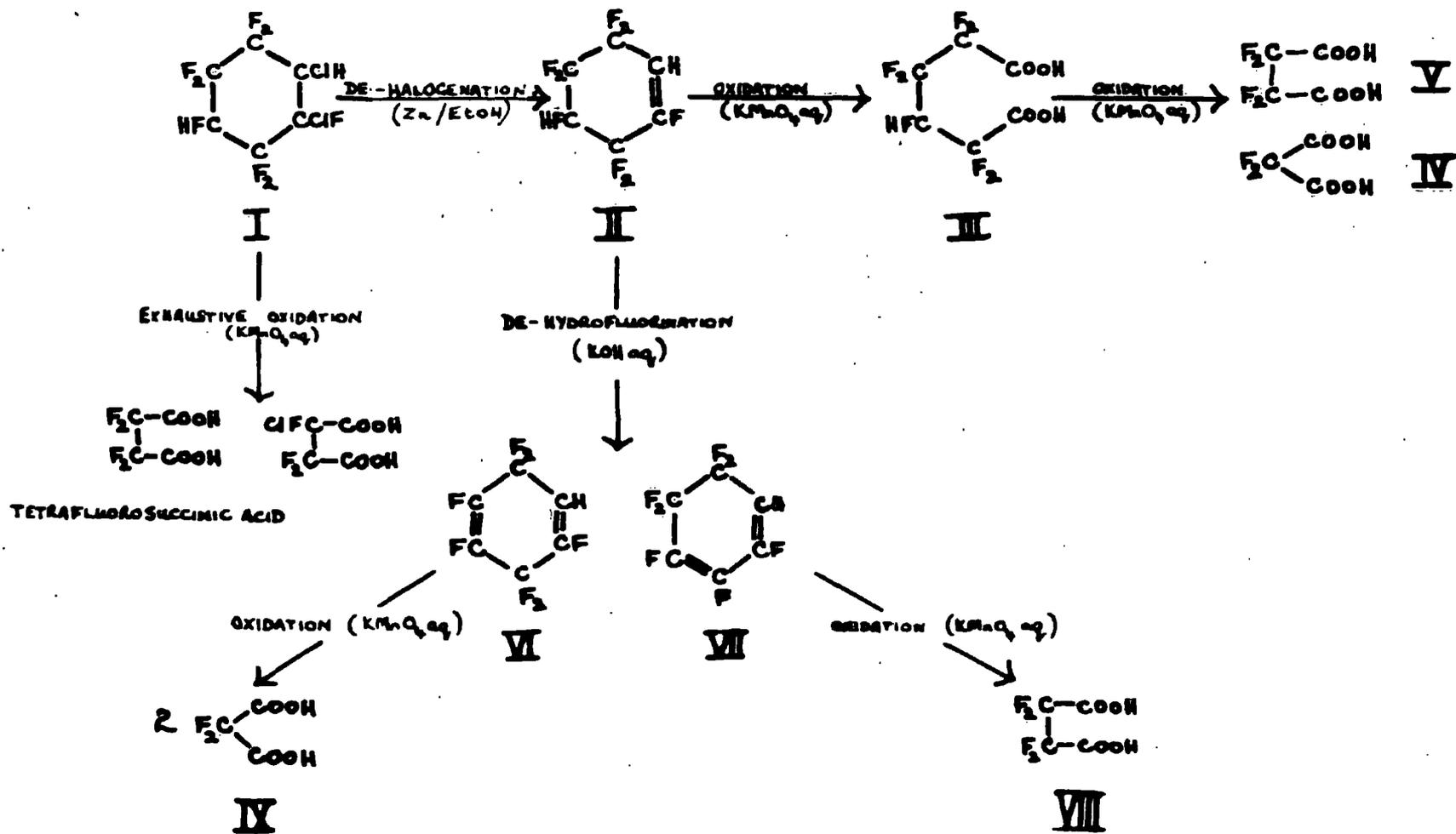
to be 1,2-dichloro-octafluorocyclohex-1-ene by oxidising it with aqueous potassium permanganate to perfluoroadipic acid. It should also be possible to carry out oxidations of this nature with ozone.

Information on reduction appears limited to the conversion of chloroundecafluorocyclohexane to undecafluorocyclohexane (see above), and dichlorodecafluorocyclohexanes to decafluorocyclohexanes: (ROYLANCE, TATLOW AND WORTHINGTON, loc. cit.) by means of lithium aluminium hydride. Besides employing this type of reduction it was also decided to attempt direct hydrogenations with molecular hydrogen at room temperature and atmospheric pressure in the presence of noble metal catalysts. It was hoped by this means to detect any double bond structures.

To demonstrate the value of the above types of reaction in the elucidation of structures their application to a hypothetical 1,2-dichloro-2,3,3,4,5,5,6,6-octafluorocyclohexane will be considered (see Reaction Scheme).

The formation of an olefine (II) containing the same number of fluorine atoms would show that the two chlorine atoms were present on adjacent carbon atoms. The positions of the hydrogen atoms could then be proved by

REACTION SCHEME (i)



oxidations of I and II. From II would be obtained the known 3H-heptafluoroadipic acid III (BARBOUR et al, J. Appl. Chem., 1954, 4, 341; FEAR AND THROWER, *ibid.*, 1955, 5, 353). Further oxidation of this acid, or exhaustive oxidation of II, would give rise to a mixture of difluoromalonic (IV) and tetrafluorosuccinic (V) acids, both of which are known (FEAR, THROWER AND VEITCH, *ibid.*, p. 589). Thus the position of one of the hydrogen atoms would be established, and it would be obvious that the other was present on a carbon atom involved in the double bond in II. The position of this hydrogen would be established by the formation of tetrafluorosuccinic acid and not difluoromalonic acid when I was exhaustively oxidised. Further proof of the structure of II would be provided by a de-hydrofluorination experiment. This could give rise to a mixture of dienes (VI and VII), although it would be expected that VII, being conjugated, would be present in greater proportion than VI. Separation of these followed by oxidations would give rise to one known perfluoro-dibasic acid in each case.

It is obvious that several stereoisomers of I would be capable of existence, and the determination of an actual

configuration would be a very difficult task. If, however, one such compound could be fully characterised then a knowledge of its reactions, notably de-hydro-halogenations, might lead to some rules regarding group types which would be of great assistance in the determination of the configurations of other like compounds.

TABLE 1

Formula of Compound	M.Pt. (°C.)	B.Pt. (°C.)	Refractive Index	Density (25°C.)	Mode of Preparation	Yield	Reference
C_6ClF_{11}	24-26	76.9-77.0	-		Fluorination of $o\text{-Cl}_2C_6H_4$ with either AgF_2 or MnF_3 at 118-323°C.	17%	LINDGREN AND McBEE, U.S. Pat. 2,480,081; Am.C.A. 1950, <u>44</u> , 2020g.
	30-31	79.4-80.1/ 754 mm.	n_D^{40} 1.301		Fluorination of C_6Cl_6 with SbF_5 at 100-300°C.		McBEE, ROBB AND LIGETT, U.S. Pat. 2,493,008; Am.C.A. 1950, <u>44</u> , 5375b.
	28	78.4-78.6			Fluorination of C_6H_5Cl and $o\text{-Cl}_2C_6H_4$ with CoF_3 at 350°C.	16%	STILMAR, U.S. Pat. 2,553,217; Am. C.A. 1951, <u>45</u> , 9079d. TATLOW AND WORTHINGTON, J.C.S., 1952, 1251.
$C_6Cl_2F_{10}$	12-14	107.5-107.7	n_D^{20} 1.3413	1.79	Chlorination of $C_{12}F_{12}$ at 600-650°C.	46%	BARLOW AND TATLOW, <i>ibid.</i> , 4695.
	18.5-20	108.0	n_D^{20} 1.338		Fluorination of $o\text{-Cl}_2C_6H_4$ with AgF_2 or MnF_3 at 118-323°C.	5%	LINDGREN AND McBEE, <i>loc. cit.</i>
	39-41	109.6-110.2/ 756 mm.	n_D^{45} 1.332		Photochlorination of C_6F_{10}	62%	TATLOW AND WORTHINGTON, <i>loc. cit.</i> BRICE AND SIMONS, J.A.C.S., 1951, <u>73</u> , 4017.
	36-37	108-109/752 mm.	n_D^{45} 1.331		Fluorination of C_6Cl_6 with SbF_5 at 100-300°C.		STILMAR, <i>loc. cit.</i>
					Fluorination of $o\text{-Cl}_2C_6H_4$ with CoF_3	16%	TATLOW AND WORTHINGTON, <i>loc. cit.</i>
					Photochlorination of C_6F_{10}	56%	Idem, <i>ibid.</i>

TABLE 1 (contd.)

Formula of Compound	M.Pt. (°C.)	B.Pt. (°C.)	Refractive Index	Density (25°C.)	Mode of Preparation	Yield	Reference
$C_6Cl_3F_9$	32.5-33.5	144-148	n_D^{45} 1.3630		Fluorination of C_6Cl_6 with PbF_4 at 300°C.		LINDGREN AND McBEE, loc. cit.
		Fluorination of C_6Cl_6 with CeF_4 at 275°C.			McBEE, ROBB AND LIGETT, U.S. Pat. 2,493,007; Am. C.A. 1950, <u>44</u> , 5375b.		
		Fluorination of C_6Cl_6 with SbF_5 at 150°C.			McBEE et al, Natl. Nuclear Energy Serv., Div. VII, 1, Ppn., Props., and Technol. of F. and Org. Fluoro Cmpds., 1951, 783-8; Am.C.A. <u>46</u> , 7987g.		
		Fluorination of o- $Cl_2C_6H_4$ with CoF_3 at 350°C.			TATLOW AND WORTHINGTON, loc. cit.		
$C_6Cl_6F_6$	94-96				Fluorination of C_6Cl_6 (in CCl_4) with elementary F. ₄	small	BIGELOW AND PEARSON, J.A.C.S., 1934, 56, 2773.
$C_6H_2Cl_6F_4$	79-80				Chlorination of 1,2,4,5- $F_4C_6H_2$	small	FINGER et al, ibid., 1951, <u>73</u> , 145.
$C_6H_4Cl_7F$	213-215				Photochlorination of C_6H_5F at room temp.		T. van der LINDEN, Rec. trav. chim., 1936, <u>55</u> , 282.
$C_6H_5Cl_6F$		112-117.5/ 0.5-0.6 mm.	n_D^{19} 1.5440		Photochlorination of C_6H_5F at room temp.		Idem, ibid.
$C_6H_{10}ClF$		138.2	n_D^{20} 1.4382		Fluorination of 1- ClC_6H_9 with HF in presence of, and in absence of, catalysts ($AlCl_3$, BF_3 , $SnCl_4$)	40%	CUTHBERTSON AND MUSGRAVE. To be published in J. Appl. Chem.

TABLE 1 (contd.)

Formula of Compound	M.Pt. (°C.)	B.Pt. (°C.)	Refractive Index	Density (25°C.)	Mode of Preparation	Yield	Reference
C_6ClF_9					Fluorination of $C_6Cl_5(CF_3)$ with SbF_5 at $150^\circ C$.		McBEE et al, op. cit.
$C_6Cl_2F_8$	-70	112.5-113.5/ 750 mm.	n_D^{20} 1.3748	1.719	Fluorination of C_6Cl_6 with BrF_3 , followed by SbF_5 treatment and subsequent dehalogenation with Zn/EtOH.	5%	Mc BEE, LINDGREN AND LIGETT, Ind. Eng. Chem., 1947, <u>39</u> , 378; McBEE, LIGETT AND LINDGREN, U.S. Pat. 2,586,364; Am. C.A. 1952, <u>46</u> , 8675d; LIGETT, McBEE AND LINDGREN, U.S. Pat. 2,509,156, Am. C.A. 1950, <u>44</u> , 7872e.
		111-113/ 749 mm.			Fluorination of C_6Cl_6 with SbF_5 at $100^\circ C$.	42%	McBEE, WISEMAN AND WISEMAN, Ind. Eng. Chem., 1947, <u>39</u> , 415.
					Fluorination of $C_6Cl_5(CF_3)$ with SbF_5 at $150-360^\circ C$.	87%	McBEE AND WISEMAN, U.S. Pat. 2,459,783; Am.C.A. 1949, <u>43</u> , 3844e.
$C_6Cl_3F_7$	-76	145.5/750 mm.	n_D^{20} 1.4013	1.774	Fluorination of C_6Cl_6 with BrF_3 (as above).	2.5%	McBEE, LINDGREN AND LIGETT, loc. cit. LIGETT, McBEE AND LINDGREN, loc. cit.
$C_6Cl_6F_4$	113-114				Fluorination of C_6Cl_6 (in CCl_4) with elementary F_2 .		BIGELOW AND PEARSON, loc. cit.
C_6ClF_7	-60- -65	88-89/ 740 mm.	n_D^{20} 1.3560	1.633	Fluorination of C_6Cl_6 with BrF_3 , etc.	8%	McBEE, LINDGREN AND LIGETT, loc. cit. LIGETT, McBEE AND LINDGREN, U.S. Pat. 2,498,891; Am. C.A. 1950, <u>44</u> , 4500d.
					Dehalogenation of $C_6Cl_2F_8-C_6Cl_3F_7$ mixtures with Zn + EtOH.		McBEE, LIGETT AND LINDGREN, U.S.Pat. 2,586,364.

TABLE 1 (contd.)

Formula of Compound	M.Pt. (°C.)	B.Pt. (°C.)	Refractive Index	Density (25°C.)	Mode of Preparation	Yield	Reference
$C_6Cl_2F_6$	-25- -30	119-120/ 750 mm.	n_D^{20} 1.4030	1.656	Fluorination of C_6Cl_6 with BrF_3 etc.	4%	See refs. for $C_6Cl_2F_8$, C_6ClF_7 .
$C_6Cl_3F_5$	0-5	156-157/ 750 mm.	n_D^{20} 1.4466	1.692	Fluorination of C_6Cl_6 with BrF_3 .	2%	Refs. as for $C_6Cl_2F_6$.

Chapter II

- (i) Discussion of the Experimental Work
and the Results.
- (ii) Theoretical Considerations.

DISCUSSION

Vapour-phase reactions between elementary fluorine and organic compounds can be moderated quite successfully by allowing the reactants to combine within the meshes of a metal packing. Very little is known as to the exact nature of the changes which occur in such a process, but, unless the metal fluorides formed take part in the reaction, the moderating effect appears to be due to the rapid conduction of heat away from the reaction zone, and the breaking up of atomic chain reactions. By analogy, the vapour-phase reactions between chlorine trifluoride and benzene have been moderated by employing this technique.

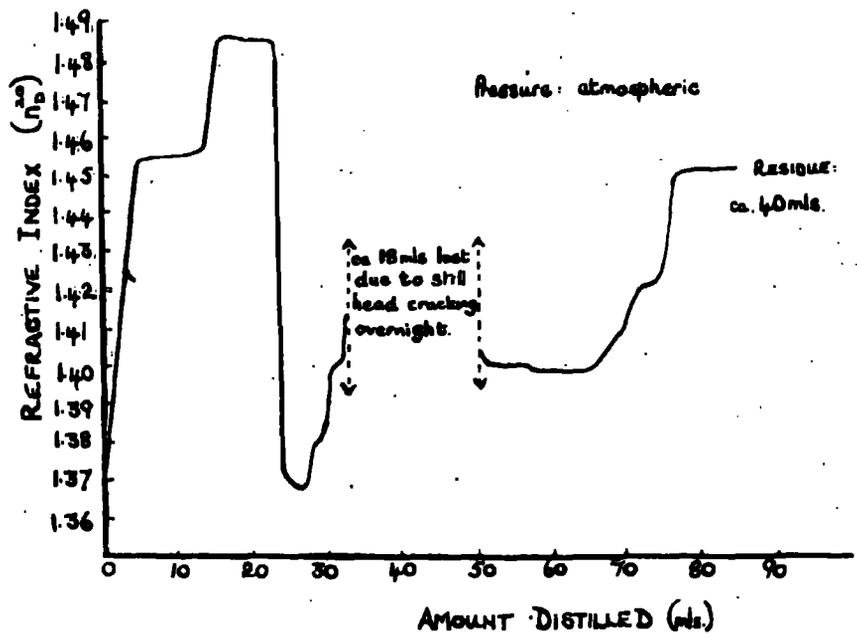
SOWLER AND MUSGRAVE (loc. cit.) made preliminary experiments using an apparatus based on that described by MUSGRAVE AND SMITH (J.C.S., 1949, 3021). The chlorine trifluoride and the benzene were diluted with nitrogen, preheated, and led into opposite sides of a heated metal tube provided with a baffle plate and packed with copper clippings. A smooth reaction ensued, and the products were condensed out of the issuing gas stream into cooled brass traps. In order to determine

which set of conditions would give the least complex, and therefore most easily separable product, twenty runs were carried out in which the ratio of chlorine trifluoride to benzene was varied between the limits 0.17 mole to 5.0 moles, and the temperature of the reactor from 100 to 250°C. For each set of conditions approximately 100 gms. of product were collected, and then distilled through a 20-plate column packed with glass helices. The distillation curves obtained showed that very little separation was being achieved, but that as the above halogenation ratio increased the amounts of material boiling below 85°C. decreased, whilst the amounts of high boiling material increased. Halogen analyses carried out on boiling fractions showed that both chlorine and fluorine were present in the products. In order to improve the separations a concentric-tube distillation column was constructed, and a further 130 mls. of product prepared at a halogenation ratio of 2.1:1 and a reactor temperature of 250°C., which conditions had been found to produce a relatively simple mixture containing less than one fifth unchanged benzene. However, Sowler did not attempt the distillation of the mixture, but abandoned the work at this stage. The present investigation

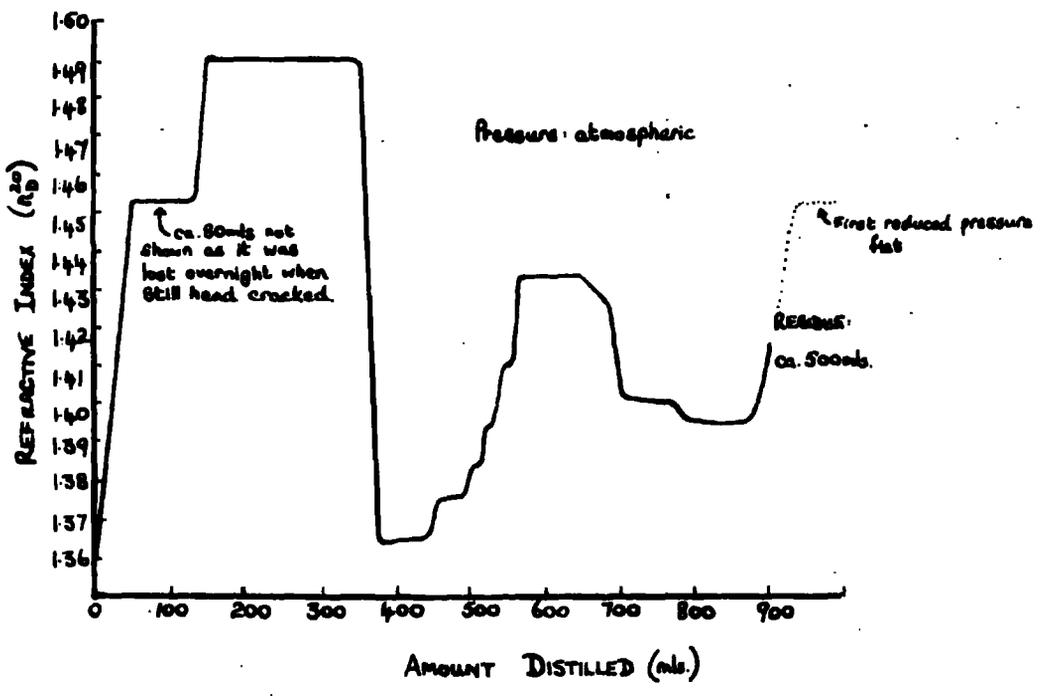
began with this operation in order to determine whether a separation could be achieved by the most powerful means then available in our laboratory.

Unknown mixtures are most profitably examined analytically in a column of the order of 100 theoretical plates; the results of such an investigation then indicate the use of a less efficient, more productive column for further work. This adequate fractionating efficiency, however, must be coupled with a small holdup so that sharp separations of components present only in small proportion can be achieved. The concentric-tube column available was, therefore, admirable for the analytical distillation of Sowler's reaction mixture. It was of the NARAGON-LEWIS type (Ind. Eng. Chem., Anal. Ed., 1946, 18, 448), with an efficiency at atmospheric pressure and total reflux of 60 theoretical plates, and a holdup of approximately 1 ml.

The distillation curve obtained is shown in DIAGRAM 1, and indicates that quite a considerable degree of separation was achieved. The analyses which were carried out on supposed "flats" (TABLE 2), however, showed that some azeotrope formation was taking place. This was not surprising because from the very nature



(a) DISTILLATION CURVE FOR SONLER'S REACTION PRODUCT



(b) DISTILLATION CURVE FOR BANKS' REACTION PRODUCT

DIAGRAM 1

TABLE 2

Analyses of Distillation "Flats" from Sowler's Reaction Product

Flat No.	B.Pt. (°C.)	n_D^{20}	% Cl (found)	% F (found)	Mol. Wt. (found)	Cl:F ratio (atoms)	Remarks
1	78.1	1.4555	6.1	32.3	100	1:9.9	Material contained benzene
2	81.2	1.4852	negligible	14.19	86	-	Material contained benzene
3	109-111	1.3715	15.5	42.16	271	1:5	
4	127	1.4025	22.1	47.6	263	1:4	
Material boiling between 130 and 155°C lost due to an accident overnight							
5	155.0	1.4037	38.78	32.0	292	1:1.55	
6	163.5	1.4203	23.3	14.16	265	1:1.14	
7	76/22 mm.	1.4653	41.1	26.4	270	1:0.83	

The analyses were carried out by the method of BELCHER et al (Mikrochim. Acta, 1953, 3, 283; *ibid.*, 1954, 4, 104) except in the case of the Cl analyses for flats 1 and 2. These were carried out argentometrically.

of the reaction between chlorine trifluoride and benzene at elevated temperatures it was expected that compounds with similar structures and close boiling points would be formed, and also this phenomenon is a well-known drawback to the separation of fluorinated mixtures by fractional distillation (see EVANS AND TATLOW, J.C.S., 1955, 1184; FEAR AND THROWER, J. Appl. Chem., 1955, 5, 353). However, it was decided to prepare litre quantities of chlorofluorinated material, and separate out either pure compounds or azeotropic mixtures in amounts suitable for investigation by chemical means.

Before proceeding with this, the type of column to be used in the separation had to be chosen. The analytical distillation graph indicated that certain materials were present only in small proportion, so that even with a large volume of product the holdup of the column must be kept below 10 mls. in order to achieve the sharpest possible separation. An efficiency of sixty theoretical plates at total reflux appeared adequate. A search of the literature revealed that the holdup of any packed column with an efficiency of sixty plates would be greater than 25 mls., the actual value depending on the type of packing and the throughput employed, so the choice was

limited to the following three types of column:-
 concentric-tube, rotating concentric-tube and spinning
 band. Some relevant operating characteristics for these
 are given below:-

	Type of column	Through- put (mls./min.)	H.E.T.P. (cms.)	Holdup for an efficiency of 60 plates (mls.)
1	Concentric-tube	1.53	0.4	1
2	Rotating concentric- tube	17.0	1.6	6
3	Spinning band	4.0	2.5	0.8

After a consideration of the technical difficulties, which included the prevention of attack on metal portions by any halogen hydracids split off from chlorofluorinated material on distillation and the operation of the columns at reduced pressure, if a column of type 2 or 3 was selected, together with the fact that a considerable time would have to be spent in acquiring the necessary operating technique, it was decided to use the concentric-tube type. In order to compensate somewhat for the small throughput two such columns were constructed so that the chlorofluorinated material could be divided between them and the distillation time halved. This also

ensured against total loss of material of a certain composition through accident.

Information was not forthcoming from the literature regarding the operating characteristics of concentric-tube type columns at reduced pressure, and since a considerable portion of chlorofluorinated material was high boiling it was necessary to be certain that the efficiencies of the columns were still superior to other types of column under all conditions. A suitable test mixture was not available, and one had to be developed which consisted of methyl benzoate and methyl caprylate. By this means it was found that the efficiencies of the concentric-tube columns decreased by 50% when the operating pressure was reduced from 760 to 50 mm. of mercury. (This work is described in CHAPTER VIII of this thesis).

The original apparatus used by Musgrave and Sowler was modified, the benzene feed being replaced with one of a much superior design, and a "cool flame" concentric-tube burner used instead of a baffle plate. Trial runs were carried out to determine optimum operating conditions, and then two large runs completed for which the details are summarised below. Run 1 duplicated Sowler's last run. The products were dense, pale yellow, somewhat

Run No.	ClF: C ₆ H ₆ (mole)	N ₂ diln. of C ₆ H ₆ (l/mole)	N ₂ diln. of reactants (l/mole)	Reactor Temp. °C.	Product (gms.)	Product (mls.)	% Cl (Found)	% F (Found)
1	1.9	16.1	96.6	260	2,090	1533	36.1	36.5
2	6.5	36.6	219.6	260	1,625	903	-	-

lachrymatory liquids. Assuming that the reaction between chlorine trifluoride and benzene in the vapour phase involves the addition of halogen to the double bonds followed by substitution of hydrogen by halogen, it is obvious that Run 1 product would be expected to contain some compounds containing hydrogen, whilst the Run 2 product should consist of fully halogenated compounds. Both reaction mixtures were split up into boiling fractions of a size suitable for the concentric-tube columns to handle, but time has only allowed for the fractions from Run 1 to be further rectified by means of the concentric-tube columns. The atmospheric pressure distillation curve is shown in DIAGRAM 1 for comparison with the analytical curve. Halogen analyses were carried out on samples from the seventeen distillation "flats" and it appeared from the results of these (TABLE 9, p. 114) that some were single substances while others were azeotropic mixtures. After carrying out several

experiments (hydrogenation, de-hydrohalogenation and oxidation) on a supposed pure compound, however, it was concluded that the analytical figures were fortuitous, and that all the distillation "flats" were mixtures. At this stage the techniques and uses of gas chromatography were becoming known, and a gas-liquid partition chromatography apparatus was built in our laboratory. It was used to analyse the distillation "flats" and discovered that all except one were mixtures, the number of components being as high as four in some cases. Following this, large-scale gas chromatographic separations were attempted on the first eight distillation "flats", and the following compounds isolated:-
dichlorodecafluorocyclohexanes, dichlorononafluorocyclohexanes, trichlorononafluorocyclohexanes, dichlorooctafluorocyclohexane, dichloroheptafluorocyclohexane, chloropentafluorocyclohexane, monochlorobenzene and monochlorofluorobenzenes. Distillation "flat" XII analysed to a dichloropentafluorocyclohexane. Each of these will be discussed separately. Owing to high and unavoidable losses of material during the distillations the above compounds were only obtained in small amounts, so it was not possible to proceed with structure

determinations. However, the ways in which these would have been carried out if material had been available are indicated.

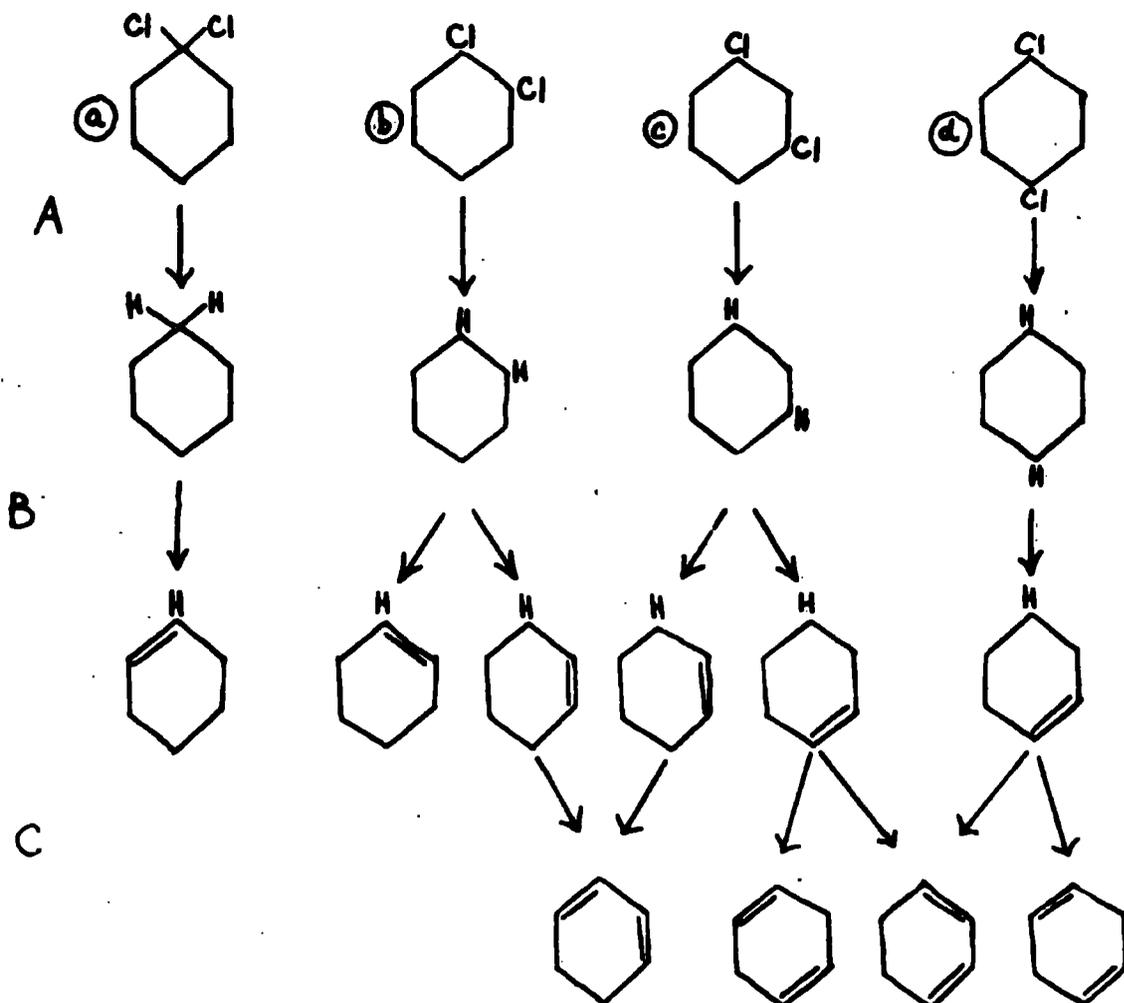
Dichlorodecafluorocyclohexanes

Distillation of the reaction product afforded an azeotrope (flat I), b.pt. 79.5°C. , which was separated by large-scale gas chromatography into benzene (90% by weight of total flat material), and two fractions which both analysed to $\text{C}_6\text{Cl}_2\text{F}_{10}$. The first, and largest of these, had the following physical constants:- m.pt. $15-25^{\circ}\text{C.}$, b.pt. $110.5^{\circ}\text{C.}/747\text{ mm.}$, n_{D}^{20} 1.3385. The melting range indicates that it is an isomeric mixture. Catalytic hydrogenation at room temperature and atmospheric pressure resulted in the replacement of 36.5% of the available chlorine by hydrogen, but negligible fluorine. The material did not react with alcoholic potassium hydroxide at room temperature. No other reactions were attempted because of lack of material. Since the second dichlorodecafluorocyclohexane fraction was only obtained in very small amount, only a halogen analysis, molecular weight determination and a refractive index measurement (n_{D}^{20} 1.3420) were made. Below are given the physical constants reported in the literature

for 1:2-dichlorodecafluorocyclohexane and also mixtures of this compound with some of its isomers.

Material	M.Pt. (°C.)	B.Pt. (°C.)	n_D^t	Authors
1:2-dichlorodecafluorocyclohexane	18.5-20	108.0	1.338 ²⁰	BRICE AND SIMONS (loc. cit.)
"	36-37	108-109/752mm.	1.331 ⁴⁵	TATLOW AND WORTHINGTON (loc. cit.)
Isomeric Mixture	39-41	109-110.2	1.332 ⁴⁵	Idem, ibid.
"	12-14	107.5-107.7	1.3413 ²⁰	LINDGREN AND McBEE (loc. cit.)

Several lines of investigations are available which will enable information regarding the number of isomers present in the two $C_6Cl_2F_{10}$ fractions, and their structures, to be obtained by future workers. Firstly, separations should be attempted using gas chromatography columns with different packings and if these are successful then the course of Reaction Scheme (ii) should be followed. After each stage separations should be attempted by means of fractional distillation and/or gas chromatography, the latter technique being preferable. Oxidations of the fluorocyclohexenes or perfluorocyclohexadienes to known



REACTION SCHEME (ii)

Stage A: REDUCTION WITH LiAlH_4

" B: DE-HYDROCHLORINATION WITH aq. KOH

" C: EXHAUSTIVE DE-HYDROCHLORINATION WITH aq. KOH

NOTE:— FLUORINE ATOMS ARE TO BE UNDERSTOOD WHERE NO
SUBSTITUENT ATOMS ARE SHOWN IN THE CYCLOHEXANE RING.

perfluoro dibasic acids would then complete the investigation. ROYLANCE, TATLOW AND WORTHINGTON (loc. cit.) used this technique to prove that the dichlorodecafluorocyclohexane, which they obtained by passing o-dichlorobenzene over heated cobaltic fluoride, was an isomeric mixture, whilst EVANS AND TATLOW have carried out both the partial (J.C.S., 1955, 1184) and exhaustive (J.C.S., 1954, 3779) de-hydrofluorinations of 1H:3H-decafluorocyclohexane. The partial reaction afforded a mixture of 3H- and 4H-nonafluorocyclohexenes which were separated by gas chromatography, and the exhaustive reaction gave a mixture of octafluorocyclohexa-1:3- and -1:4-dienes which were separated by fractional distillation.

Dichlorononafluorocyclohexanes

Material analysing to $C_6HCl_2F_9$ was obtained from distillation "flats" II (b.pt. $81.0^\circ C.$), III (b.pt. $109-110.0^\circ C.$), V (b.pt. $118.0^\circ C.$), VI (b.pt. $121.0^\circ C.$) and VII (b.pt. $124.0^\circ C.$).

"Flat" II was a benzene azeotrope (containing 90% by weight C_6H_6), and complete separation of the dichlorononafluorocyclohexane by gas chromatography with a "dinonyl" phthalate-Kieselguhr packing was impossible. Thus only a halogen analysis was carried out on this material.

"Flat" III was separated into two fractions which analysed to dichlorononafluorocyclohexane (b.pt. 110.0°C; n_D^{20} 1.3610) and dichlorooctafluorocyclohexane (b.pt. 108.0°C; n_D^{20} 1.3700) respectively. The analytical "peak" for the dichlorononafluorocyclohexane had the same nitrogen retention volume as the dichlorononafluorocyclohexane "peak" of flat II. The results of the hydrogenations of the "flat" III $C_6HCl_2F_9$ material indicate that, given sufficient time and with a more active catalyst than the 5% palladium carbon used, both chlorine atoms, and also two or more fluorine atoms, can be completely replaced by hydrogen. Reaction with bromine and also iodine monochloride resulted in considerable replacement of the hydrogen atom. Infra-red measurements supported the conclusion that the material contained hydrogen but no double bond structures. Treatment of the material with alcoholic potassium hydroxide at room temperature effected the elimination of 18% of the available fluorine and 1.0% of the available chlorine as halogen hydracids. De-hydrohalogenation to a lesser extent could also be brought about by dilute aqueous sodium hydroxide (N/10), and this phenomenon, which occurred with all the hydrogen-containing chlorofluoro-

cyclohexanes isolated, added further complications to the interpretation of the results from the hydrogenation experiments.

ROYLANCE, TATLOW AND WORTHINGTON (loc. cit.) found that the dibromo-addition product of 1H-nonafluorocyclohexene lost both bromine and fluorine from the -CBrF- grouping on treatment with aqueous potassium hydroxide at room temperature. Since a negligible amount of chlorine was removed from the dichlorononafluorocyclohexane by such treatment it is most probable that the grouping -CClF- is not adjacent to a $\overset{|}{\text{C}}\text{H-}$ grouping, and one or both of the following structures may be present.



and



Lack of material again made it impossible to carry out a full investigation into the isomeric nature of the material and the actual structures present. The method of approach would have been similar to that described for the dichlorodecafluorocyclohexanes.

"Flats" V, VI and VII contained different proportions of dichlorononafluorocyclohexane material, but absolute separations were not achieved in any case. Analytical figures indicated that the material (b.pt. 122.0-122.7°C.; n_D^{20} 1.3551) from "flat" V was the most pure, and experiments

were carried out on this. Hydrogenation did not effect the replacement of either chlorine or fluorine to the same extent found for the dichlorononafluorocyclohexane material from "flat"III; neither did bromination or reaction with iodine monochloride proceed to the same extent. De-hydrohalogenation at room temperature, however, resulted in the elimination of 21.3% of the available chlorine and 28.5% of the available fluorine, the reaction mixture darkening considerably. This cannot be explained totally by the mechanism suggested by ROYLANCE, TATLOW AND WORTHINGTON (loc. cit.) because one hydrogen atom in the molecule is not sufficient for the above quantity of halogen to be eliminated as hydracid. Thus it must be postulated that simple replacement of halogen by hydroxyl can also occur via $S_N 1$ or $S_N 2$ mechanisms. On refluxing a de-hydrohalogenation mixture for six hours elimination of 37.1% chlorine and 58.6% fluorine occurred.

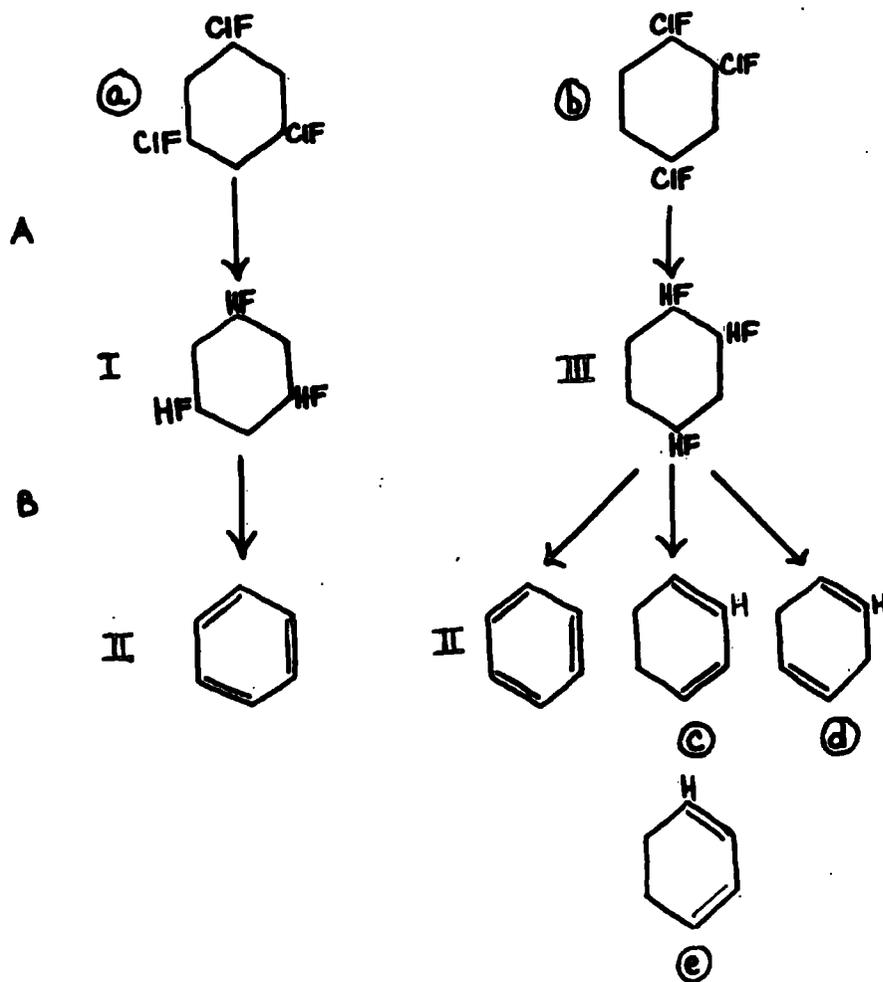
Trichlorononafluorocyclohexanes

A tedious gas-chromatographic procedure, in which fractions were recirculated several times, led to the isolation of a material (b.pt. $128.5^{\circ}\text{C}.$; n_D^{20} 1.3733) analysing to $\text{C}_6\text{Cl}_3\text{F}_9$ from distillation "flat" VIII

(b.pt. 129°C .). Evidence that this was an isomeric mixture was obtained when the cold trap in which the fraction had been condensed was allowed to warm up. The major portion was liquid, but a small amount of solid material, which did not melt at 26°C ., was found on the sides of the trap. A sufficient amount could not be recovered for purification and analysis.

TATLOW AND WORTHINGTON (loc. cit.) obtained small yields of trichlorononafluorocyclohexane by the action of cobaltic fluoride on o-dichlorobenzene, and quote the following physical constants for the material:- m.pt. $32.5-33.5^{\circ}\text{C}$, b.pt. $140.7-141.2/758$ mm, n_D^{45} 1.363.

Catalytic hydrogenation at room temperature effected the replacement of 29.3% of the available chlorine and a small amount of fluorine (4.2%) by hydrogen; no double bond structures were detected. No reaction occurred with bromine, iodine monochloride or alcoholic potassium hydroxide (at room temperature). When the de-hydrohalogenation mixture was refluxed for eight hours, however, 45.3% of the available chlorine and 51.0% of the available fluorine were hydrolysed off with considerable darkening of the reaction mixture. Infra-red analysis confirmed that the material did not



REACTION SCHEME (III)

Stage A: REDUCTION WITH LiAlH_4

B: DE-HYDROFLUORINATION WITH KOH/aq

Note:- FLUORINE ATOMS ARE TO BE UNDERSTOOD WHERE NO
SUBSTITUENT ATOMS ARE SHOWN IN THE RINGS.

contain hydrogen or double-bond structures.

It should be possible to determine the isomeric nature of this material and the structures present by means of reduction with lithium aluminium hydride, followed by de-hydrofluorination of the products, and oxidations of the unsaturated perfluoro compounds so obtained. It is interesting to note that two of the six possible structural isomers of $C_6Cl_3F_9$ should give rise to perfluorobenzene if treated so (see Reaction Scheme (iii)). In the case of an isomer with structure b it might be expected that dienes c, d, and e would accompany the perfluorobenzene, since BUXTON AND TATLOW (J.C.S., 1954, 1177) found that hydrogen fluoride is preferentially eliminated from the two adjacent $-CHF-$ groups of 1H:2H-hexafluorocyclobutane. This might not be the case with fluorohydrocarbons with a different ring size, and especially with III since the aromatic product should be more stable than the dienes and so formed preferentially.

Dichlorooctafluorocyclohexane

Dichlorooctafluorocyclohexane was the second component of distillation "flat" III. The physical constants of the material isolated were:- b.pt. 107.8-108.0°C.,

n_D^{20} 1.3700. The presence of 10% unsaturation was indicated by catalytic hydrogenation, which also effected the replacement of 35% of the available chlorine by halogen. Infra-red analysis also indicated the presence of unsaturation in the material. The explanation of this, and also the low halogen analysis (see TABLE 10), could be that the dichlorooctafluoro-cyclohexane was contaminated with some nonene originating from slow decomposition of the "dinonyl" phthalate, which was used as column liquid in the gas chromatographic separation of "flat" III, into nonene and phthalic anhydride. The latter compound was found in the cool outlet tubes of the large-scale column. Dehydrohalogenation at room temperature resulted in the removal of 12.8% of the available chlorine and 48% of the available fluorine from the molecule. As in the case of the dichlorononafluorocyclohexane from flat V, this amount of halogen could not have been eliminated in the form of halogen hydracids.

Dichloroheptafluorocyclohexane (b.pt. 114.0°C.; n_D^{20} 1.3796)

This formed an azeotrope (distillation "flat" IV, b.pt. 117°C.) with monochloropentafluorocyclohexane.

Catalytic hydrogenation effected the replacement of chlorine (38% of that available) by hydrogen, but no fluorine, and indicated that the material was saturated. Room temperature de-hydrohalogenation effected the removal of chlorine (8.0%) and fluorine (19.7%), presumably as hydracids. Infra-red analysis confirmed the presence of hydrogen in the molecule, but no double bond structures. Further investigations were not carried out, but they need to take the course indicated for the dichlorodecafluorocyclohexanes.

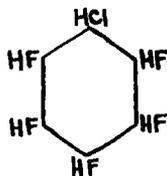
Dichloropentafluorocyclohexane

Distillation "flat" XII (b.pt. 157°C.; n_D^{20} 1.3957) analysed to a Cl:F ratio of 2:5, and the molecular weight found was 243. Since analytical gas chromatograms showed only one "peak" it is tentatively suggested that this material is a dichloropentafluorocyclohexane or a mixture of its isomers. Catalytic hydrogenation resulted in the replacement of both chlorine and fluorine by hydrogen, and indicated that 10% unsaturation existed in the material. Further proof of the constitution of the material needs obtaining by means of large-scale gas chromatography.

Monochloropentafluorocyclohexane (b.pt. 114.5°C.; n_D^{20} 1.3608)

This was the second component of distillation "flat" IV. Catalytic hydrogenation resulted in the replacement of both chlorine (24.3%) and a small amount of fluorine (3.1%) by hydrogen. No indication of any unsaturation was given, and this was confirmed by infra-red measurements which also showed that this material contained far more hydrogen than the other cyclohexane derivatives which were examined. The material only reacted slightly with bromine and iodine monochloride, but de-hydrohalogenation at room temperature resulted in the elimination of 36.3% of the available fluorine and 19.5% of the available chlorine.

If this compound was not formed by the addition of halogen hydracid to a halo-cyclohexene or -cyclohexadiene intermediate in the reaction between chlorine trifluoride and benzene, then one hydrogen atom must be attached to each carbon atom, and there is only one possible structure for the molecule, namely:-



Exhaustive de-hydrohalogenation should lead to a mixture of isomeric chlorodifluorobenzenes and isomeric trifluorobenzenes.

Chlorobenzene

This compound was only present in very small amount

in the reaction product, and its isolation and characterisation present a big achievement. The purest sample was obtained from distillation "flat" VII although it is apparent from a study of the analytical data shown in TABLE 10 p. 142, and the hydrogenation data in TABLES 11 and 13, that it was also present in "flats" V and VI. The physical constants of the material from flat VII were:- b.pt. 131.0°C/764 mm., n_D^{20} 1.5158; those quoted in the literature for chlorobenzene are:- b.pt. 132°C; n_D^{20} 1.5248. Nitration of 0.5 gms. of the suspected chlorobenzene yielded a sample of 2:4-dinitrochlorobenzene, which appeared from its m.pt. to be mostly of the β variety. This was then reacted with aniline to produce 2:4-dinitrodiphenylamine, the m.pt. of which agreed exactly with that quoted in the literature.

Chlorofluorobenzenes

Distillation "flat" VIII was very complex material, and, besides trichlorononafluorocyclohexanes ("peak" 1), a sample was isolated from "peak" 4 which analysed exactly to chlorofluorobenzene. The physical constants of the material, however, did not agree with any of those quoted for o-, m-, or p-chlorofluorobenzene (see list

below), and it was decided that it was most probably a mixture of m- and p-isomers.

Material from reaction product :-b.pt. 129.7,

n_D^{20} 1.4920.

o-chlorofluorobenzene :-b.pt. 137.6°C, n_D^{20} 1.4968.

m-chlorofluorobenzene :-b.pt. 128.0°C, n_D^{27} 1.4910.

p-chlorofluorobenzene :-b.pt. 130.0°C, n_D^{20} 1.4965.

The results of a catalytic hydrogenation were almost identical with those obtained when an authentic specimen of p-chlorofluorobenzene was hydrogenated under the same conditions, so it was decided to identify the presence of p-chlorofluorobenzene by hydrolysing the sample with sodium methylate and preparing suitable derivatives of the resulting p-chlorophenol. This was first carried out on an authentic specimen of p-chlorofluorobenzene, a good yield of p-chlorophenol was obtained and a benzoyl and dibromo derivative prepared which had physical properties corresponding to those reported in the literature. When the same procedure was carried through using the suspected m- and p-chlorofluorobenzene mixture, however, the product showed the properties of a mixture which contained some phenolic constituent. No derivatives could be isolated,

although qualitative phenol tests were positive. Infra-red analysis was resorted to, and the spectrogram obtained showed that the material from "flat" VIII contained o-, m- and p-chlorofluorobenzenes. It is apparent now that the mixture of isomers should have been distilled through a concentric-tube column when at least a separation of the o- from the m- and p-chlorofluorobenzenes would have been achieved in the absence of azeotrope formation.

No attempt was made during the preparation of the chlorofluorinated mixture to trap any very low boiling breakdown products which might have been formed. This would have been a difficult proposition because almost thirty litres of nitrogen were passing through the apparatus per hour. In future runs, however, if an efficient potassium fluoride trap, followed by a train of glass traps cooled in liquid nitrogen, is attached to the outlet of the last brass trap on the chlorofluorination apparatus, a large proportion of any low boiling products should be trapped. Distillation of the material through a low-temperature column can then be carried out.

The gas chromatogram for the material (b.pt. 58.0-79.0°C.) which distilled prior to "flat" I showed that benzene,

dichlorodecafluorocyclohexanes and several other components were present. A large-scale separation was attempted, and the material split into three fractions (see DIAGRAM 25, p.137). The first consisted of 0.5 gms. of highly volatile material with refractive index 1.3170 (n_D^{20}). A halogen analysis was not obtained because the bomb containing the only available sample "blew". The second fraction contained the two dichlorodecafluorocyclohexane "peaks" shown by distillation "flat" I. It analysed to a Cl:F (atom) ratio of 1:8, and had a refractive index of 1.3305 (n_D^{20}). The third fraction was benzene.

The distillation curve for the reaction product from Chlorofluorination Run 1 indicated that, unless involved in the azeotropes "flat" I or "flat" II, fluorobenzene was not present (see CHAPTER IX). Analytical gas chromatograms showed no sign of a fluorobenzene peak for either distillation "flat" I or II. If it was present in very small amount, however, this would be expected from a consideration of the shape of the chromatogram obtained for a benzene-fluorobenzene mixture with a "dinonyl" phthalate-kieselguhr column packing. Thus any fluorobenzene would have been condensed into the benzene traps during the large-scale separations, so the material from these was taken and investigated by the nitration method described by FEAR AND THROWER (J. Appl. Chem., 1955, 5, 353).

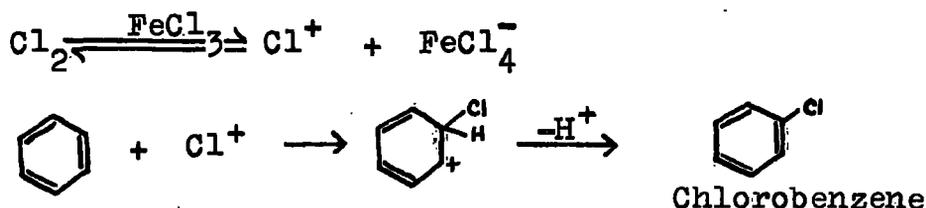
Any fluorobenzene present would have been converted to 2:4-dinitrophenol via 2:4-dinitrofluorobenzene, but no phenolic material was isolated or even recognised in the products from the reactions.

It is obvious that a tremendous amount of work remains to be done before the reaction product from Run 1 is fully solved. In future, however, workers need not carry out such a tedious distillation prior to the gas-chromatographic separations but use a distillation column which is more productive, though less efficient, than the concentric-tube type to split the product up into appropriate boiling ranges only. The higher boiling fractions will need the development of suitable high-temperature packings for the gas-chromatographic separations, and since "dinonyl" phthalate is liable to cause contamination of fractions through its decomposition, the low-temperature separations recorded in this thesis might be carried out with different packings to advantage. Once completed, however, the solution of Run No. 2, which, from a study of the preliminary distillation graphs, appears to be less complex, should be a relatively simple matter.

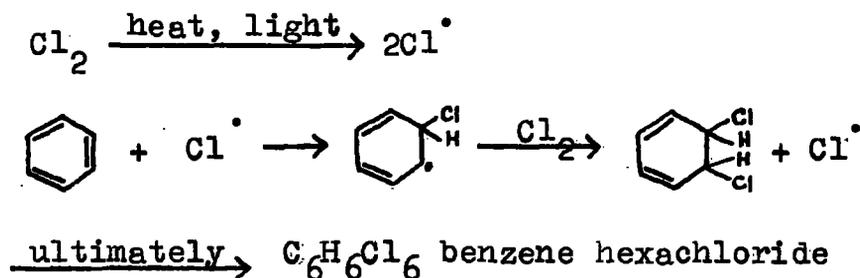
THEORETICAL CONSIDERATIONS

Depending on the conditions employed any halogen may react with an organic compound to form either substitution or addition products. Substitution occurs via an ionic, carrier-catalysed mechanism, while addition is due to light- and heat- catalysed formations of atomic halogen. Considering then the direct chlorination of benzene, the following two reactions can occur:-

1) Substitution via an ionic mechanism



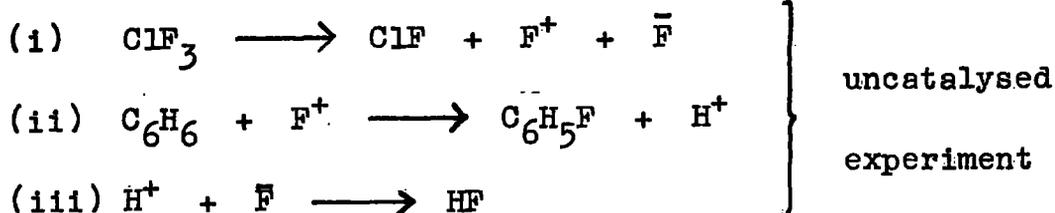
2) Addition via an atomic mechanism

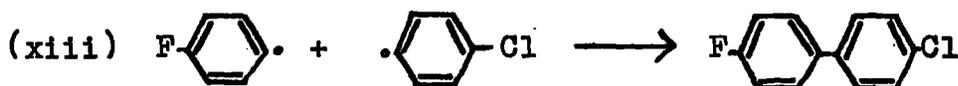
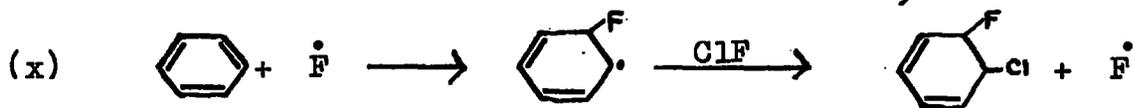
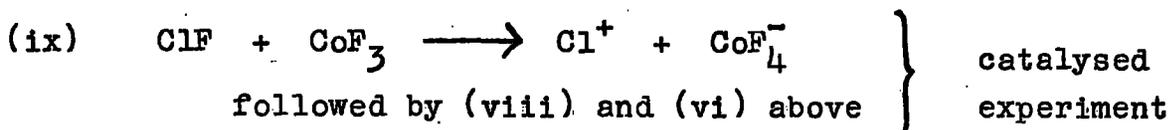
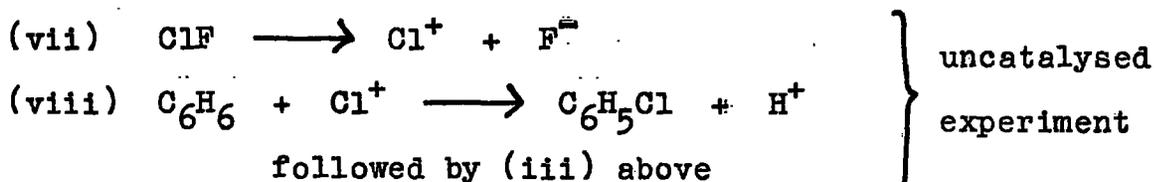
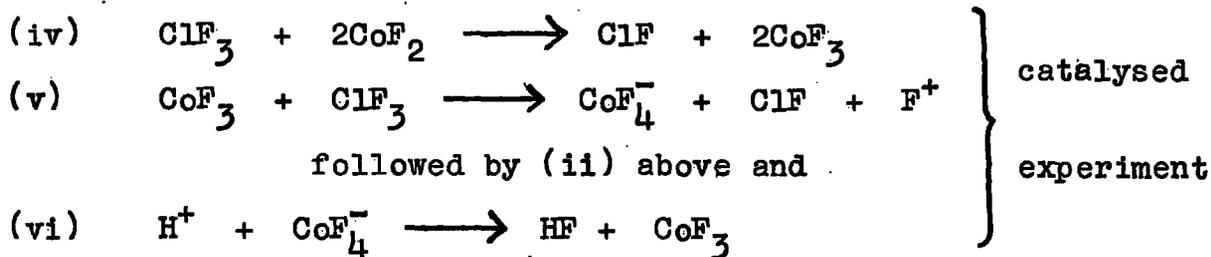


Direct fluorination of benzene, however, only occurs via atomic and free radical processes because fluorine is the most electronegative element and it is extremely

difficult to remove an electron from a fluorine atom to form a positive ion F^+ . The products of the reaction are CF_4 , C_2F_6 , C_3F_8 , C_4F_{10} , C_5F_{10} , C_6F_{12} , C_6HF_{11} and $C_{12}F_{22}$ (FUKUHARA AND BIGELOW, J.A.C.S., 1941, 63, 2792). These are formed through addition of fluorine to the double bonds followed by substitution, fragmentation and polymerisation. The initial step-wise addition reactions to an aromatic nucleus were demonstrated by BIGELOW, THOMPSON AND TARRANT (Ind. Eng. Chem., 1947; 39, 360) through a study of the direct fluorination of 4-chloro-1,3-bis-(trifluoromethyl)-benzene, which has a highly deactivated nucleus. The progressive products isolated were $C_6H_3ClF_2(CF_3)_2$, $C_6H_3ClF_4(CF_3)_2$ and $C_6H_3ClF_6(CF_3)_2$. Further fluorination resulted in the substitution of the chlorine then the hydrogen by fluorine, and, finally, fragmentation and polymerisation.

The reaction between chlorine trifluoride and benzene in the liquid phase required a mechanism which explained the formation of chlorobenzene and fluorobenzene, together with small amounts of addition products and diphenyls. The following reaction mechanisms were postulated by ELLIS (Ph.D. thesis, Durham, 1952; see also ELLIS AND MUSGRAVE loc. cit.):—





Although the formation of an F^+ ion was postulated originally to account for the formation of fluorobenzene from benzene, it later became essential to explain directive influences in the cobaltous fluoride - catalysed, liquid-phase reactions between chlorine trifluoride and benzene homologues and halo-benzenes. In the catalysed experiments this formation seems feasible, but in the uncatalysed benzene experiment is more doubtful, and a mechanism of the following type would be more acceptable.

- a) $\text{ClF}_3 \longrightarrow \text{ClF} + \text{F}^\bullet + \text{F}^\bullet$
- b) $\text{C}_6\text{H}_6 + \text{F}^\bullet \longrightarrow \text{C}_6\text{H}_5^\bullet + \text{HF}$
- c) $\text{C}_6\text{H}_5^\bullet + \text{ClF} \longrightarrow \text{C}_6\text{H}_5\text{Cl} + \text{F}^\bullet$ or
 $\text{C}_6\text{H}_5\text{F} + \text{Cl}^\bullet$
- d) $\text{C}_6\text{H}_5^\bullet + \text{F}^\bullet \longrightarrow \text{C}_6\text{H}_5\text{F}$
- e) $\text{C}_6\text{H}_5^\bullet + \text{Cl}^\bullet \longrightarrow \text{C}_6\text{H}_5\text{Cl}$
- f) $\text{C}_6\text{H}_5^\bullet + \text{C}_6\text{H}_5^\bullet \longrightarrow (\text{C}_6\text{H}_5)_2$
- g) Reactions x, xi, xii and xiii.

It can, of course, be argued that even if a catalyst was not added as such to the reaction mixture it would be provided by the steel reaction vessel containing the mixture. The proof obtained by Ellis for the production of positional isomers in the halogenations of benzene derivatives seems good, but it would be interesting to subject, say, his chlorofluorobenzene fraction to infra-red analysis.

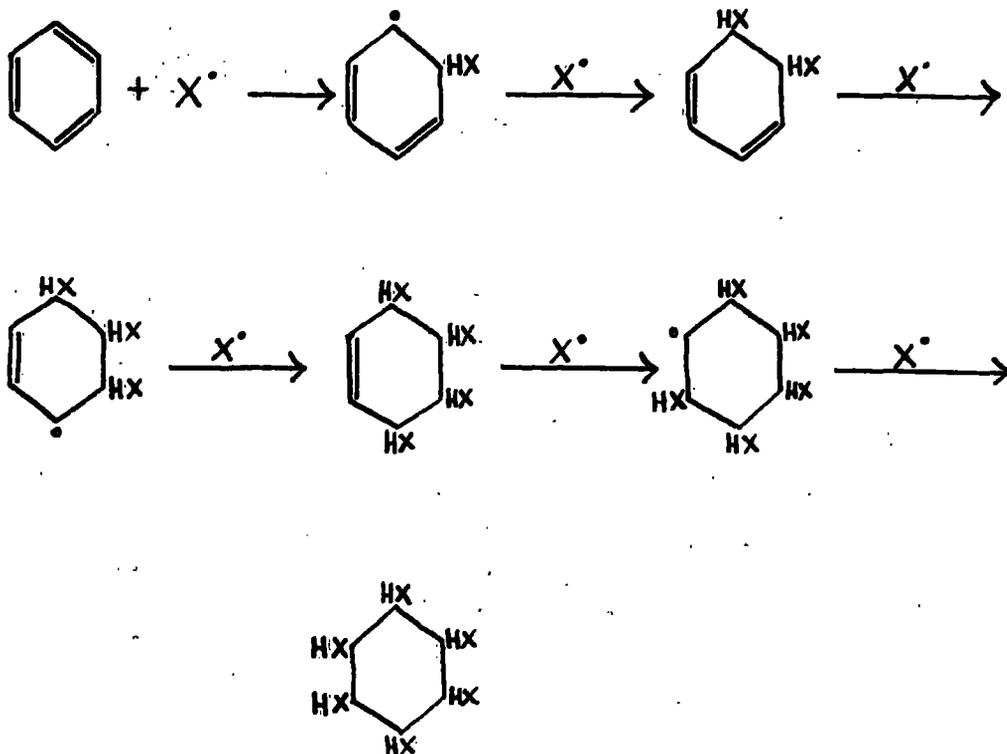
The vapour-phase reaction between chlorine trifluoride and benzene must proceed entirely via atomic and free radical processes. Only in this way can the complexity of the reaction product be explained. Two initial dissociations need to be postulated, namely:-

1. $\text{ClF}_3 \longrightarrow \text{ClF} + \text{F}^\bullet + \text{F}^\bullet$
2. $\text{ClF} \longrightarrow \text{Cl}^\bullet + \text{F}^\bullet$

By analogy with direct chlorinations and fluorinations of

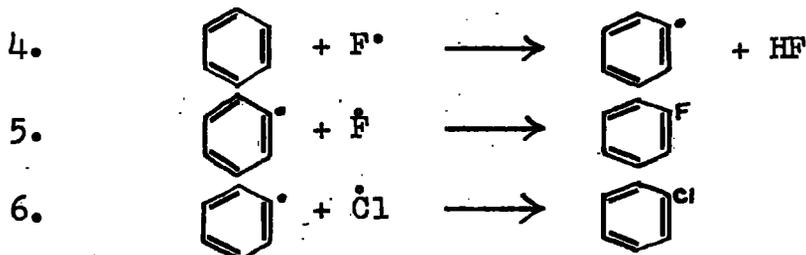
benzene in the vapour-phase, the entities thus produced will add on to the double bonds to produce hydrochloro-fluorocyclohexanes. Once the initial addition (see below) has taken place with the formation of dienes, further addition of halogen must be extremely rapid and occur with greater ease than the preliminary addition to an aromatic double bond. This would explain why, as yet, no unsaturated products or polymeric materials have been isolated in any amount from the reaction product. Writing X for halogen (Cl or F), the processes involved are:-

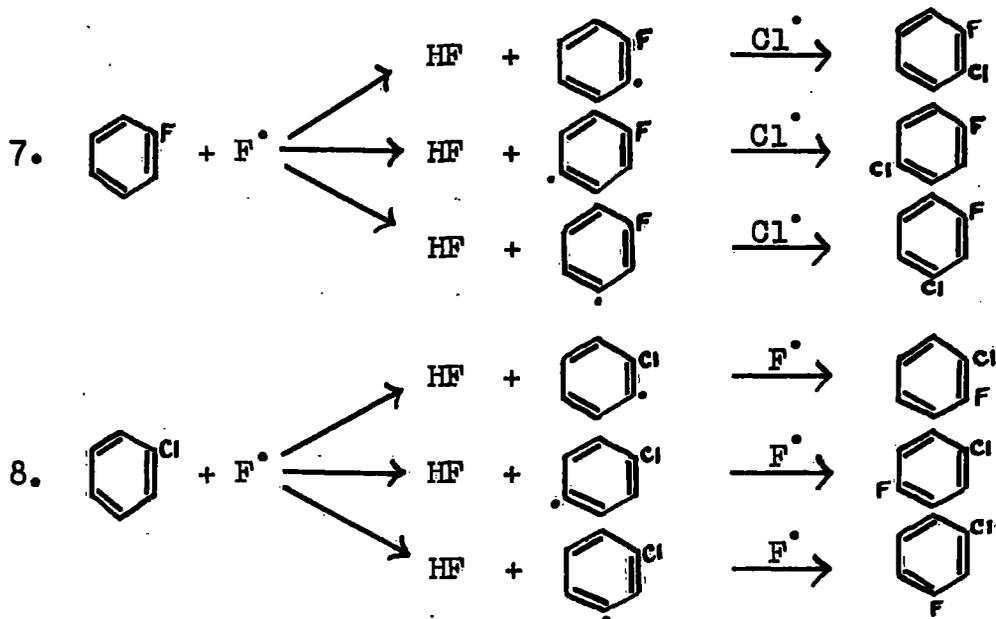
3.



One example of the type of product produced finally by stage 3 has so far been isolated, namely, monochloropentafluorocyclohexane. Further substitution of hydrogen by chlorine and fluorine, and of chlorine by fluorine, can then occur in a variety of ways such that any one molecular formula is capable of being represented in the reaction mixture by numerous isomers, both structural and stereo. It would not be expected from a consideration of the halogenation ratio employed in Run 1 that much total substitution of hydrogen would occur. This is borne out by the fact that the fully halogenated products $C_6Cl_2F_{10}$ and $C_6Cl_3F_9$ are present only in small proportion, and the analytical figures for azeotropes not separated indicate that no other fully halogenated compounds are present.

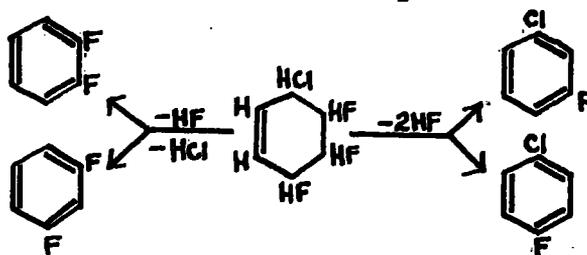
The explanation of the formation of chlorobenzene and o-, m- and p- Chlorofluorobenzenes presents difficulties, and a mechanism of a type suggested previously (a-f) must be postulated.





Reactions of this type would be expected to give rise to other chlorofluorobenzenes together with more highly chlorinated or fluorinated benzenes. However, this mechanism must compete with the main mechanism (3), which can also employ halo-benzenes as starting material, so that poor yields of the simpler aromatic compounds only would be expected. This agrees with the fact that up to the present time only chlorobenzene and chlorofluorobenzenes have been isolated from the reaction product, and these in small amounts. Considering reaction stages 5-8 it is obvious that these could lead to the formation of diphenyls also (see reaction stages xi, xii, xiii and f). If these are present to any extent in the reaction product they will be found in the higher boiling fractions which have not yet been fully separated.

A further source of aromatic compounds, again in small amounts, would be any very easily de-hydrohalogenated hexahydrochlorofluoro-cyclohexanes, -cyclohexenes and -cyclohexadienes present in the crude reaction product. The de-hydrohalogenations would have occurred when the crude material was either washed with water and dilute sodium carbonate solution to free it from hydrogen fluoride, or when it was distilled. For example:-



Since only traces of unsaturated compounds, if any, have been detected in the reaction product, and no fluorobenzenes have been isolated, it is not very likely that the chlorobenzene or chlorofluorobenzenes were produced by such reactions.

Summarising briefly, the main reaction between chlorine trifluoride and benzene in the vapour phase is one of step-wise addition of both chlorine and fluorine to the double bonds. This is followed by a variety of substitution reactions which give rise to a complex mixture of chlorofluorocyclohexanes. Subsidiary primary substitutions also occur to a small extent and produce aromatic halogen compounds.

EXPERIMENTAL SECTION

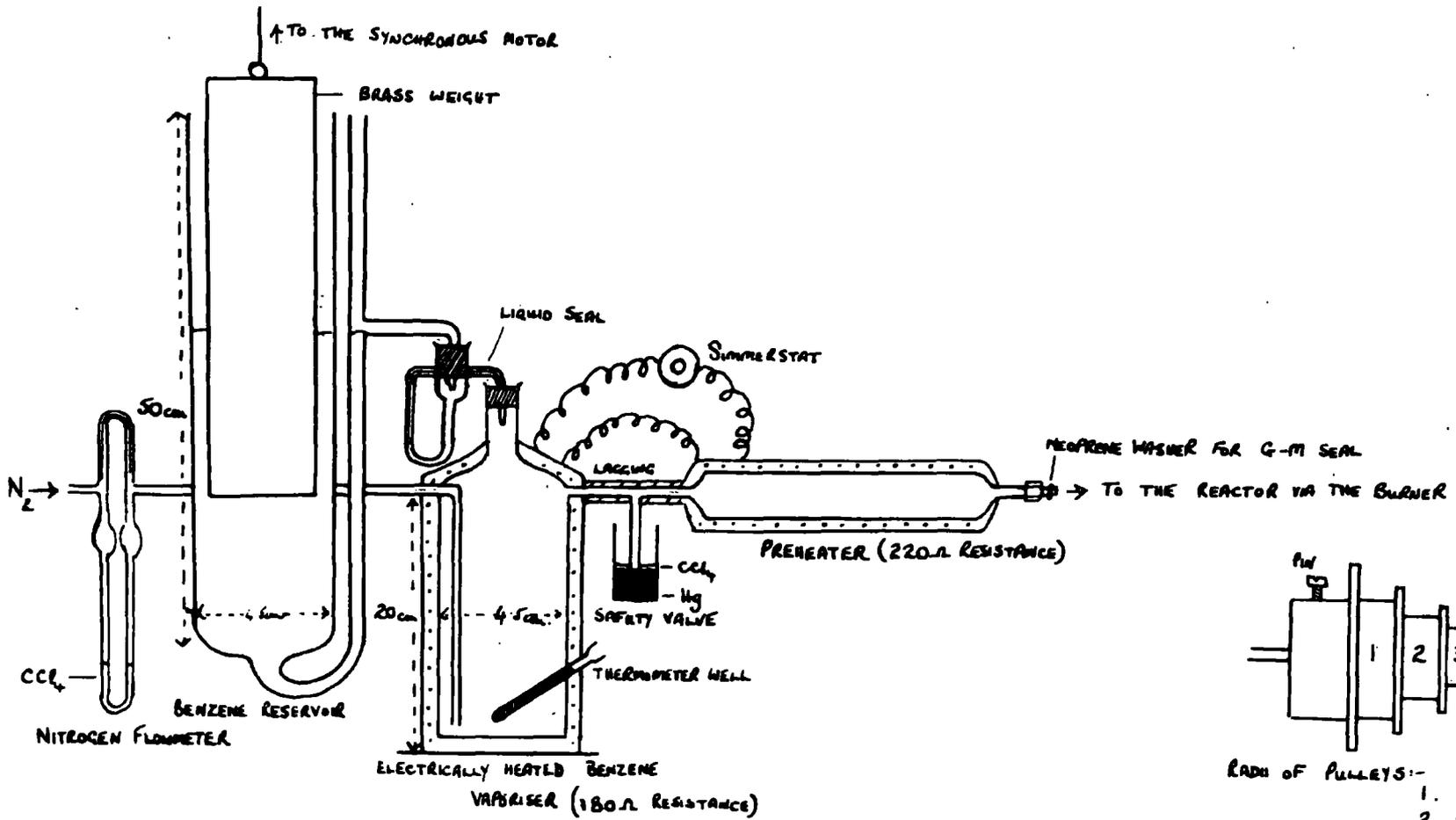
Chapter III

The Chlorofluorination of Benzene in the
Vapour Phase

The benzene and the chlorine trifluoride, suitably diluted with nitrogen, were allowed to react in a heated wrought-iron tube packed with copper clippings, and the products condensed out of the gas stream in cooled brass traps.

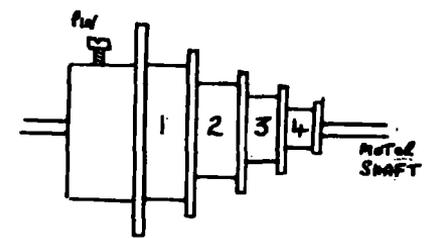
Apparatus

The benzene input was regulated and kept constant by means of the apparatus shown in DIAGRAM 2A, which worked on the same principle as the hydrocarbon feed described by BARBOUR et al (J. Appl. Chem., 1952, 2, 127). Pure, dry, benzene contained in a "U" shaped vessel was displaced into a liquid seal by a metal cylinder which was lowered into one arm of the "U" tube at a constant rate by means of a synchronous electric motor, the shaft of which rotated at the rate of 0.4 rev./hr.. The benzene discharged from the liquid seal into an electrically heated vaporiser kept at 150°C., and was carried into the reactor, via a pre-heater at 250°C., on a metered stream of nitrogen. Almost any required amount of benzene between the limits 28 gms./hr. to 4 gms./hr. could be introduced by using metal cylinders of different diameters and a bakelite pulley system (DIAGRAM 2B).



A

ELECTRICALLY HEATED BENZENE VAPORISER (180 Ω RESISTANCE)



RADI OF PULLEYS:-

- 1. 0.9 cm
- 2. 0.6 cm
- 3. 0.45 cm.
- 4. 0.25 cm.

B.

DIAGRAM 2

A) BENZENE VAPORISER

B) PULLEY SYSTEM.

Chlorine trifluoride was led into the reactor from a cylinder via a flowmeter (DIAGRAM 3), which was calibrated as accurately as possible by weighing the cylinder before and after metering the gas into the apparatus for known times.

In order to moderate the reaction between the benzene and the chlorine trifluoride, and so ensure smooth running coupled with good yields of product, they were introduced into the reactor by means of a concentric-tube "cool flame" burner constructed out of mild steel (DIAGRAM 4 ; PLATE 1). This type of burner, described by TYCZKOWSKI AND BIGELOW (J.A.C.S., 1953, 75, 3523), is an alternative to a baffle plate in a reactor and was shown by them, when used in a direct fluorination, to produce a mild reaction in which both cleavage and polymerisation were reduced.

The burner was packed with copper wool to keep the annular spaces clear of copper clippings, and fastened to the reactor by means of six bolts and a lead to knife-edge seal. It was extended somewhat by placing a $4\frac{1}{2}$ " wide strip of strong copper foil in the outer annular space to ensure that the reactants were well inside the copper packing before meeting. A small perforated table

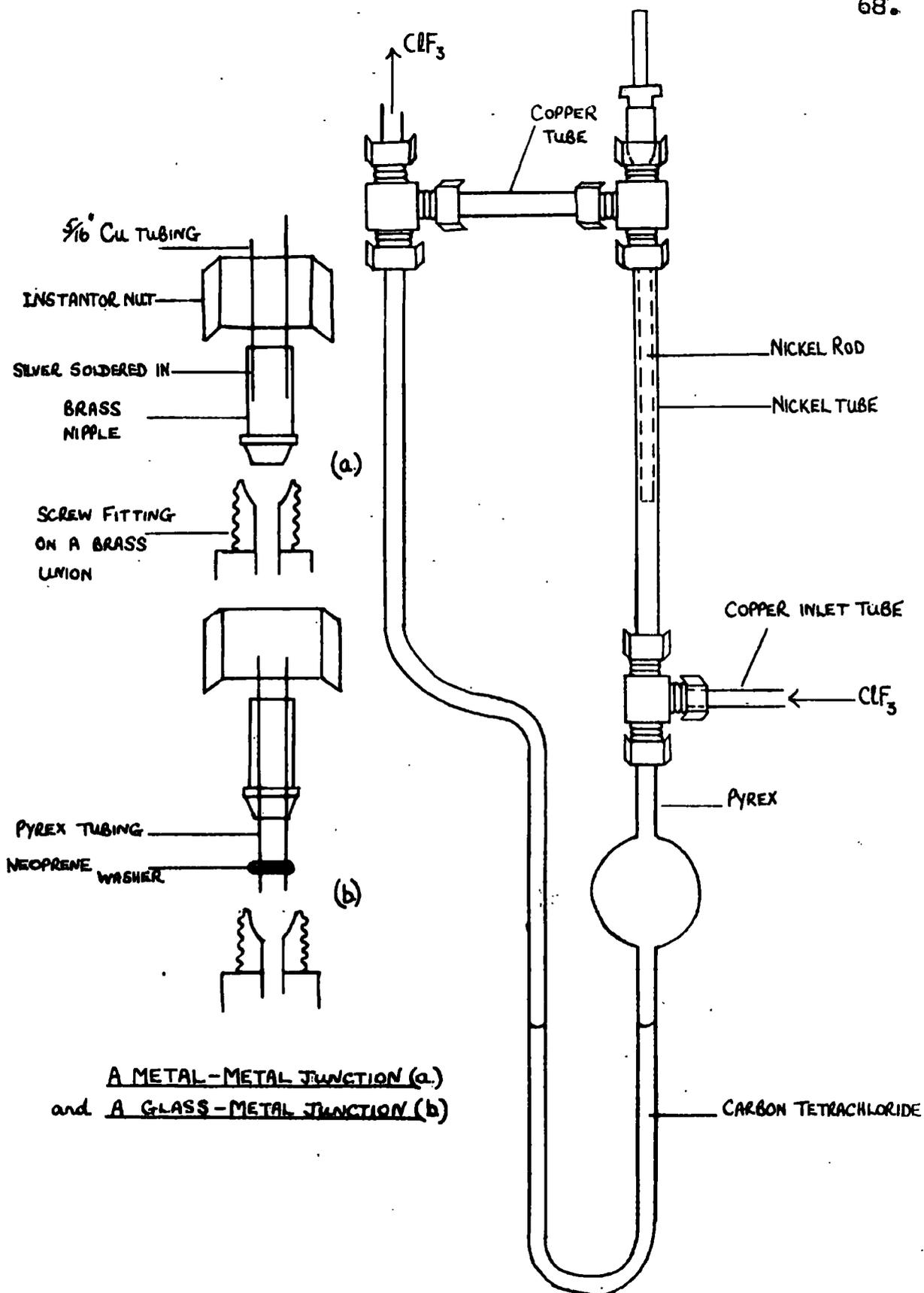


DIAGRAM 3 A CHLORINE TRIFLUORIDE FLOWMETER.

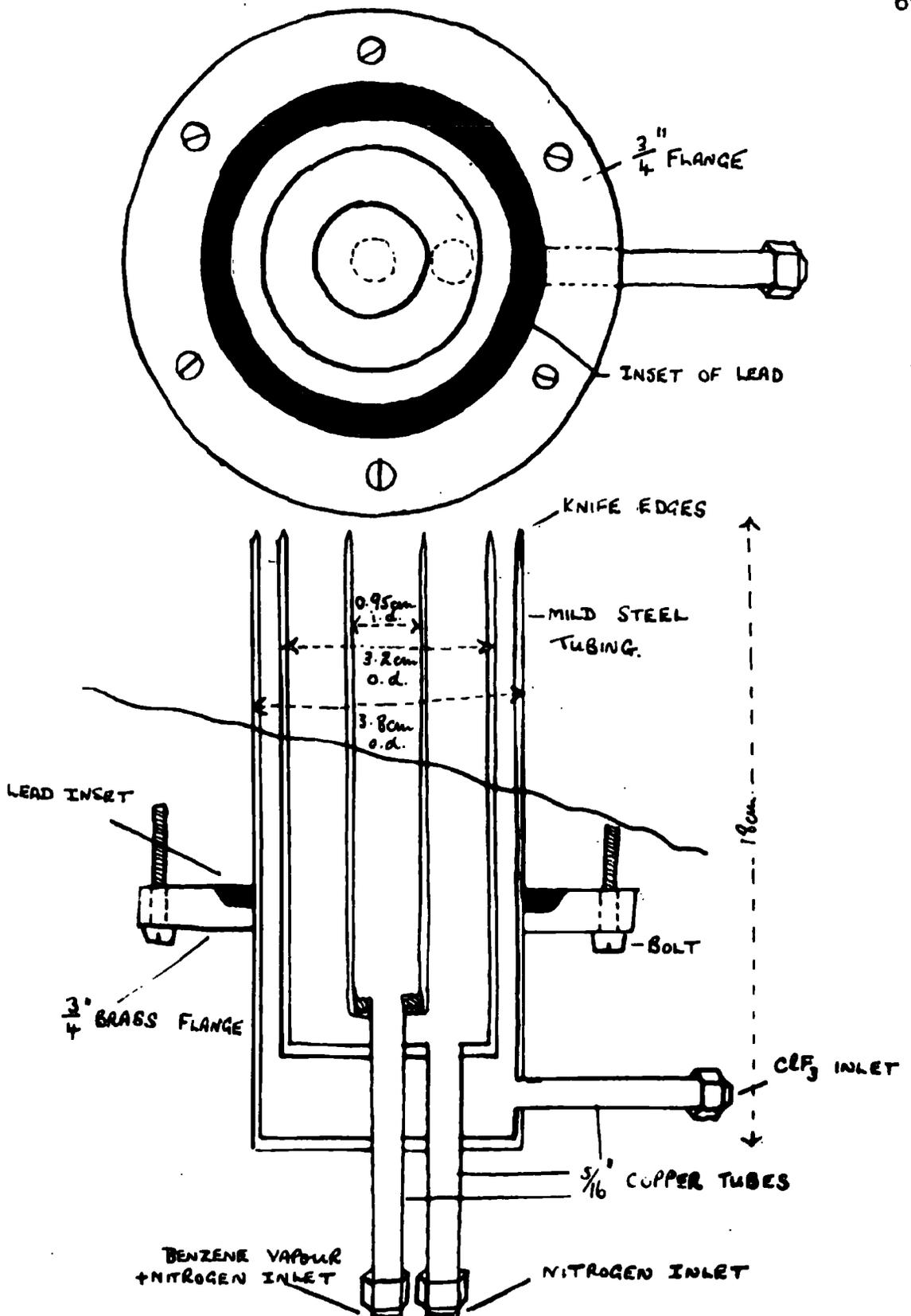




PLATE 1 The Concentric-tube Burner

(DIAGRAM 5) supported the $3\frac{1}{2}$ kilograms of copper clippings with which the vertical reactor was packed, thus preventing them from blocking up the outlet tube. The reactor was heated by means of six 60Ω sectional heaters of the Massingham type, three pairs being connected in parallel and run off the 250 v. Mains via an 8 amp. "Variac" transformer. The reactor was provided with three evenly spaced thermometer pockets (DIAGRAM 5).

The reaction products were condensed in a series of brass traps. Trap A (DIAGRAM 6) was water-cooled, and traps B and C (DIAGRAMS 7 and 6) were cooled with ethanol-"Drikold" mixtures. The inlet tube of trap B was maintained at 50°C . by a small electrical heater to prevent products solidifying there and causing a blockage.

DIAGRAM 8 shows the complete set up of the apparatus, and PLATE 2 some of the component parts.

Operation

When the heated parts of the apparatus, namely vaporiser, pre-heater, and reactor, had attained the required temperatures, the whole apparatus was flushed with nitrogen. Then, before any benzene was admitted, chlorine trifluoride was passed into the reactor to remove organic material and form a halide surface on the metal.

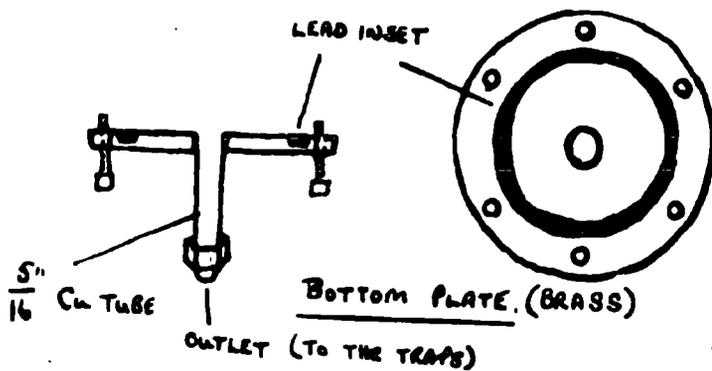
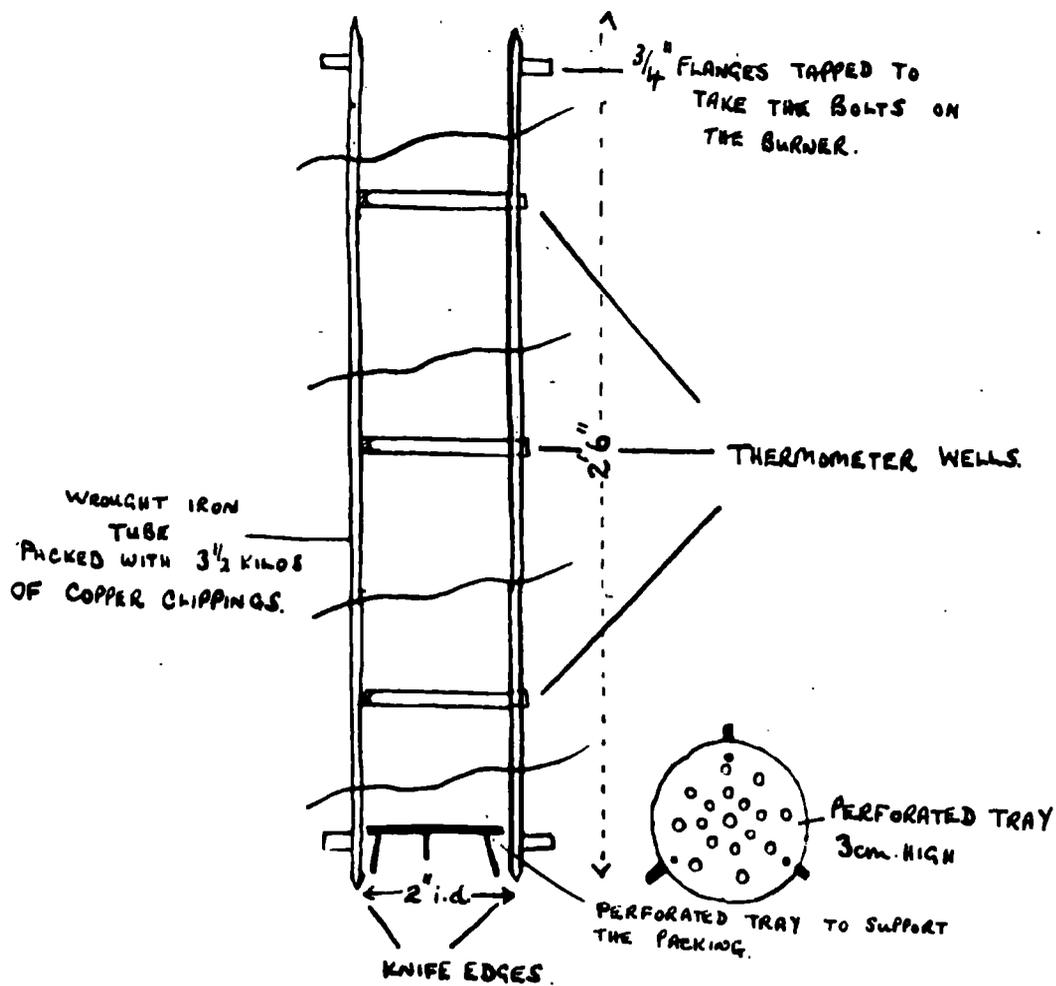
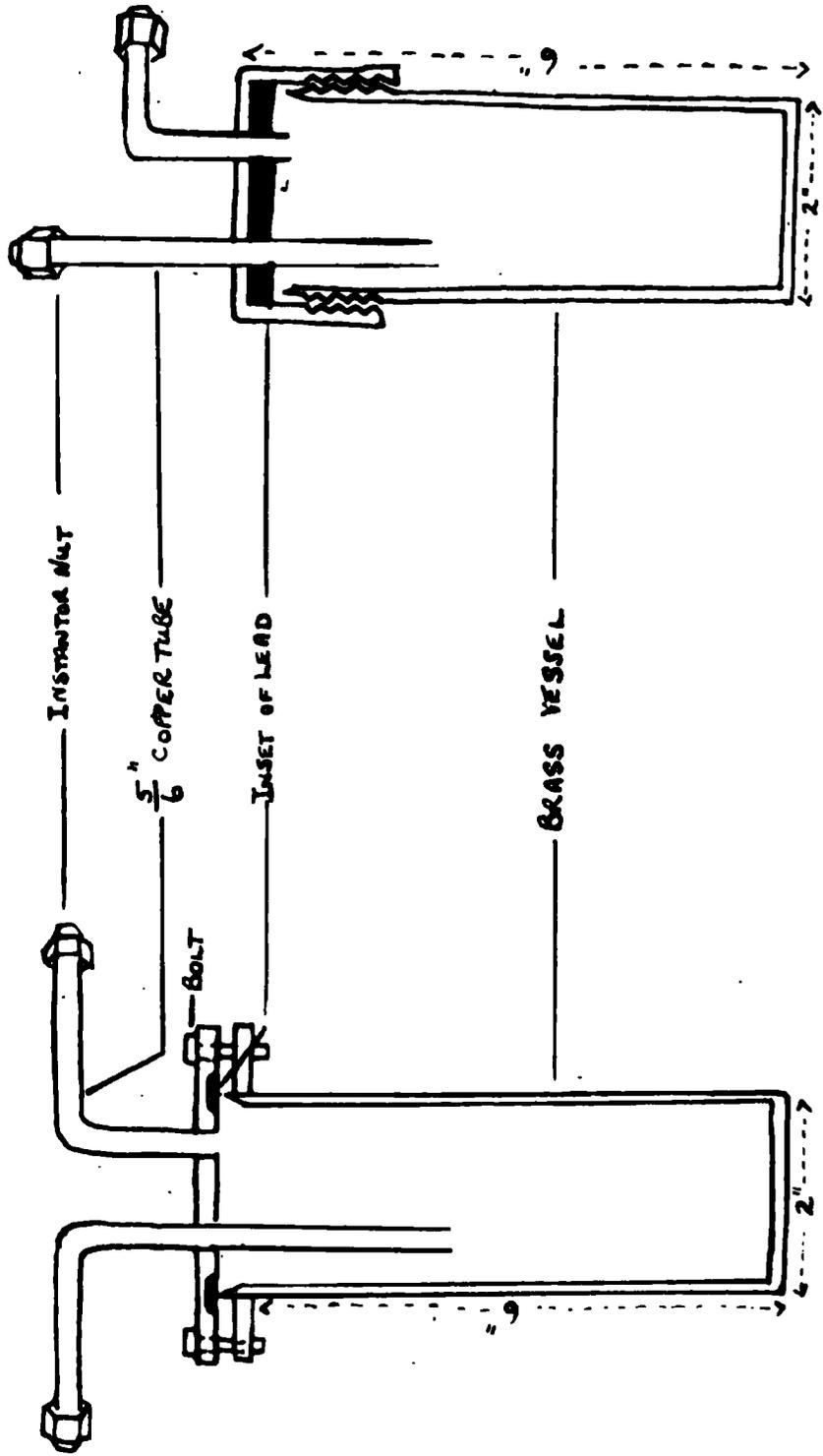


DIAGRAM 5

THE WROUGHT IRON TUBE REACTOR AND ACCESSORIES.

DIAGRAM 6



TRAP A - WATER COOLED.

TRAPS C AND D

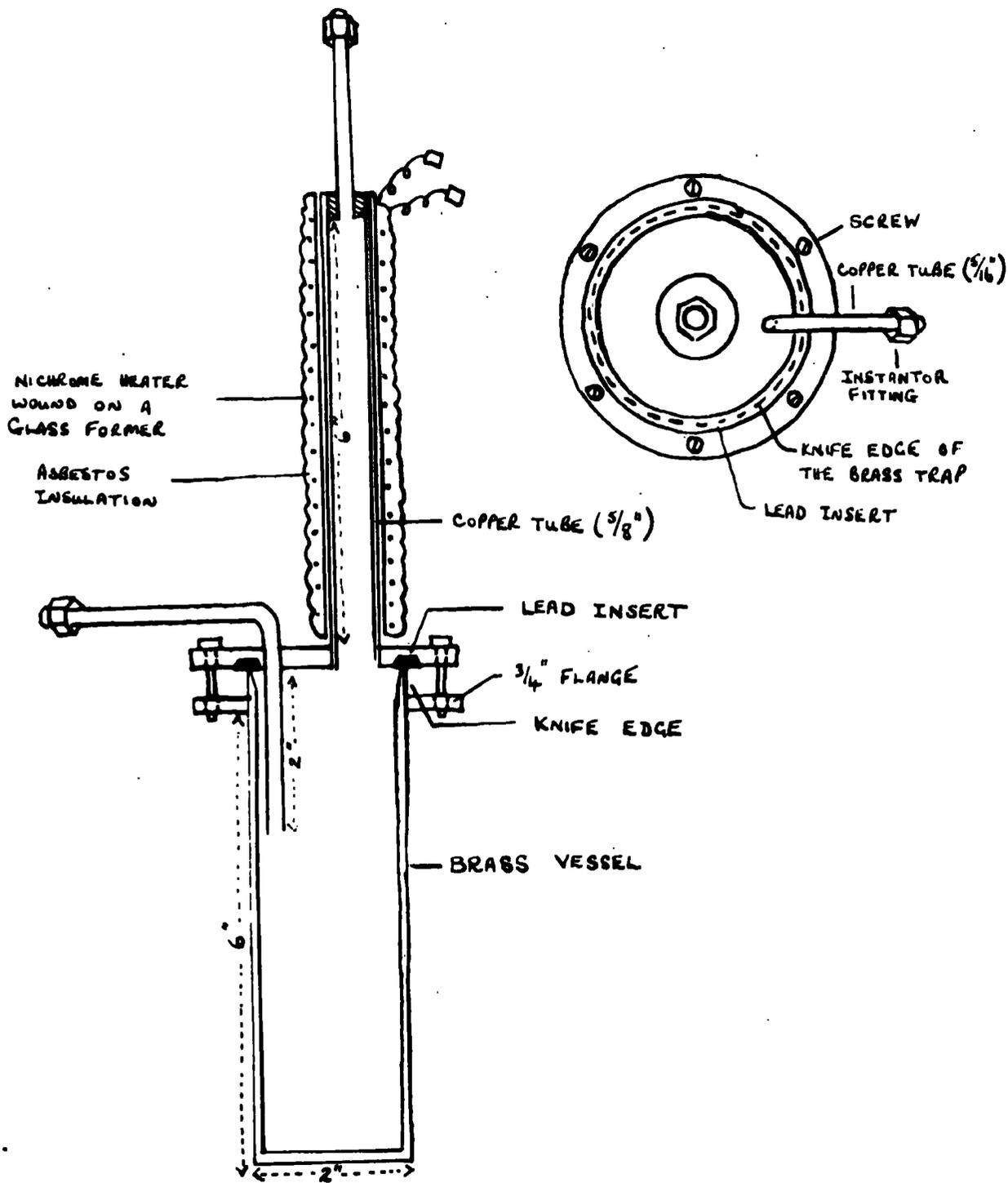


DIAGRAM 7

PLAN AND ELEVATION OF TRAP B

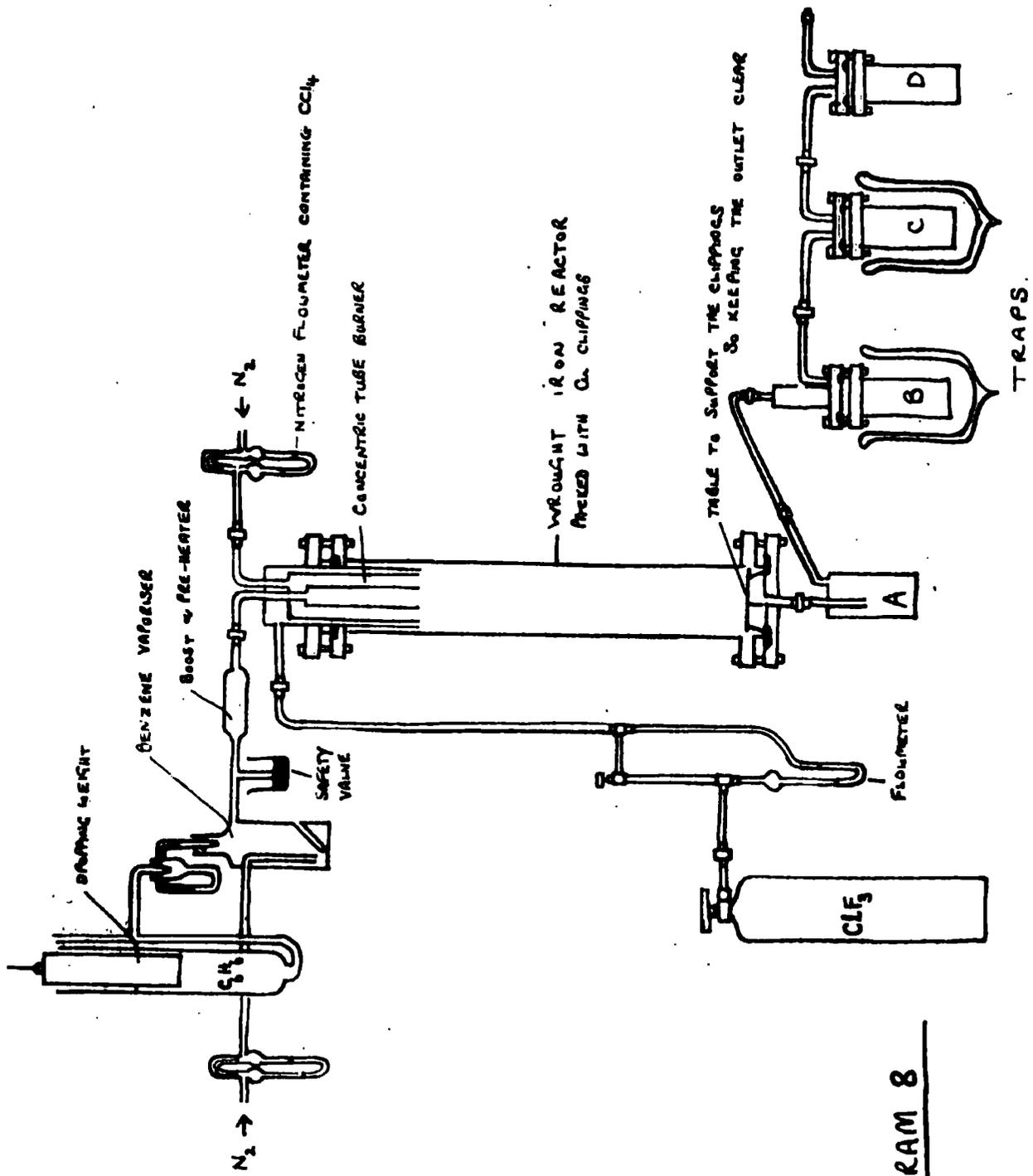


DIAGRAM 8

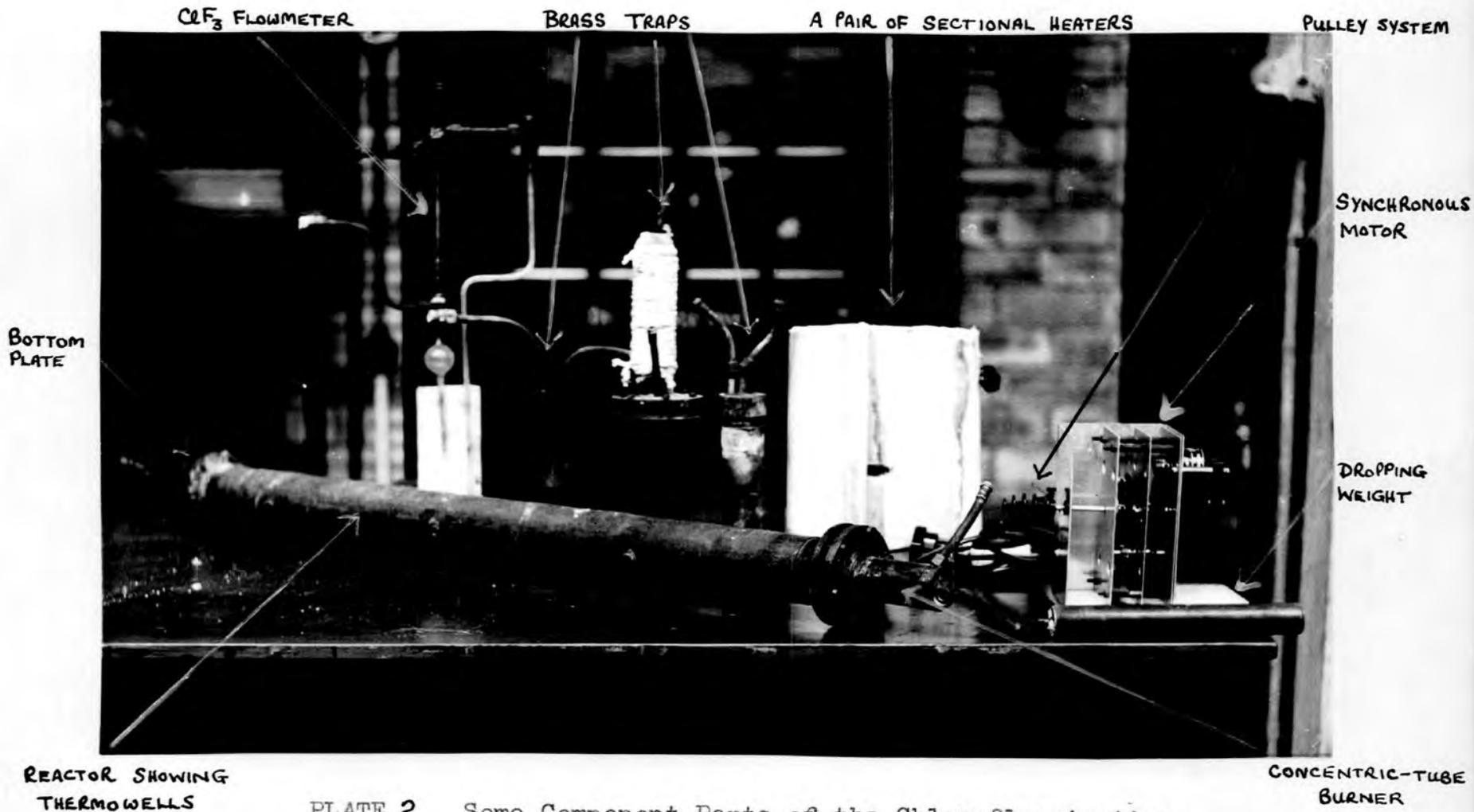


PLATE 2 Some Component Parts of the Chlorofluorination
Apparatus

The apparatus was then flushed again with nitrogen, after which the reactants were admitted essentially at the same time. After the first hour of each run the chlorine trifluoride feed was turned off and the cylinder weighed to check on the input rate. The reaction between the benzene and the chlorine trifluoride was highly exothermic, so the power supply to the reactor heaters was reduced as the run proceeded to keep the temperature reading of the top thermometer at a pre-determined value.

The apparatus ran quite smoothly, stoppages only occurring when leaks developed at the glass to metal seals on the chlorine trifluoride flowmeter, or when slight explosions took place inside the reactor so causing a gas block in the liquid seal on the benzene input. However, after running for about 70 hours pressure began to build up in the reactor due to caking of the copper clippings, so at this stage it was taken down and re-packed. During this operation it could be seen that the reaction flame was only about one foot long so that a considerable proportion of the packing was still in good condition and was used again.

The products which collected in the cold traps were

washed with distilled water, neutralized by washing with sodium carbonate solution, washed again with distilled water then dried over anhydrous magnesium sulphate. In the majority of runs most of the products condensed in water-cooled trap A, but this was not always the rule and traps B and C proved quite necessary. Large quantities of hydrogen fluoride and hydrogen chloride were formed during the reaction, and these, except for some of the former which remained in the cold traps and was subsequently neutralized, passed out of the train of traps with the nitrogen and down the vents of the fume cupboard in which the apparatus was assembled. Only traces of chlorine trifluoride were detected in the effluent gases, but as a precaution traps B and C were allowed to warm up overnight before they were emptied.

A phenomenon which could not be accounted for occurred when the contents of trap A were poured out. They appeared at first as a black liquid, but the colour gradually changed through shades of green to a light amber. This change took place over a period of several minutes.

TABLE 3 gives details of trial runs which were carried out to determine which conditions gave optimum

yields. It appeared that the nitrogen dilution flow-rate did not affect yields to any great extent, so it was made as large as was convenient in order to obtain a long reaction flame. Conditions 9 and 12 were chosen for building up large quantities of material for investigation. Details of the runs carried out are given in TABLES 4 and 5 .

TABLE 3

TRIAL CHLOROFLUORINATION RUNS

RUN NO.	C ₆ H ₆ FEED Gm/hr	ClF ₃ FEED Gm/hr	ClF ₃ C ₆ H ₆ RATIO (wt/wt)		N ₂ (1) (2)		TEMPS. ON REACTOR (°C.)	Gms. ClF ₃ FED IN	Amount PRODUCT (Gms.)	DENSITY OF PRODUCT (Gm/ml)	AMOUNT OF PRODUCT (mls)	AMOUNT C ₆ H ₆ FED IN (mls)
			C ₆ H ₆	ClF ₃	N ₂	N ₂						
1	10.7	24.75	2.31	3.8	8.5	220 215 170	78.3	31.2	1.3	30	24	
2	10.7	25.5	2.33	3.7	6.4	212 216 174	217.3	84	1.4	60	78	
3	10.7	24.0	2.25	3	6	170 165 108	72	17.28	1.44	12	31	
4	10.7	21.4	2.0	3.8	6	325 350 240	107	50.4	1.26	40	60	
5	10.7	20.33	1.9	3.8	6	255 250 180	81.3	34.16	1.22	28	48	
6	10.7	40.13	3.75	3.8	12	280 250 160	120.5	46.8	1.56	30	36	
7	10.7	26	2.42	4	12	248 245 168	104	58	1.35	43	48	
8	10.7	25.3	2.4	4	18	240 240 164	80	41.6	1.3	32	36	
9	19.35	44	2.28	4	24	275 250 168	103	59.5	1.29	46	51	
10	8.53	59.7	7	4	24	260 230 200	254	137.3	1.76	78	42	
11	8.53	59	7	4	24	190 160 140	177	54	1.7	32	29.1	
12	8.53	60	7	4	24	270 240 210	166	102.6	1.8	57	26.4	
13	8.53	60.3	7	4	24	360 310 280	150.8	50.4	1.8	28	24.3	

N₂(1) = Rate of flow of nitrogen through the benzene vaporiser in litres per hour.

N₂(2) = Rate of flow of nitrogen into centre annular space of the burner in litres per hour.

TABLE 4

CHLOROFLUORINATION RUN NUMBER ONE

	C ₆ H ₆ FEED gm/hr.	ClF ₃ FEED gm/hr.	ClF ₃ C ₆ H ₆ RATIO (wt./wt.)	N ₂ N ₂ (1)(2)	TEMPS. ON REACTOR (°C.)	LENGTH OF RUN	Gms. C ₆ H ₆ FED IN	Gms. ClF ₃ FED IN	AMOUNT PRODUCT (gms.)	DENSITY OF PRODUCT (gm/ml)	AMOUNT PRODUCT (mls)	AMOUNT C ₆ H ₆ FED IN (mls)
(1)	19.35	43	2.28	4 24	270 220	5 hrs.	96.75	215	129.2	1.36	95	110
(2)	19.35	43	2.28	4 24	260 210	4hrs. 38mins.	87	198	105	1.5	70	99
(3)	19.35	42	2.18	4 24	260 210	5hrs.	96.75	210	144.8	1.4	102	110
(4)	19.35	46	2.37	4 24	270 215	4hrs.	77.4	184	113.6	1.42	80	88
(5)	19.35	42.7	2.21	4 24	260 210	6hrs.	116.1	256.2	165.6	1.38	120	132
(6)	19.35	43	2.28	4 24	260 210	6hrs. 10mins	126.8	286	187.7	1.38	136	147

TABLE 5

SUMMARY OF CHLOROFLUORINATION RUN NUMBER TWO

	C ₆ H ₆ FEED gm/hr	ClF ₃ FEED gm/hr	ClF ₃ C ₆ H ₆ RATIO (wt./wt.)	N ₂ (1)	N ₂ (2)	TEMPS. ON REACTOR (°C.)	LENGTH OF RUN	Gms. C ₆ H ₆ FED IN	Gms. ClF ₃ FED IN	AMOUNT PRODUCT (gms)	DENSITY OF PRODUCT (gm/ml)	AMOUNT PRODUCT (mls)	AMOUNT C ₆ H ₆ FED IN (mls)
(1)	8.53	66	7.75	4	24	260 230 200	9hrs. 10mins.	78.19	600	252	1.8	140	89
(2)	8.53	66	7.75	4	24	260 230 200	9hrs. 25mins.	78.9	613	308.95	1.85	167	90
(3)	8.53	66	7.75	4	24	260 235 200	8hrs. 30mins.	72.51	557	248.4	1.8	138	82.5
(4)	8.53	65	7.68	4	24	260 235 200	8hrs. 20mins.	71.08	542	277.2	1.8	154	80.8
(5)	8.53	66	7.75	4	24	260 235 200	13hrs. 10mins.	112.18	869	376.2	1.8	209	128
(6)	8.53	66.7	7.75	4	24	260 235 200	6hrs. 5mins.	51.18	408	171	1.8	95	58.7
SUMMARY	8.53	66	7.75	4	24	260 235 200	54hrs. 40mins.	464	3,589	1,625.4	1.8	903	429

Chapter IV

The Distillation of the Chlorofluorinated
Products.

"Now I am come to the arts and I shall begin from distillation, an invention of later times, a wonderful thing to be praised beyond the power of men; not that which the vulgar and unskilled men use, for they do but corrupt and destroy what is good; but that which is done by skillful artists Let one that loves learning and to search nature's secrets, enter upon this; for a dull fellow will never attain to this art of distilling."
PORTA, 1589.*

* DELLA PORTA, *Magia Naturalis*, Naples, 1589; quoted by EGLOFF AND LOWRY, *Ind. Eng. Chem.*, 1929, 21, 920.

Two types of column were employed in the attempt to effect a separation of the components of the reaction mixtures by means of batch fractional distillation. Preliminary distillations of both Chlorofluorination Run No. 1, and No. 2, were carried out using two columns packed with glass helices, whose efficiencies were 14 and 20 theoretical plates respectively. By this means the reaction mixtures were split up into fractions of a size and boiling range suitable for more efficient stills, namely 60 plate concentric-tube columns, to handle. Time only allowed, however, for the cuts from Run No. 1 to be further rectified. In each set of distillations two columns were operated side by side in order to (a) reduce the chance of losing all material of a certain composition, and (b) to save time.

Constructions of the Columns

(a). PACKED. (See DIAGRAM 9). These consisted of lengths of pyrex tubing (13 mm. internal diameter) provided with B.14 ground glass joints at each end, and packed with $\frac{1}{8}$ -inch, single-turn, Fenske glass helices. Funnel systems were placed in the tubes immediately above and below the packed sections to enable boil-up rates and reflux ratios to be estimated. The packed sections of the tubes were wound with fine asbestos rope over which were fitted sheathes

of thin copper foil. These, in turn, were covered with layers of asbestos paper, and asbestos rope again wound on. Counter-wound on to this asbestos rope were electrical heaters, of approximately 200 ohms resistance, consisting of lengths of oxynichrome tape (25 ohms/yd.). Rheostats were connected in series with these heaters, and the circuits operated from Simmerstats. Lengths of cellular asbestos pipe lagging were clamped on to the columns to insulate them.

In conjunction with these columns were employed total-condensation - partial take-off still heads of the Whitmore-Lux design (WHITMORE AND LUX, J.A.C.S., 1932, 54, 3451), and three-necked 650 ml. capacity still pots. These were heated by means of "Isomantles", the heat input being controlled through constant voltage regulators of the carbon pile type, and "Variac" transformers in series.

(b). CONCENTRIC-TUBE. (See DIAGRAM 10). These were made according to the instructions given by NARAGON AND LEWIS (Ind. Eng. Chem., Anal. Ed., 1946, 18, 448.) with the following exceptions:-

- (i) Internal expansion sections were introduced to allow for differential expansions between the inner tubes and the vacuum jackets of the columns. Intolerable strains and breakages were thus minimised.

(ii) The vacuum jackets were left with two diametrically-opposite unsilvered strips, in order that the interior portions of the columns could be examined.

Both columns contained eleven inches of precision-bore tubing, the relative sizes of the tubes being:-
inner tube 6.5 mm. O.D., outer tube 8.0 mm. I.D.

The stages in the fabrication of a still head for one of the columns are shown in DIAGRAM II. The glass valve was ground into its seat by means of coarse carborundum, fine carborundum, and finally, "Sira" fine optical abrasive powder, the whole operation taking some eight hours to complete. The sizes of the valve and seating were such that when the valve was lifted by means of a solenoid, 0.25 ml. of distillate collected in the graduated receiver which was attached to the still head. A double surface condenser effected total condensation of vapour.

The columns had compensating heaters (400 ohms resistance) of the Massingham type clamped on to the vacuum jackets, and three-necked 100 ml. capacity still pots, which were heated as described above in (a).

PLATE 3 shows how the concentric-tube columns were mounted. To prevent strains due to the columns:

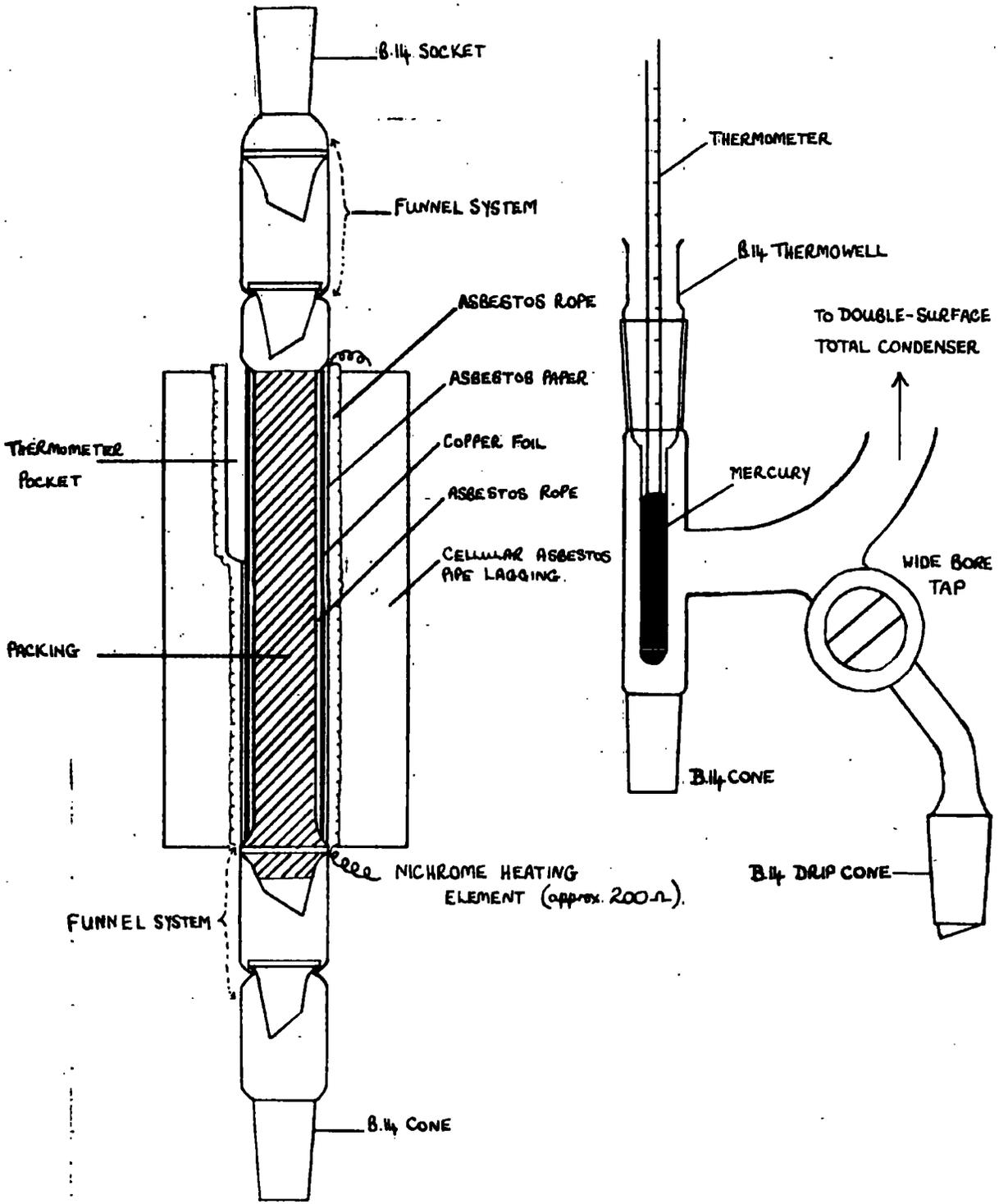


DIAGRAM 9 PACKED COLUMN AND STILL HEAD.

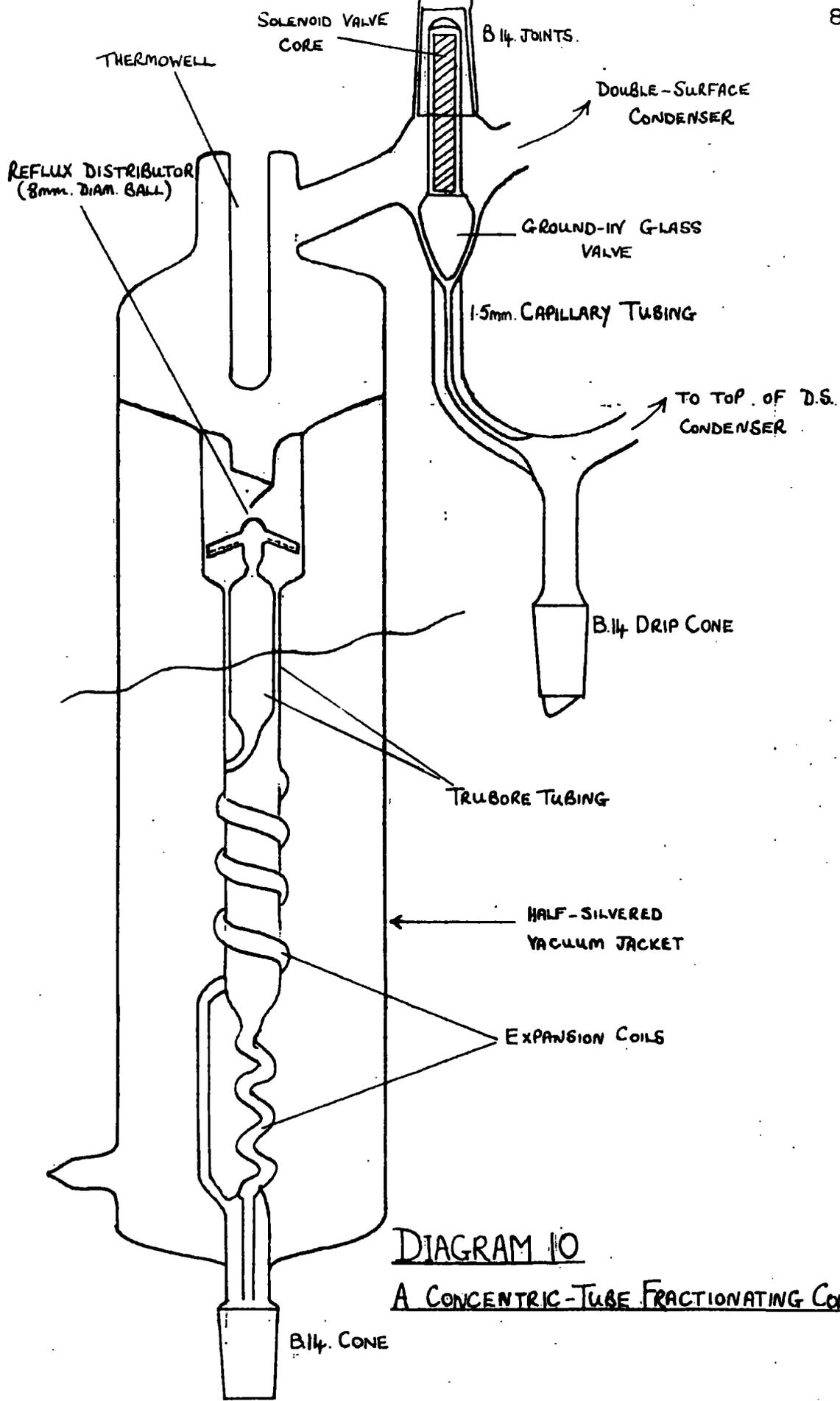


DIAGRAM 10
A CONCENTRIC-TUBE FRACTIONATING COLUMN

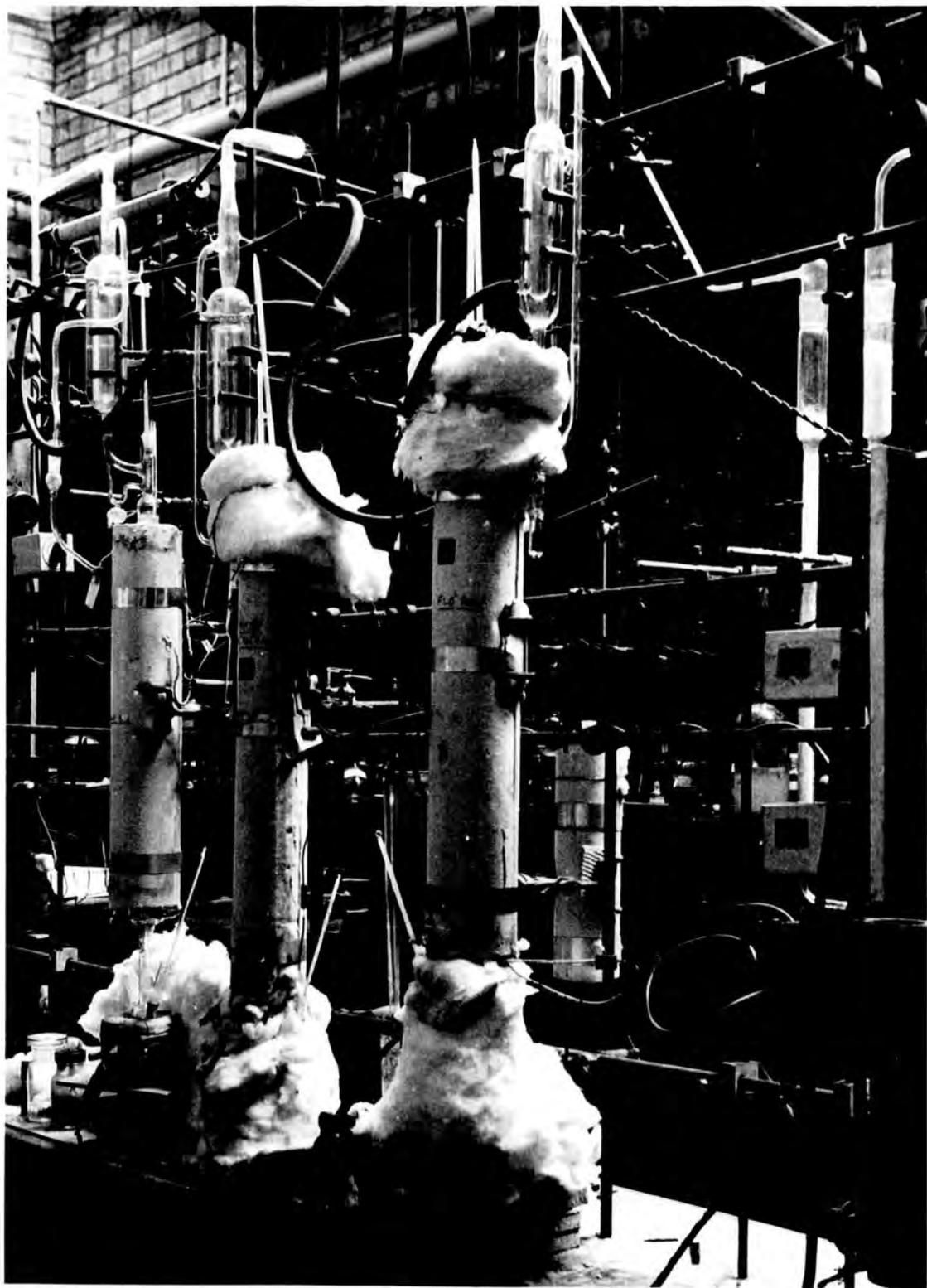


PLATE 3

The Concentric-tube Columns

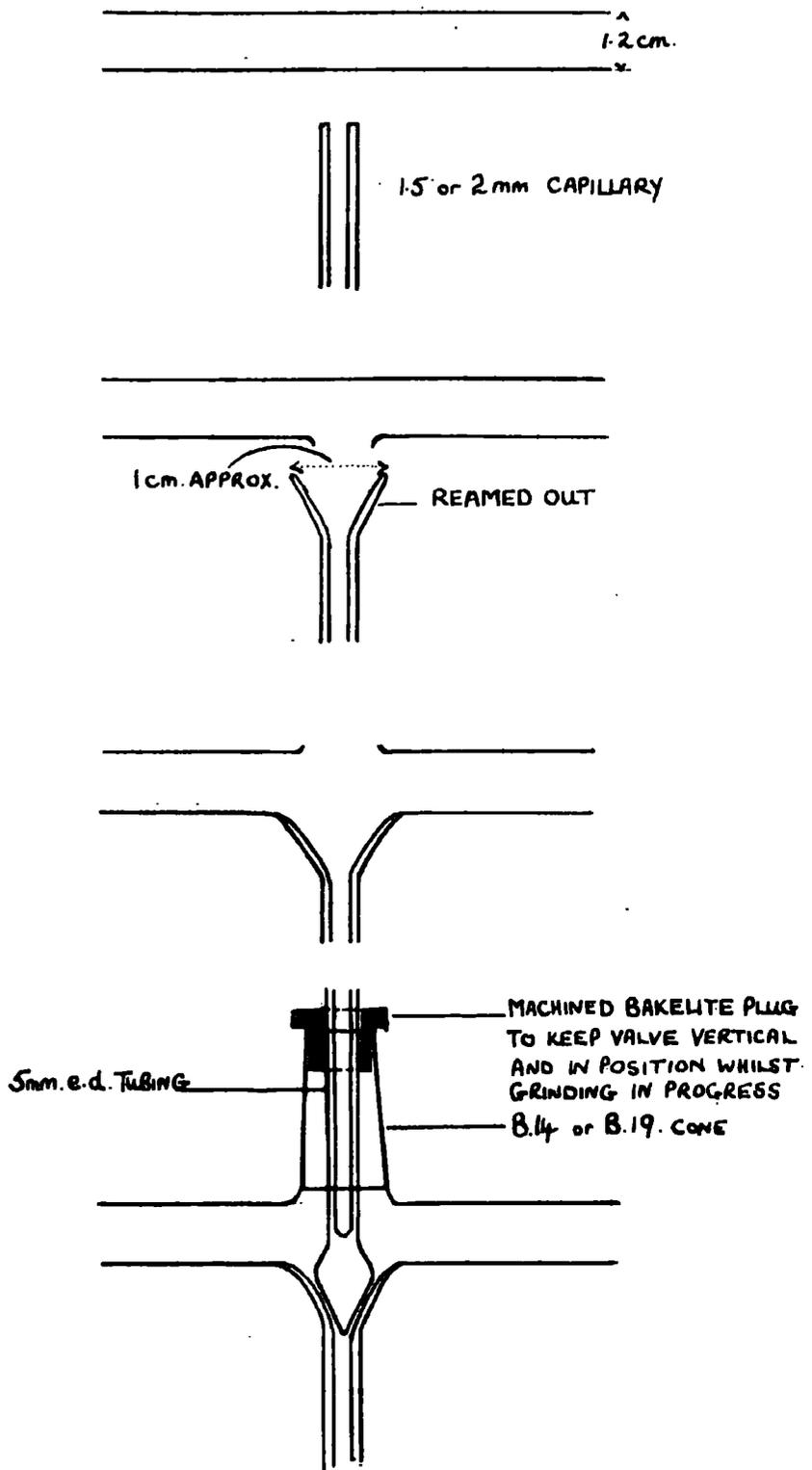


DIAGRAM II STAGES IN THE FABRICATION OF A PYREX TAKE-OFF VALVE

expanding at elevated temperatures, or movement of the framework, the condensers were only lightly clamped to the same vertical member of the framework as the respective column. The base of the framework was in the form of a cabinet in which the variable transformers and voltage regulators were mounted.

Accessory Equipment

(a). For distillation at atmospheric pressure.

PREVOST POT SAMPLER (PREVOST, M.S. Thesis, Pennsylvania State College, 1948; described by ROSE AND ROSE, "Technique of Org. Chem.", Ed. by Weissberger, Intersc. Publ., Inc., N.Y. and London, 1951, Vol. IV, p. 34). This device (DIAGRAM 12) enabled still pot liquids to be sampled for analysis during test runs without interrupting the distillations. It was so placed in the still pot that samples could be taken from the lowest part of the still.

(b). For distillation at sub-atmospheric pressures.

INTERNAL POT HEATER. (See DIAGRAM 13a). Numerous devices have been suggested to prevent the tendency for liquids to "bump" when boiled under vacuum (See survey by BOWMAN AND TIPSON, op.cit, p. 491). However, having tried them all I found that a small inner heating coil, placed at the very bottom of the still pot, was the most satisfactory. By

this means the concentric-tube columns were operated continuously for periods of 100 hours or more at reduced pressure. The heaters for the two columns were connected in series, and run off a "Variac" transformer.

TAKE-OFF ADAPTOR. (See DIAGRAM 13A). This was a modification of the normal Perkin triangle arrangement employed to enable distillate to be removed from a still head without affecting the equilibrium of the distillation process. It was designed to prevent distillate coming into contact with the lubricant on the joints and stopcocks associated with a take-off system. This was necessary because although the grease used was insoluble in the liquids being distilled (see below), it tended to run if distillate was allowed to flow over it during long continuous periods of distillation.

DIAGRAM 14 shows the vacuum system employed in all the work at reduced pressure, and also the "Cartesian Diver"-type manostats which kept the pressure in the system constant to ± 0.5 mm. Both concentric-tube columns were operated from the one system. (See PLATE 4).

Lubricant

All ground glass joints and stopcocks which were integral parts of the stills or accessory equipment, and which came into contact with the liquids being distilled,

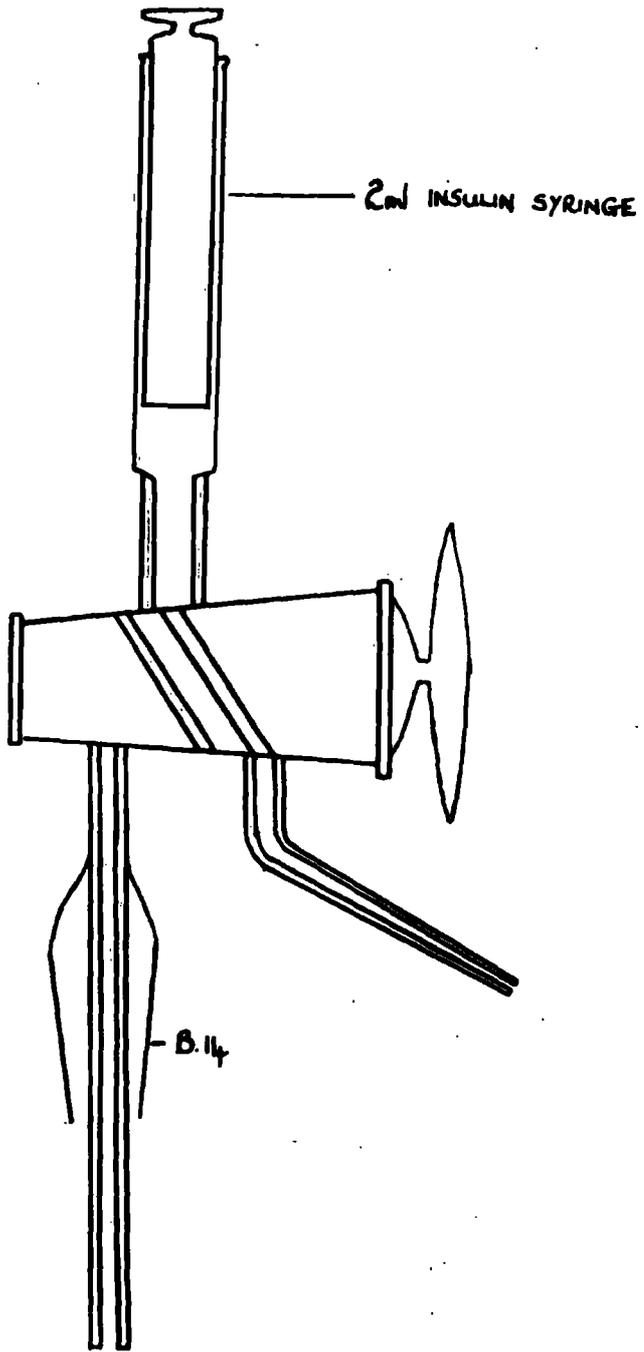
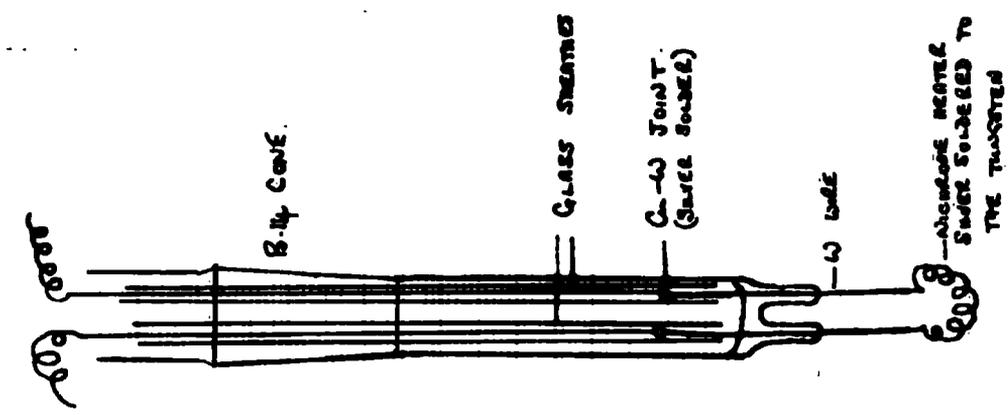


DIAGRAM 12 A STILL POT SAMPLER.



B. INTERNAL STILLPOT HEATER

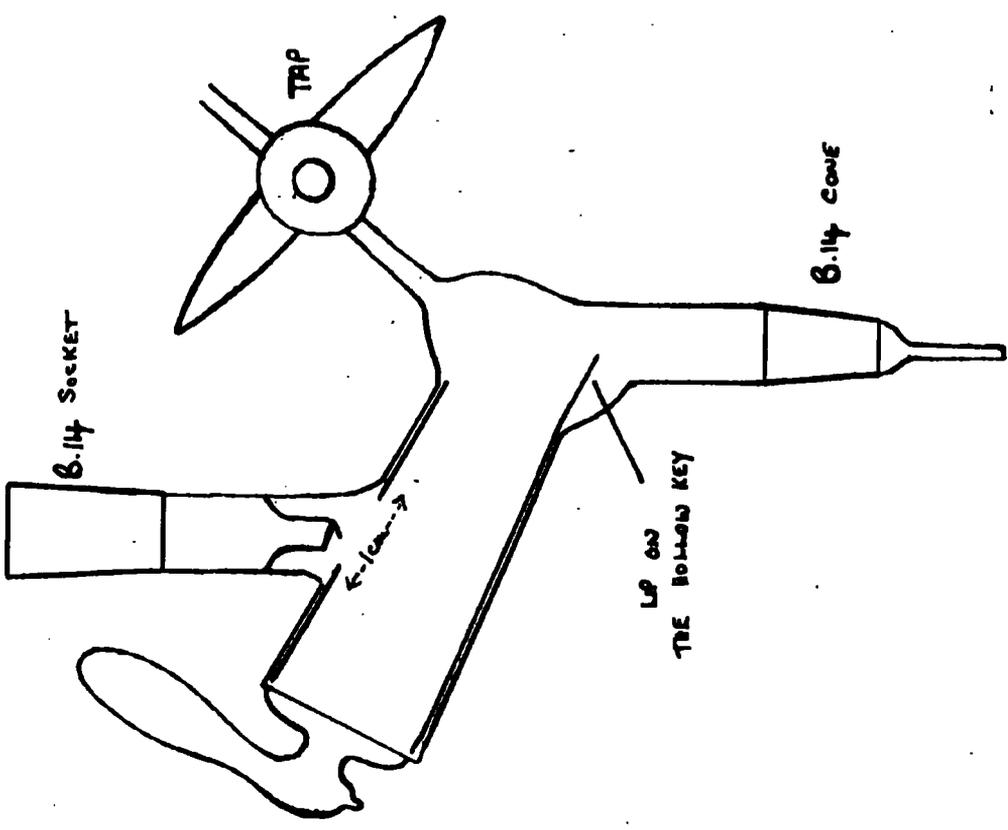
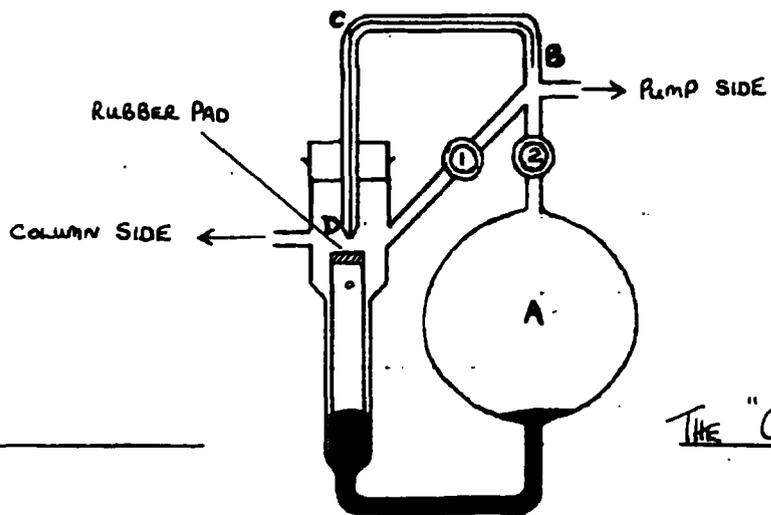


DIAGRAM 13 A TAKE-OFF ADAPTOR



D = ORIFICE GROUND PLAT
A = OPERATING PRESSURE

DIAGRAM

THE "CARTESIAN-DIVER" TYPE MANOSTAT

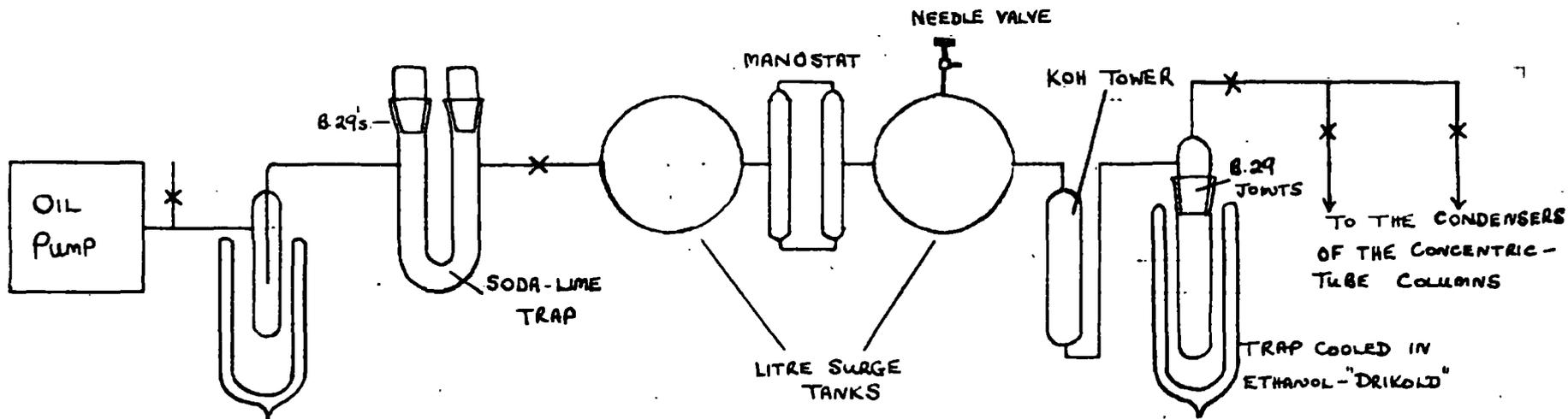


DIAGRAM 14

A SCHEMATIC REPRESENTATION OF THE APPARATUS USED FOR DISTILLATION UNDER REDUCED PRESSURE.

M = MANOSTAT
N = NEEDLE VALVE
T = TAKE-OFF ADAPTOR

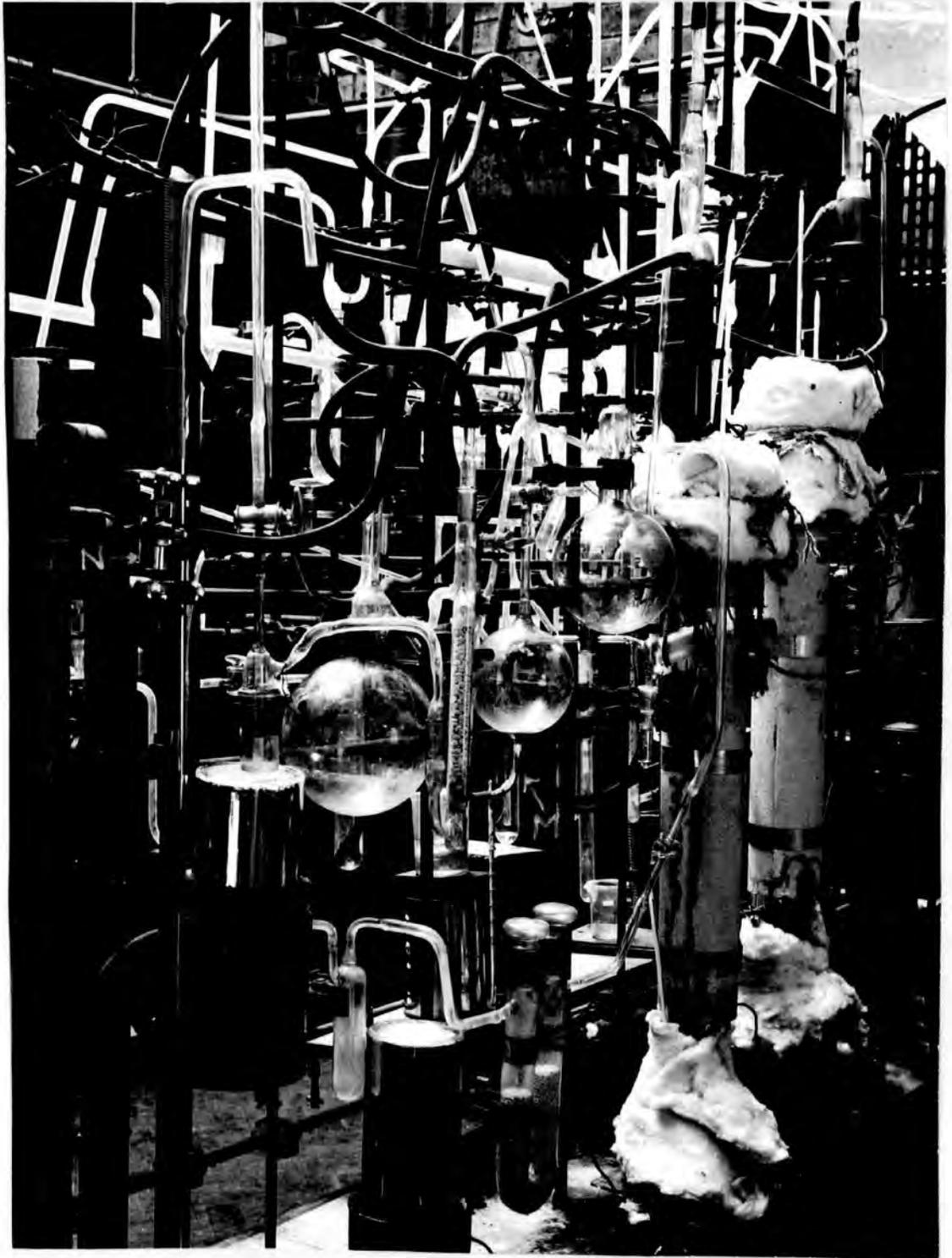


PLATE 4 The Concentric-tube Columns showing the
Vacuum System used for Reduced Pressure Distillations

or their vapours, were lubricated with a hydrocarbon-insoluble mannitol grease. This was prepared as follows:- 1 part of mannitol, 2 parts of dextrin, and $2\frac{1}{2}$ to 3 parts of glycerol were heated together, but NOT boiled, and the molten mass stirred well whilst it was cooling. This grease was quite stable up to temperatures of 170°C . When kept at this temperature for more than three days it began to carbonise.

Cleaning of the Columns:

To clean the columns before use the usual laboratory chromic acid mixture was allowed to stand in them overnight, after which they were drained, then washed out with water, alcohol, and ether in that order. The heating jackets were then brought up to about 150°C ., and a stream of air blown through them to remove the last traces of ether. This procedure was carried out, in the case of the concentric-tube columns, at the end of each long distillation, e.g. distillation of Chlorofluorination Run No. 1. at atmospheric pressure. At other times, e.g. after testing the columns at atmospheric pressure with the n-heptane-methyl cyclohexane test mixture, they were cleaned out by distilling ether through them at total reflux, then dried with a stream of air as before.

Operation of the Columns

(a) PACKED TYPE. In starting a distillation the material to be fractionated was charged into the still pot, and a few small pieces of porous pot added. Mannitol grease was then applied to the ground glass joint at the base of the column, the still pot placed in position and its "Isomantle" fitted on. A thermowell and a stopper were then greased and inserted into the two remaining necks of the still pot, and cotton wool wrapped round the top of the pot and the lower end of the column for insulation. When the column jacket had been pre-heated to a temperature 15-20°C. below the boiling point of the pot charge, the still pot heater was switched on, and the heat input slowly increased over a period of 30 minutes until reflux appeared in the condenser section. At this point the boil-up rate was increased sharply to cause the column to flood. This flooding was continued for 5 minutes to ensure that the packing was thoroughly wetted, then the boil-up rate slowly decreased until liquid was refluxing normally once more just inside the condenser. Adjustments were then made to the temperature of the heating jacket so that it was 2 degrees below that of the refluxing liquid, and the boil-up rate was set at a pre-determined value

which was kept constant throughout the distillation by means of the "Variac" transformer. The column was left at total reflux for 2 hours to ensure that it reached equilibrium before distillate was collected. Take-off was continuous, and made by partially opening the stopcock on the still head so that the reflux ratio was $P:1$, P being the plateage of the column. (Note:- REFLUX RATIO as used here is defined as the ratio of amount of material returned to the column during a known time to that removed as distillate during the same time.)

(b) CONCENTRIC-TUBE TYPE. Distillations employing this type of column were started exactly as described above for a packed column. No pre-flooding was necessary, so, after pre-heating the jacket, the heat input to the still pot was adjusted so that a boil-up rate of approximately 80 drops per minute into the still pot was obtained within 30 minutes. After refluxing at this rate for one hour the heat input was adjusted to give the desired boil-up rate which was then kept constant throughout the distillation. The column was left at total reflux for 3-4 hours to ensure that equilibrium had been established before distillate was removed. The take-off valve was operated every 15 minutes, and at the same time the temperatures recorded

by the thermometers located in the still pot, the heating jacket, and the still head, were noted. When distillations were being carried out at reduced pressure the still pot contents were heated almost to their boiling point by means of the "Isomantle", then the small internal pot heater switched on and the heat input to it adjusted until even boiling commenced. The heat input to the "Isomantle" was then adjusted to give the desired boil-up rate.

The columns were left at total reflux overnight, but in the case of the packed columns the heating jackets were turned off. This ensured that the liquids being distilled refluxed in the packed sections of the columns, and therefore no loss of material occurred through the easing of a joint or stopcock in the still heads.

At the end of a week's continuous running, and more frequently when elevated temperatures were reached, the columns were shut off, allowed to cool, and the grease on the joints and stopcocks renewed.

Testing the Columns

The efficiencies of both the packed and the concentric-tube columns were determined at atmospheric pressure using the standard n-heptane - methylcyclohexane test mixture of BROMILEY AND QUIGGLE (Ind. Eng. Chem., 1935, 35, 1136),



which is useful for columns with about ten to ninety plates. Although they studied this mixture at a pressure of 760 mm. of mercury, little error is involved if their data is applied to test runs carried out between 700 and 800 mm. Analysis of distillate and distilland was carried out refractometrically using an Abbé refractometer which was kept at $20 \pm 0.1^{\circ}\text{C}$. by circulating water from a thermostat through the prism jackets. The efficiencies of the columns were calculated from a graph of refractive index vs. theoretical plates which was constructed from the data of LECKY AND EWELL (Ind. Eng. Chem., Anal. Ed., 1940, 12, 544.). The concentric-tube columns were also tested at a pressure of 50 mm. of mercury, for which purpose a test mixture containing methyl benzoate and methyl caprylate was developed. A record of this work, together with the details of other distillations of known mixtures at reduced pressures, is to be found in CHAPTER VIII.

The atmospheric pressure test mixture was made up by mixing n-heptane (n_{D}^{20} 1.3878) and methylcyclohexane (n_{D}^{20} 1.4234) in the ratio of 4:21 (vol:vol.), and the reduced pressure test mixture by mixing methyl benzoate (n_{D}^{20} 1.5172) and methyl caprylate (n_{D}^{20} 1.4173) in the ratio of 26:4 (vol:vol.).

The packed columns were set up using a plumb line, the 100 ml. still pots used when testing the columns charged with 75 mls. of test mixture, brought to equilibrium after pre-flooding, and samples of distillate and distilland taken. The following table gives the details of two typical test runs, one for each column.

Column Length (cms.)	Boil-up Rate (mls./min.)	n_D^{20}		Theoretical Plates	H.E.T.P. (cms.)
		Distillate	Distilland		
45	1.5	1.4061	1.4140	14	3.2
65	3.6	1.4077	1.4169	20	3.2

The concentric-tube columns were set up, likewise using a plumb line, and their efficiencies determined at atmospheric pressure. They were then moved very slightly into different positions, their efficiencies determined in each position, and rigidly clamped into place when the optimum positions were found. This procedure was necessary because the concentric-tube portions of the columns were not necessarily concentric with respect to the vacuum jackets. The efficiencies were then determined at different boil-up rates, the still pots removed, the columns cleaned by

refluxing ether in them, and dried. Their efficiencies were then determined at 50 mm. using the vacuum system already described (p. 93 , and DIAGRAM 14), and the small internal pot heater to prevent uneven boiling of the methyl benzoate - methyl caprylate test mixture. The receiver on the take-off adaptor was evacuated to 50 mm. pressure using a secondary vacuum system which was operated by a water pump. TABLE 6 gives the details of the test runs. The back pressures were determined by direct reading, the still pot being connected to the still head through a manometer containing di-n-butyl phthalate.

Distillation of the Reaction Mixtures

GRAPHS A and B indicate the course of the preliminary distillations of Chlorofluorination Runs No. 1 and No. 2. The cuts made, the amounts of material in them, their boiling ranges and refractive indices, are given in TABLES 7 and 8 .

The still pot residues from the preliminary distillation of Run No. 1, i.e. the material boiling above 165°C., was split up into fractions of convenient size and boiling range before being distilled through the concentric-tube columns by crudely distilling it at reduced pressure from a Claisen flask. The fractions collected were:-

- 1). 120 mls. B.Pt. range 60-100°C. at 6.5cm. Hg.
 - 2). 150 mls. B.Pt. range 100-120°C. at 6.5cm. Hg.
- Residue c. 80 mls.

GRAPH C shows the course of the precise distillation of the cuts described in TABLE 7 using concentric-tube columns. The refractive index measurements were carried out on every 0.5 mls. of distillate in regions between "flats", and on every 1.0 ml. when a "flat" was reached. This operation, coupled with the storing of the distillate in separate, small, stoppered tubes, meant quite a considerable loss of material. Thus means were sought for determining the refractive index of distillate without loss. For this purpose the air-cell refractometer shown in DIAGRAM 15 was suggested. By attaching this to the take-off line of a column it was hoped to determine the refractive index of distillate in situ before it was allowed to collect in a receiver. However, for this particular distillation the refractive index measurements needed to be accurate to 0.0004, and a Vernier scale some three feet in diameter would be required for such accuracy. This was plainly impracticable. Another means by which distillate could be analysed without loss was thought to be the determination of dipole moment by means

of a heterodyne capacitance meter of the type described by HILL AND SUTTON (J.C.S., 1953, 1482.). The drawback here is that a very small condenser would be needed. An apparatus is under construction at the present moment, but will not be completed in time for its value to be assessed.

TABLE 9 gives details of the analyses carried out on samples taken from the "flats" shown on the graph. Also indicated in the table is the nature of each "flat" as discovered by means of gas-chromatographic analysis, the details of which are given in CHAPTER V .

TABLE 6Column Efficiencies at Atmospheric and Reduced Pressures

<u>Head Pressure</u> (Mm. Hg)	<u>Back Pressure</u> (Mm. di-n-butyl phthalate ^a)	n_D^{20}		<u>Theoretical</u> <u>Plates</u>
		Pot	Head	
Column A.				
50 ^b	28	1.5005	1.4350	29
50 ^b	29.5	1.5010	1.4360	27
50 ^b	34	1.5010	1.4390	24
762 ^c	3.5	1.4180	1.3910	60
762 ^c	4.0	1.4180	1.3915	58
Column B.				
50 ^b	23	1.5020	1.4360	28
50 ^b	37	1.5020	1.4440	21
50 ^b	47	1.5060	1.4680	11
752 ^c	1.5	1.4195	1.3910	65
752 ^c	3.0	1.4190	1.3915	61

- a. 1 mm. di-n-butyl phthalate = 0.077 mm. Hg.
- b. Methyl benzoate - methyl caprylate test mixture.
- c. Methyl cyclohexane-n-heptane test mixture.

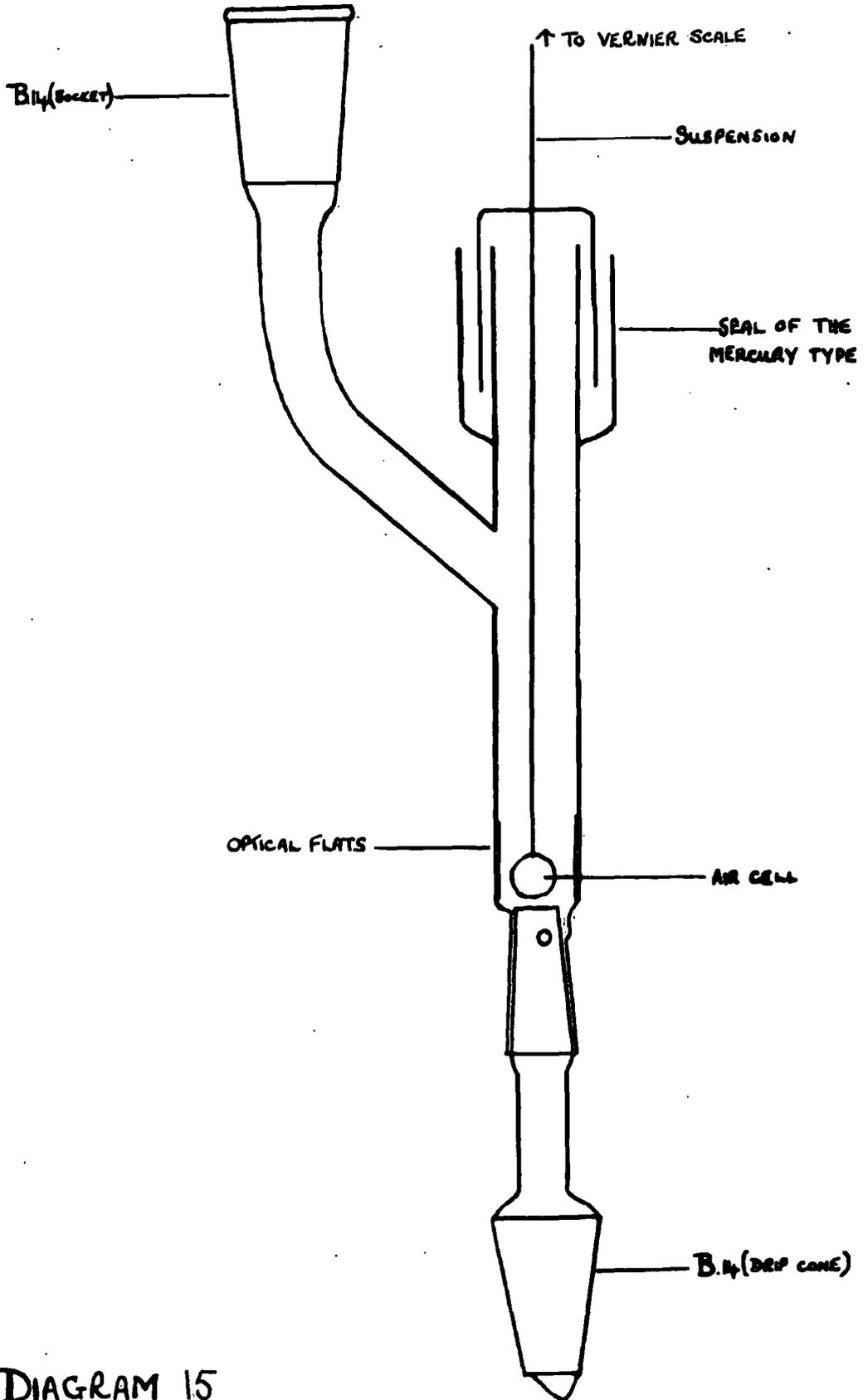


DIAGRAM 15

TABLE 7

Summary of the Preliminary Fractionation of 1.574 mls.
of Product from Chlorofluorination Run Number One using
Columns packed with Glass Helices

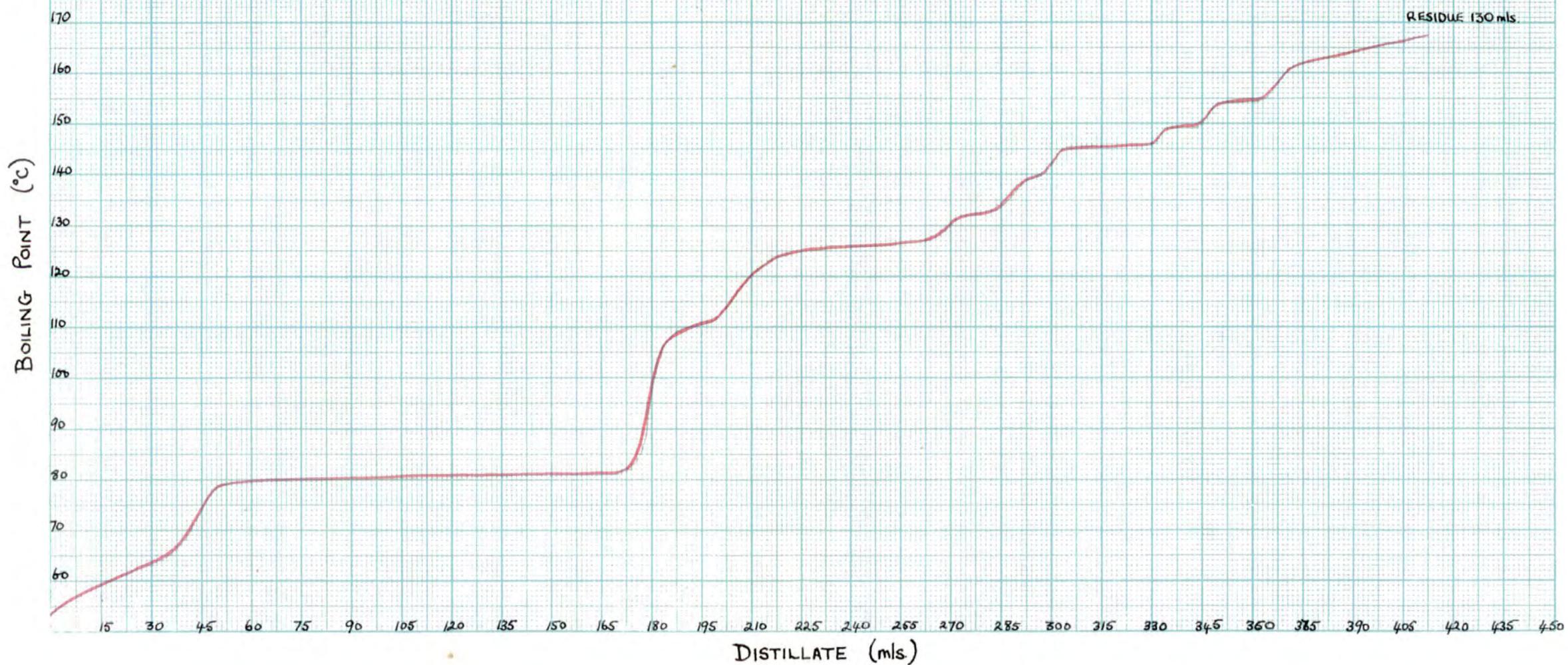
Fraction Number	Boiling Range (°C.)	n_D^{20}	Size of the Fraction (mls.)
1	52- 78	1.4552	216
2	78- 81	1.4848	295
3	81-120	1.3937	120
4	120-130	1.4214	170
5	130-140	1.3966	85
6	140-150	1.3980	65
7	150-160	1.4202	120
8	160-170		125
Residue	B.Pt. 166°C.		350

Total 1,541 mls.

Recovery = 98%

DISTILLATION CURVE FOR 550mls. OF REACTION PRODUCT FROM CHLOROFLUORINATION RUN NUMBER ONE

COLUMN: 20-plate, glass helices packed.
PRESSURE: atmospheric
TAKE-OFF RATIO: 1:20
REFLUX RATIO: 20:1



GRAPH A

110.

TABLE 8

Summary of the Preliminary Fractionation of 910 mls.
of Product from Chlorofluorination Run Number Two
using Columns packed with Glass Helices

Fraction Number	Boiling Range (°C.)	n_D^{20}	Size of the Fraction (mls.)
1	64-100	1.3240	44
2	100-110	1.3400	45
3	110-120	1.3462	66
4	120-130	1.3580	78
5	130-150	1.3760	220
6	150-165	1.3960	140
Residue	B.Pt 165°C.		222
Total			815 mls.

Recovery = 90%

This poor recovery was due to two accidents, both occurring when a column flooded violently.

DISTILLATION CURVE FOR 440mls. OF REACTION PRODUCT FROM CHLOROFUMORINATION RUN NUMBER TWO

COLUMN: 14-plate, packed with glass helices.
PRESSURE: atmospheric
TAKE-OFF RATIO: 1:14
REFLUX RATIO: 14:1

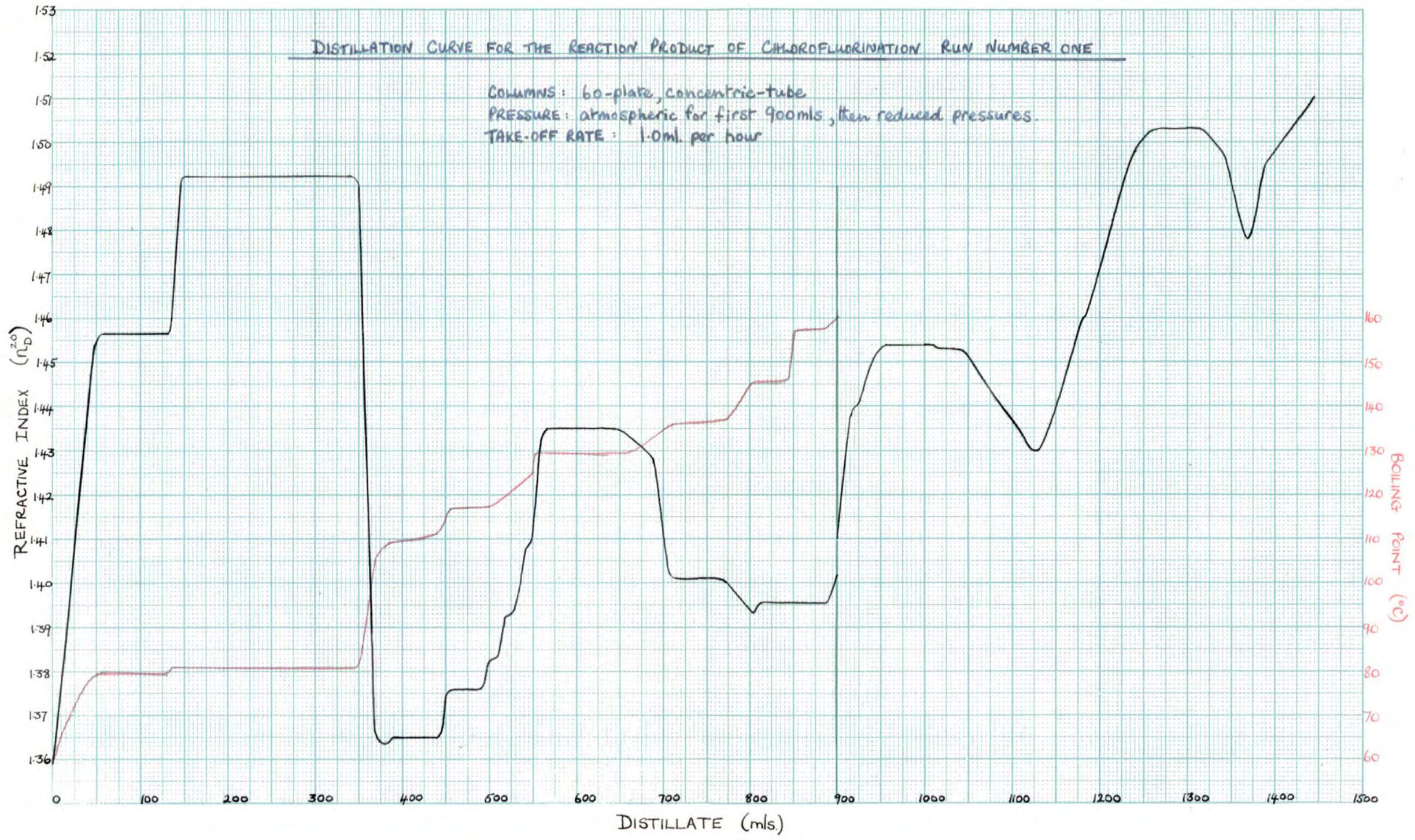


GRAPH B.

112.

DISTILLATION CURVE FOR THE REACTION PRODUCT OF CHLOROFLUORINATION RUN NUMBER ONE

COLUMNS: 60-plate, concentric-tube
PRESSURE: atmospheric for first 900mls, then reduced pressures.
TAKE-OFF RATE: 1.0ml. per hour



GRAPH C

113.

TABLE 9

Details of the Analyses carried out on the Distillation "Flats".

(Halogen analyses by method described in Chapter VII, pp. - , and mol. wts. by the method of Victor Meyer using the apparatus shown in DIAGRAM 16)

Flat Number	B.Pt. (°C.)	n_D^{20}	% Cl (found)	% F (found)	Cl:F ratio (atoms)	Mol.wt. (found)	Nature of Material	Number of Components.
I	79.5	1.4565	7.0	18.0	1:4.84	113	azeotrope	2
II	81.0	1.4920	2.04	5.2	1:4.7	85	azeotrope	2
III	109-111	1.3650	16.4	50.9	1:5.8	254	azeotrope	2
IV	117	1.3762	17.45	46.7	1:5.0	250	azeotrope	2
V	118	1.3830	21.5	44.9	1:3.9	249	azeotrope	4
VI	121	1.3930	22.9	42.5	1:3.46	244	azeotrope	4
VII	124	1.4087	24.04	39.5	1:3.07	203	azeotrope	4
VIII	129.5	1.4350	26.4	33.9	1:2.4	204	azeotrope	4
IX*	131-135	1.4310	27.0	33.9	1:2.35	220	mixture	4 or more
X	136-137	1.4010	27.06	42.8	1:2.96	263	azeotrope	3
XI	145.5	1.3955	29.57	40.5	1:2.56	243	azeotrope	3
XII***	157	1.3957	29.5	41.0	1:2.6	243	single compound	
XIII	109/92 mm.	1.4440	36.3	15.1	1:0.78	263	azeotrope	3
XIV	94/63 mm.	1.4540	38.8	26.0	1:1.25	256	azeotrope	3
XV	95/61 mm.	1.4505	38.4	32.2	1:1.57	241	azeotrope	3
XVI	106/60 mm.	1.4298	69.2	14.8	1:0.4	271	azeotrope	3
XVII	115/49 mm.	1.5032	46.5	20.8	1:0.84	258	B.Pt. too high for material to be examined by gas chromatography.	

By filtering the tarry residue from the still pots under suction a solid residue was recovered. This was re-crystallised from methylated spirits to yield material with a m.pt. 132-137°C., and the following analysis:-

(i) By combustion, C 33.0%; H 0.9%.

(ii) By Na fusion, Cl 65.0%; F negligible

Cl:C ratio (atoms) = 1:1.5.

The mol. wt. (determined by an ebullioscopic method) was 136.

* Flat IX is in reality a slope (n_D^{20} 1.4350-1.4266) and the analysis sample was taken from the material as a whole.

*** This analysis may be compared with the following:-

$C_6Cl_2F_5$ Cl, 29.84%; F, 39.9%; mol. wt. 238

$C_6H_5Cl_2F_5Cl$, 29.22%; F, 39.1%; mol. wt. 243.

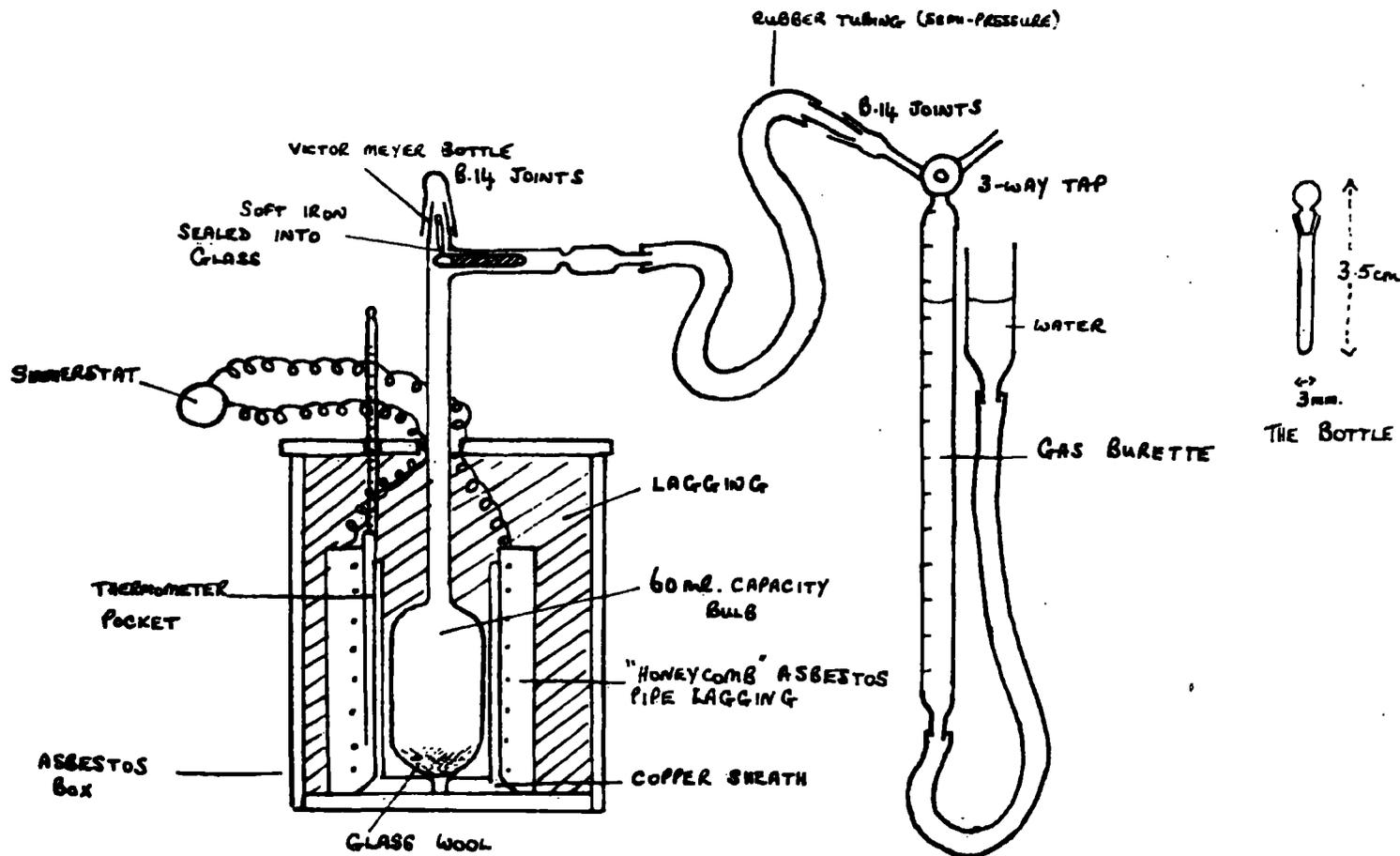


DIAGRAM 16 A MODIFIED VICTOR MEYER APPARATUS

Chapter V

The

Analysis and Separation of the Distillation

"Flats" by means of Gas-Liquid Partition

Chromatography.

The "flats" described in TABLE 9, p. 114 were analysed using small-scale columns packed with the following liquids adsorbed on Kieselguhr (Celite 545, Johns Manville Co. Ltd.) in proportions by weight of 1 part:2.5 parts respectively: "dinonyl" phthalate (Boake, Roberts & Co. Ltd.), high vacuum pump oil (8A, Edwards & Co. Ltd.), high vacuum pump oil + 10% by wt. stearic acid, and silicone fluid (M.S. 550) + 10% by wt. stearic acid. The chromatograms obtained gave information on the complexity of the "flats", the relationships between them, and the possibility of separating the components. Using large-scale columns the latter was attempted, but time has only allowed for this to be done for flats I-VIII inclusive.

Apparatus

The small columns (120 cm. x 5 mm. internal diameter) were similar in design to that of RAY (J. Appl. Chem., 1954, 4, 21), samples being injected through rubber serum-bottle caps from an "Aglia" micrometer syringe. They took the form of compact U-shaped tubes (see DIAGRAM 17) heated electrically by a jacket constructed out of a 2 ft. x 1 in. internal diameter wrought-iron tube. This

was insulated with asbestos paper, and wound with a heater consisting of 12 yds. of nichrome tape (24.8 ohms/yd.) run off a Simmerstat. The columns were packed in the following manner:- the packing was introduced into the arms of the U tubes and allowed to settle down under the influence of vibrations set up by tapping the tubes with a rubber-covered rod. In this way tight, uniformly-packed columns were made up without having to recourse to tamping methods. To ensure that the injected samples were totally flashed onto the packings just after the moment of injection, small 18-ohm heaters, run off Variac transformers, were clamped on to the columns just below the nitrogen inlets. The sections of the columns covered by these were packed with glass wool and kept at temperatures some 15-20°C. higher than the boiling points of the materials being analysed.

The large column (16 ft. x 1 in. internal diameter) was in the form of four parallel lengths joined together by short sections of 3 mm.-bore tubing, and arranged in the form of a compact, folded W (see DIAGRAM 17). It was mounted vertically in a 4 ft. 6 in. x 4 in. internal diameter cast-iron pipe, which was insulated with asbestos paper and wound electrically with 19 yds. of Vachrom wire

(4.16 ohms/yd.) run off a Simmerstat. Material was fed to the column, via a vaporiser packed with glass wool and heated by a 1,000-ohm Variac-controlled heating tape, from a small burette in which gas pressures could be equalised before admission. All the ground-glass joints on the column were sealed with black wax.

The presence of organic material in the gas stream issuing from a column was detected by the thermal conductivity cell which is described in every detail by DIAGRAM 18 . PLATE 5 shows how it was housed in a heating box which, however, was never used because the outlet pressure of a column could be adjusted so that no condensation of material occurred in the channel through the copper block. The detector circuit is shown in DIAGRAM 19 , the Tinsley galvanometer G (resistance 900 ohms; sensitivity 50 mm./micro-amp) measuring the lack of balance of the Wheatstone bridge formed by the four nickel resistance wires of the detector, which were arranged to give maximum sensitivity. A 2-volt accumulator was used to drive the bridge, and the initial balance-point adjusted by means of the variable resistance R, which was placed in series with one of the arms. S is a mercury switch.

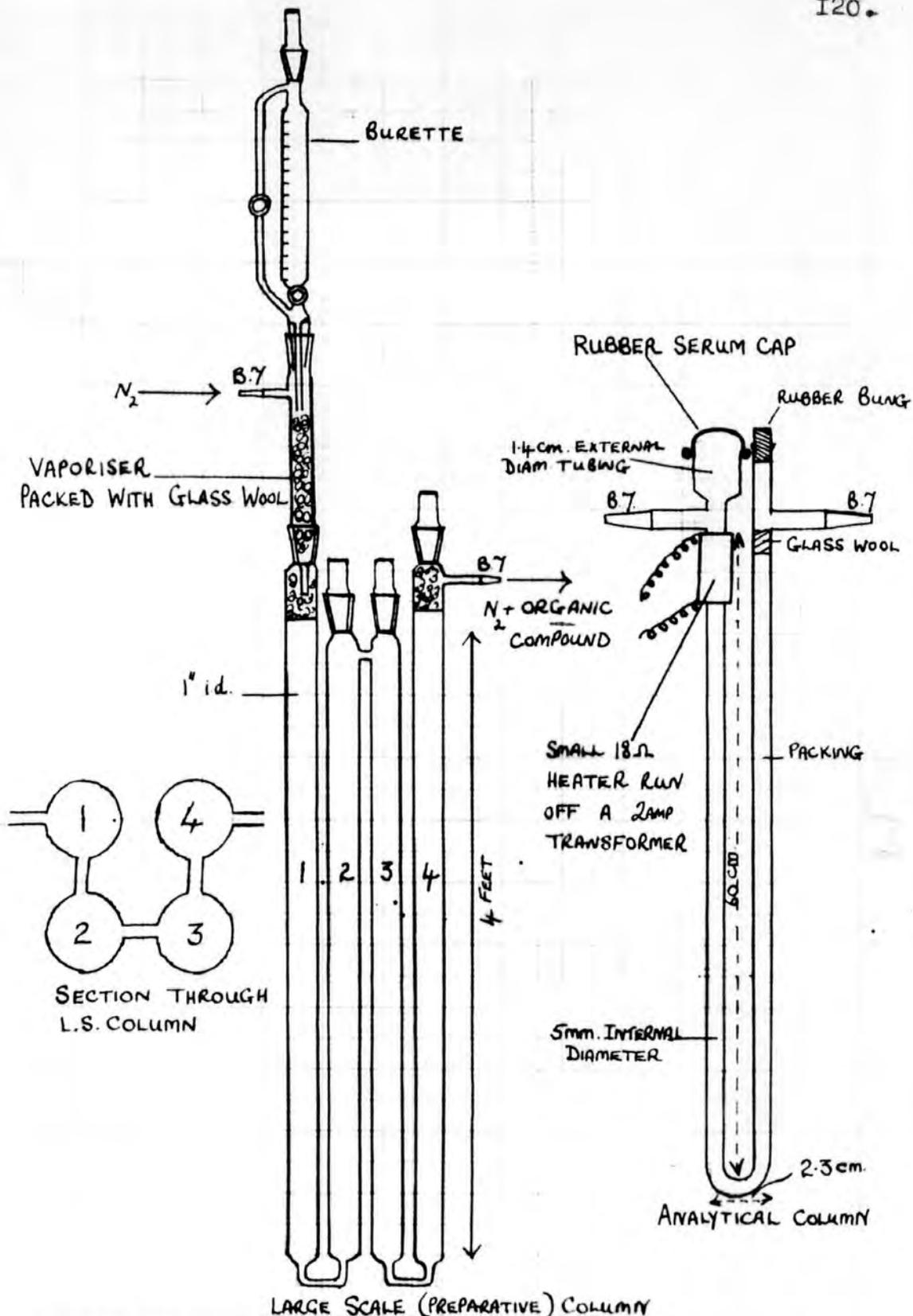
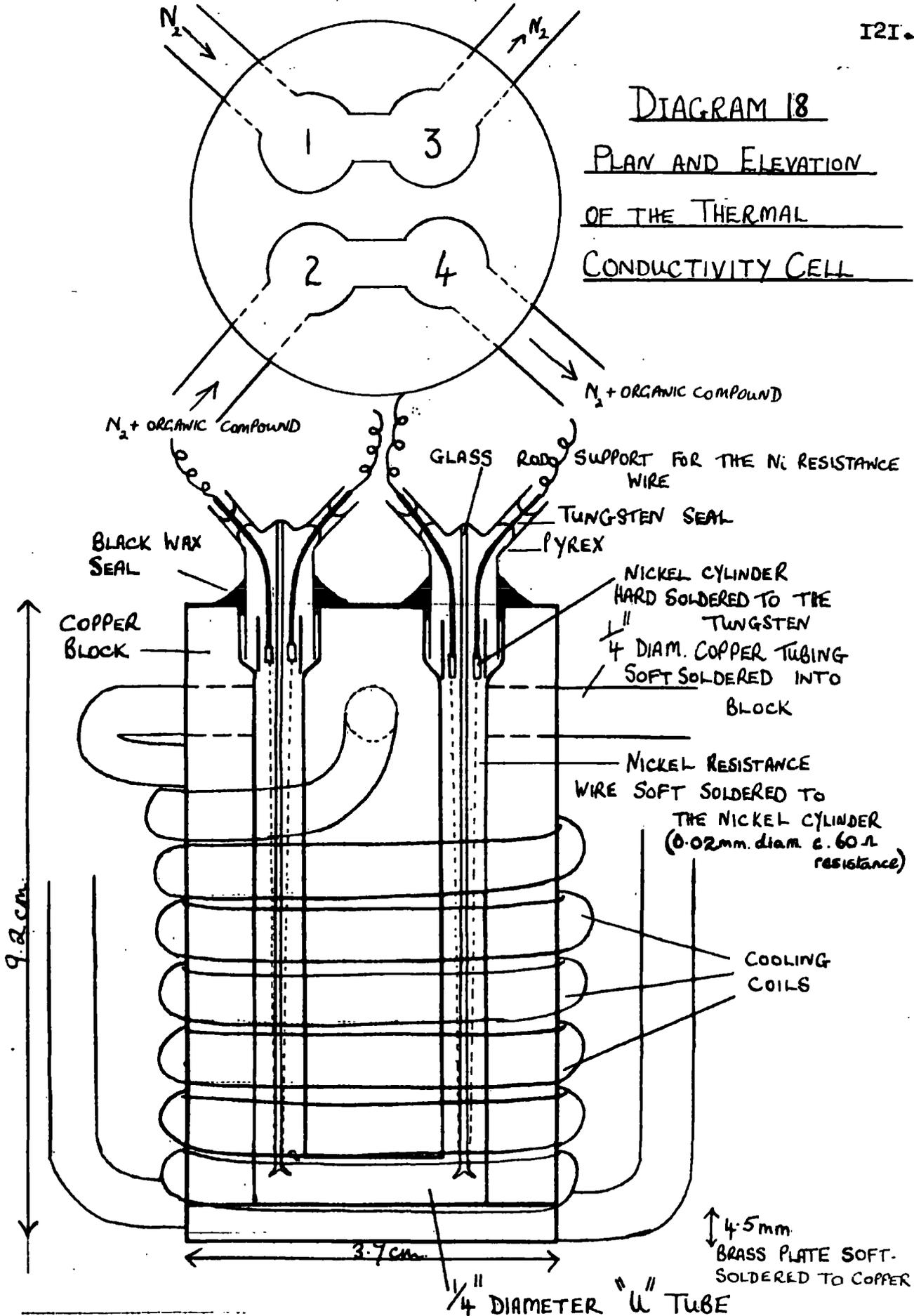


DIAGRAM 17 GAS CHROMATOGRAPHY COLUMNS

DIAGRAM 18

PLAN AND ELEVATION OF THE THERMAL CONDUCTIVITY CELL



BLACK WAX SEAL

COPPER BLOCK

9.2 cm

3.7 cm

$\frac{1}{4}$ " DIAMETER "U" TUBE

GLASS RODS SUPPORT FOR THE Ni RESISTANCE WIRE

TUNGSTEN SEAL

PYREX

NICKEL CYLINDER

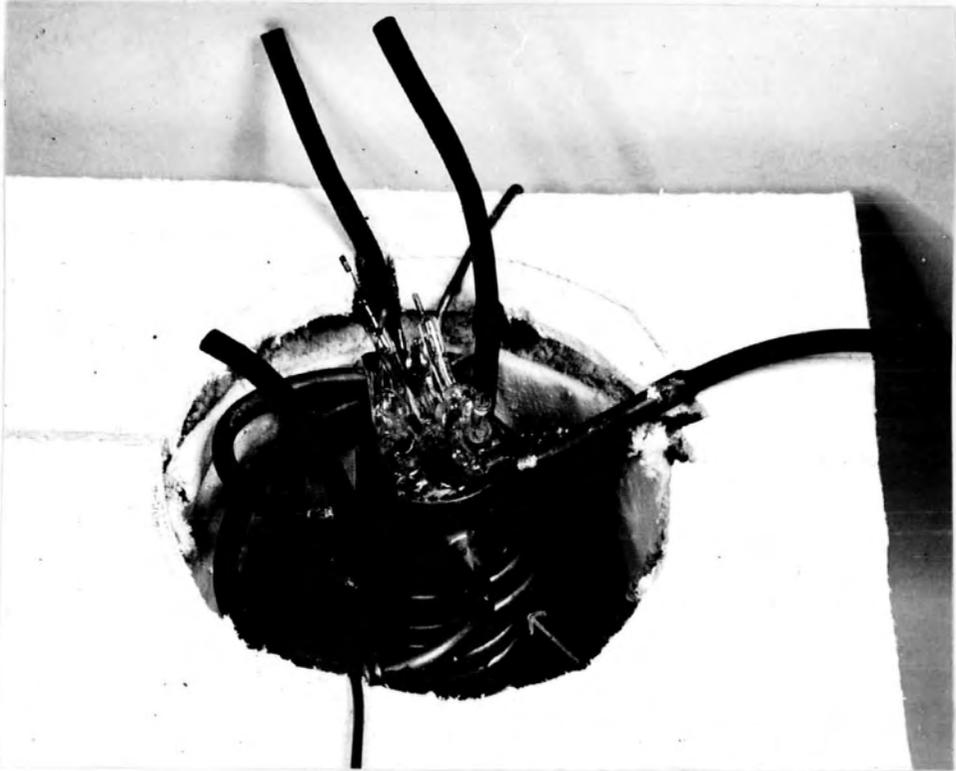
HARD SOLDERED TO THE TUNGSTEN

$\frac{1}{4}$ " DIAM. COPPER TUBING SOFT SOLDERED INTO BLOCK

NICKEL RESISTANCE WIRE SOFT SOLDERED TO THE NICKEL CYLINDER (0.02 mm. diam. 6.60 Ω resistance)

COOLING COILS

4.5 mm BRASS PLATE SOFT-SOLDERED TO COPPER



COOLING COILS ARROWED

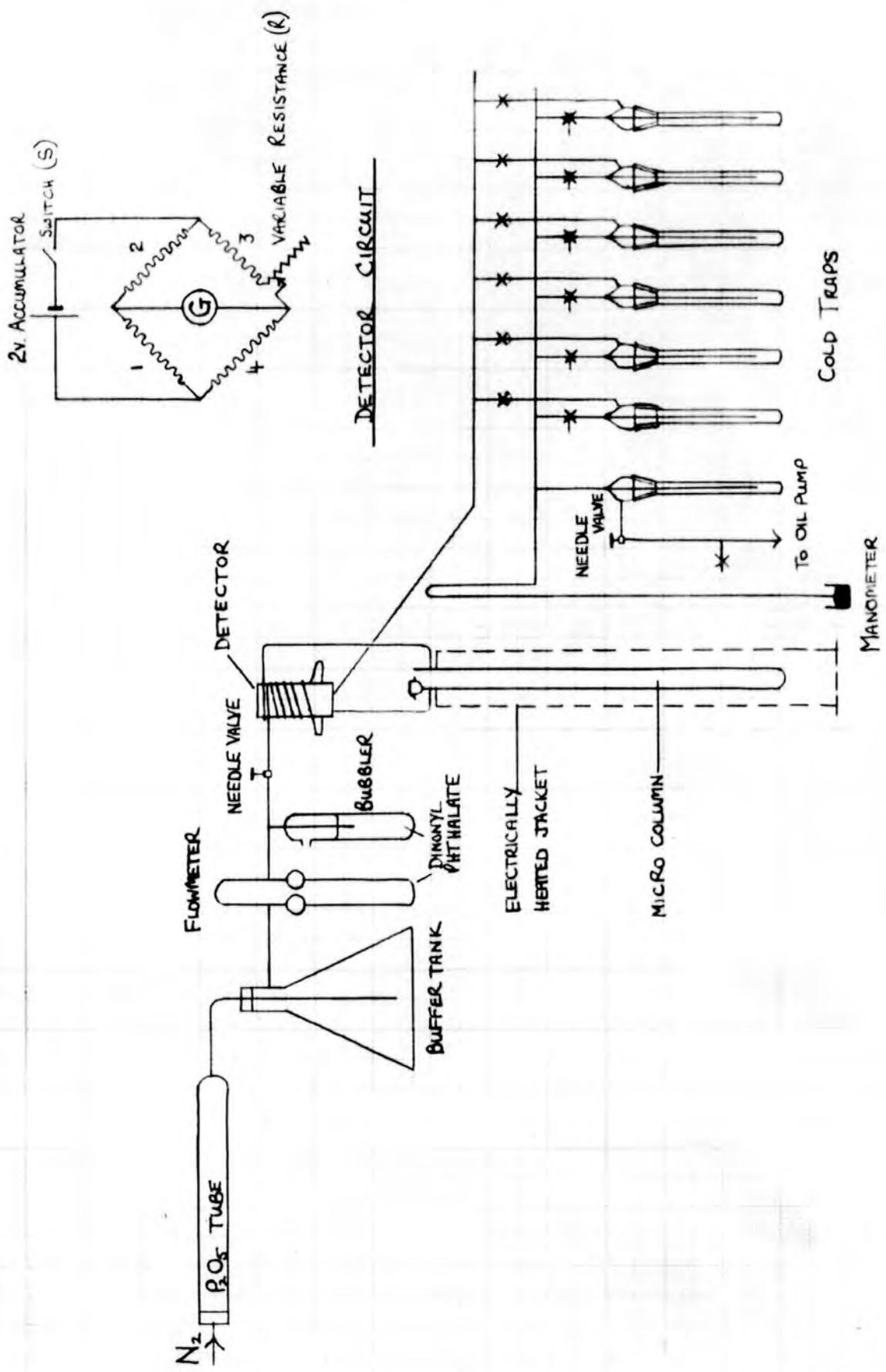


DIAGRAM 19 SCHEMATIC LAYOUT OF THE GAS CHROMATOGRAPHY APPARATUS

When an analytical run, or a calibration of the large column, was being carried out the galvanometer deflections were recorded and plotted manually, but when actual separations were under way the detector was used merely to indicate when fractions were passing, so that each could be collected separately in a trap which was one of a series arranged in parallel and cooled in liquid nitrogen. The ground-glass joints on the traps were lubricated with a light mannitol grease.

DIAGRAM 19 shows the complete apparatus in Schematic form.

Results and Discussion

GRAPHS D, E, F and G show the analytical chromatograms on which the choice of column liquids for the large-scale separations of the components of flats I-VIII inclusive was based. An overall picture of the complexity of the material from the reaction mixture which boils between 60 and 160°C. is obtained by examination of GRAPHS D, E, and F; the last two are directly comparable. DIAGRAM 20 further illustrates the fact that some preliminary fractional distillation of the reaction mixture was necessary before the separations by gas-chromatographic methods could have been achieved. It

shows the chromatograms obtained for a mixture of flats V and VIII, and for a fraction, b.pt. 85-135°C., distilled from a reaction mixture obtained by W.K.R. Musgrave using the same conditions under which Chlorofluorination Run No. One mixture was prepared.

"Dinonyl" phthalate was used as column liquid in the attempt to separate the components of flats I, II, III, IV, VIII and the material which distilled prior to flat I. The peaks of flats I, III, and IV were separated (see DIAGRAMS 21, 22, and 23), but in the case of flat II which was "slightly impure" benzene the cuts shown in DIAGRAM 24 had to be made in order to obtain a sample of peak 1 which was not greatly contaminated with benzene. It was found impossible to separate the peaks of the material prior to flat I (see DIAGRAM 25). Flat VIII proved extremely troublesome, but by making the cuts shown in DIAGRAM 26, recycling the fractions obtained at a lower column temperature, making more cuts (DIAGRAM 27) and re-cycling again, analysis samples for peaks 1 and 4 were obtained.

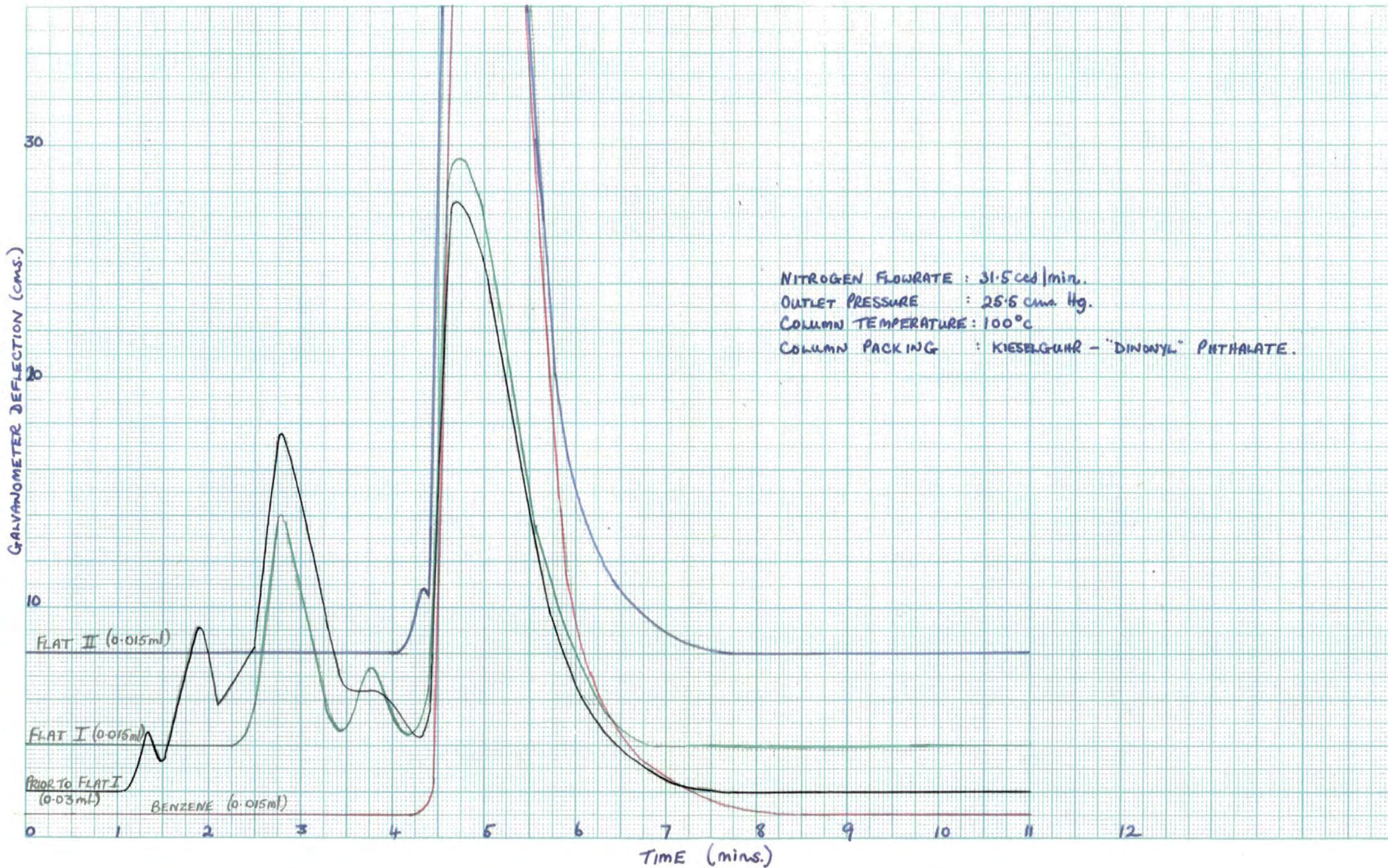
Silicone fluid and stearic acid was the most efficient of the column liquids for the separation of the components of flats V, VI and VII. DIAGRAM 28 shows how these

materials were separated into fractions. The peak 2 fractions were recycled to obtain analysis samples.

GRAPH H shows the chromatograms obtained for flats XIII, XIV, XV and XVI using pump oil + stearic acid. Silicone fluid + stearic acid was also experimented with, but similar chromatograms showing no better degree of separation were obtained.

The conditions under which the analytical chromatograms were obtained, and the large scale separations carried out are listed on the graphs and diagrams.

TABLE IO gives full details concerning the amounts of material separated, and the analyses carried out on the peaks.

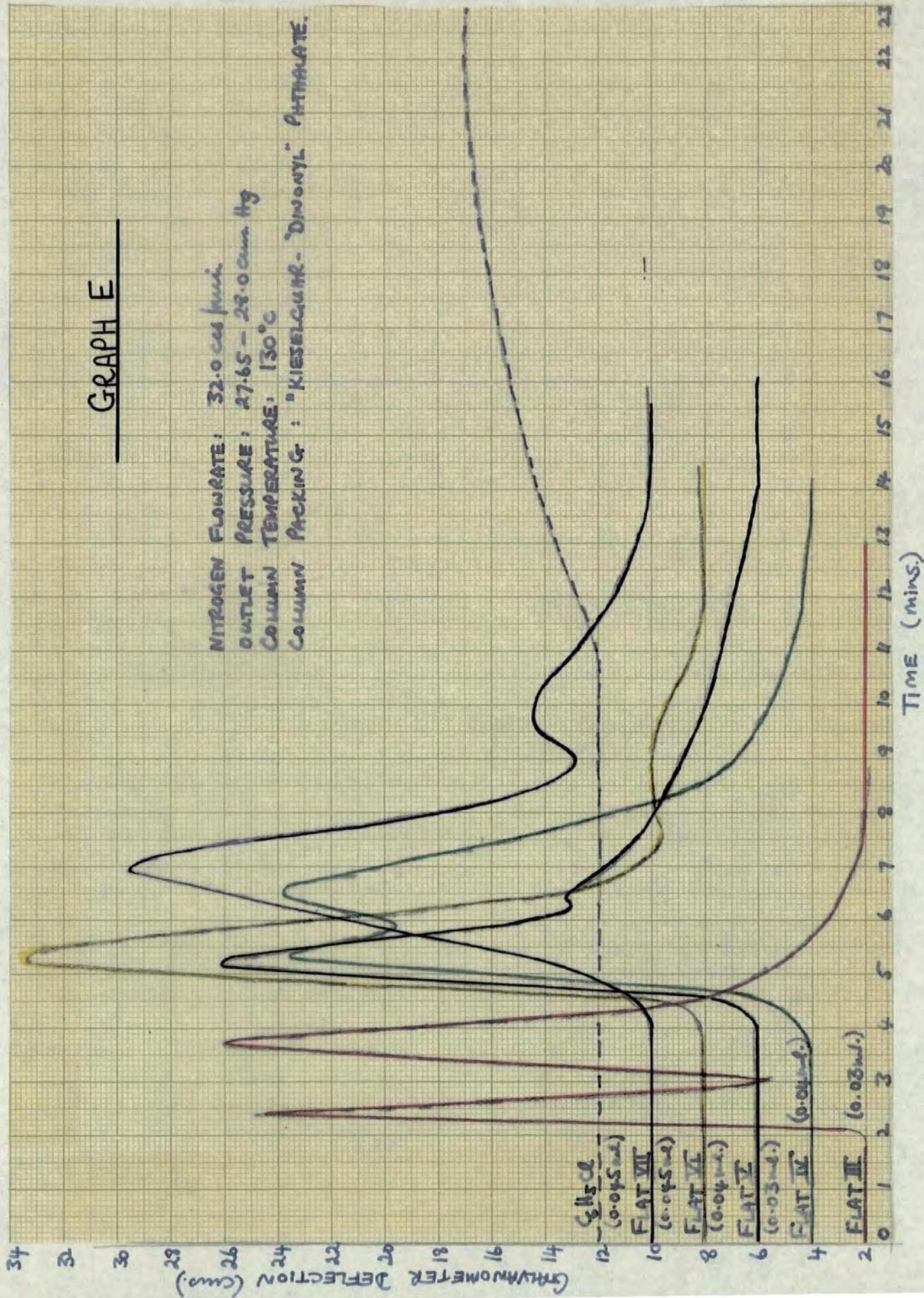


GRAPH D

127.

GRAPH E

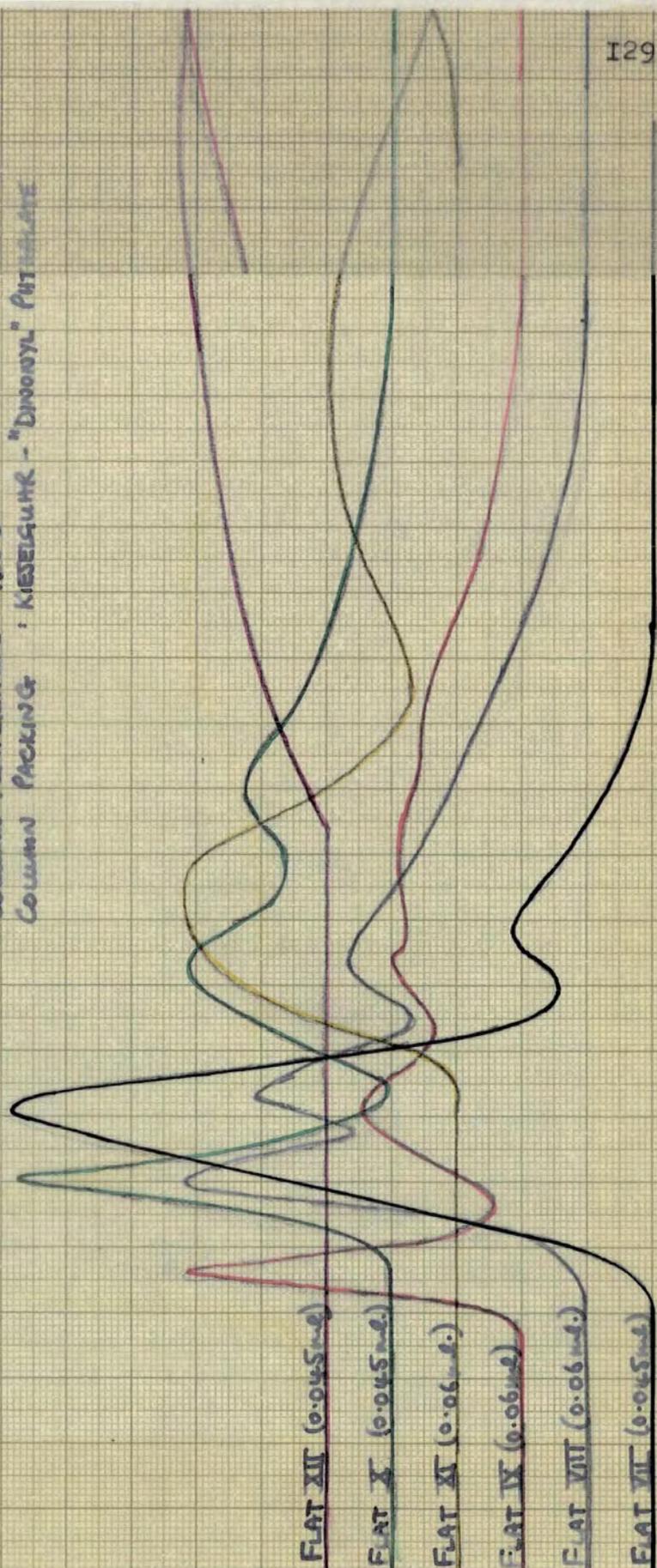
NITROGEN FLOWRATE: 32.0 cc/min
 OUTLET PRESSURE: 27.65 - 28.0 cm Hg
 COLUMN TEMPERATURE: 130°C
 COLUMN PACKING: "KIESELGUHR-DIMONYL PHTHALATE."



GRAPH F

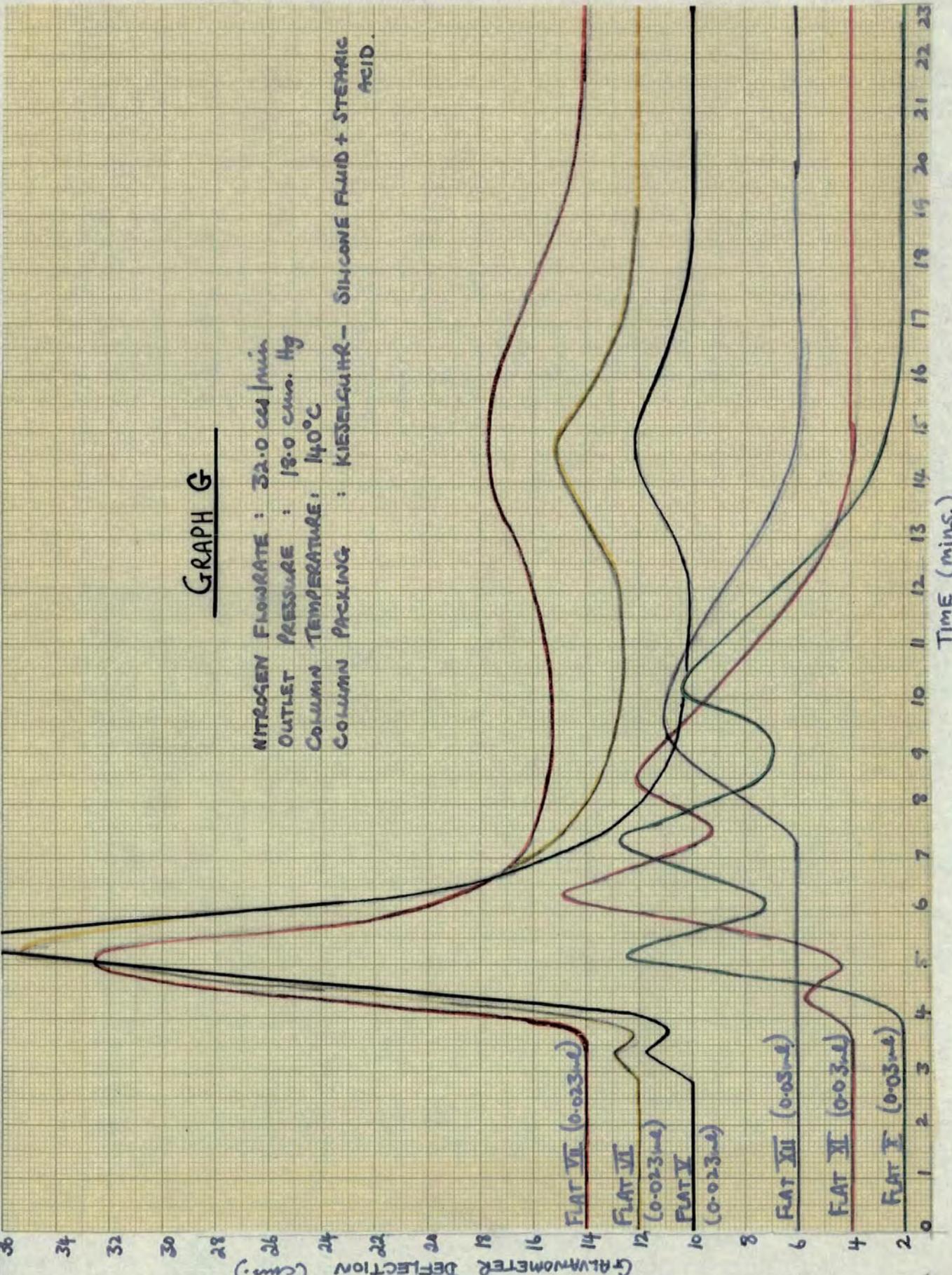
NITROGEN FLOWRATE : 32.0 cc/min
OUTLET PRESSURE : 27.65 - 29.0 cm Hg
COLUMN TEMPERATURE : 130°C
COLUMN PACKING : KIESELGUHR - "DIPONYL" PUTIDOLATE

GRAVIMETER DEFLECTION (mg.)



GRAPH G

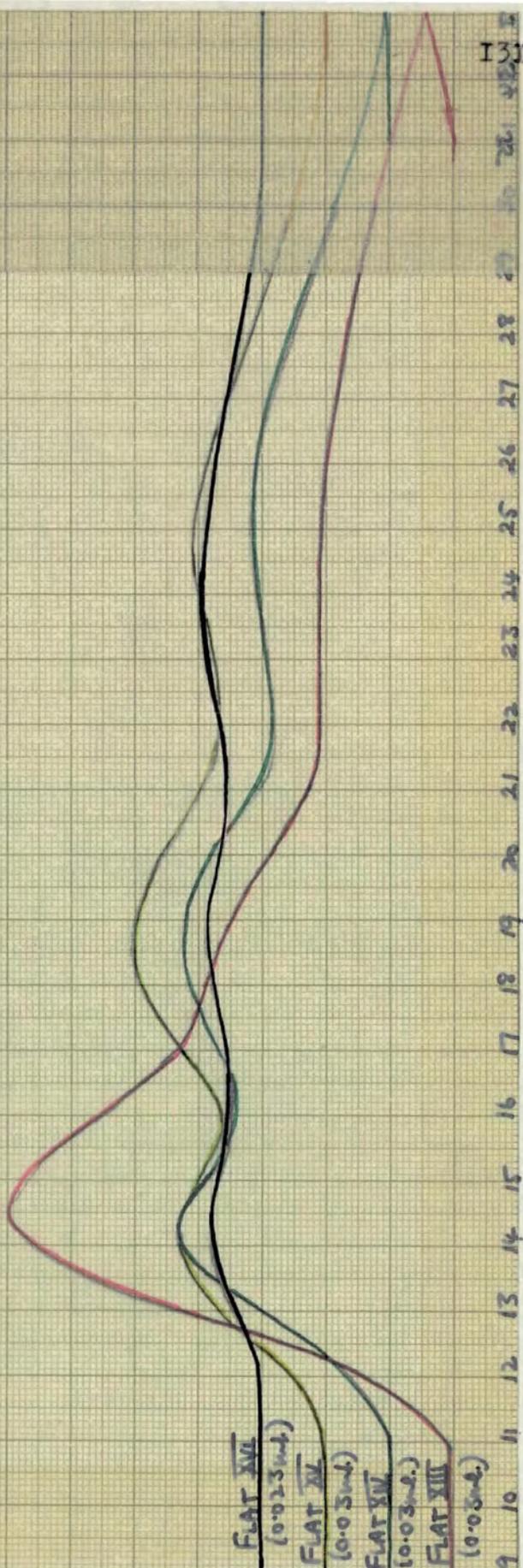
NITROGEN FLOWRATE : 32.0 cc/min
 OUTLET PRESSURE : 18.0 cm. Hg
 COLUMN TEMPERATURE : 140°C
 COLUMN PACKING : KIESELGUR - SILICONE FLUID + STEARIC ACID.



GRAPH H

NITROGEN FLOWRATE: 34.0 cc/min
OUTLET PRESSURE: 4.0 cm. Hg
COLUMN TEMPERATURE: 140°C
COLUMN PACKING: KIESELGURK-SUMP OIL

GALVANOMETER DEFLECTION (C.M.S.)



TIME (mins.)

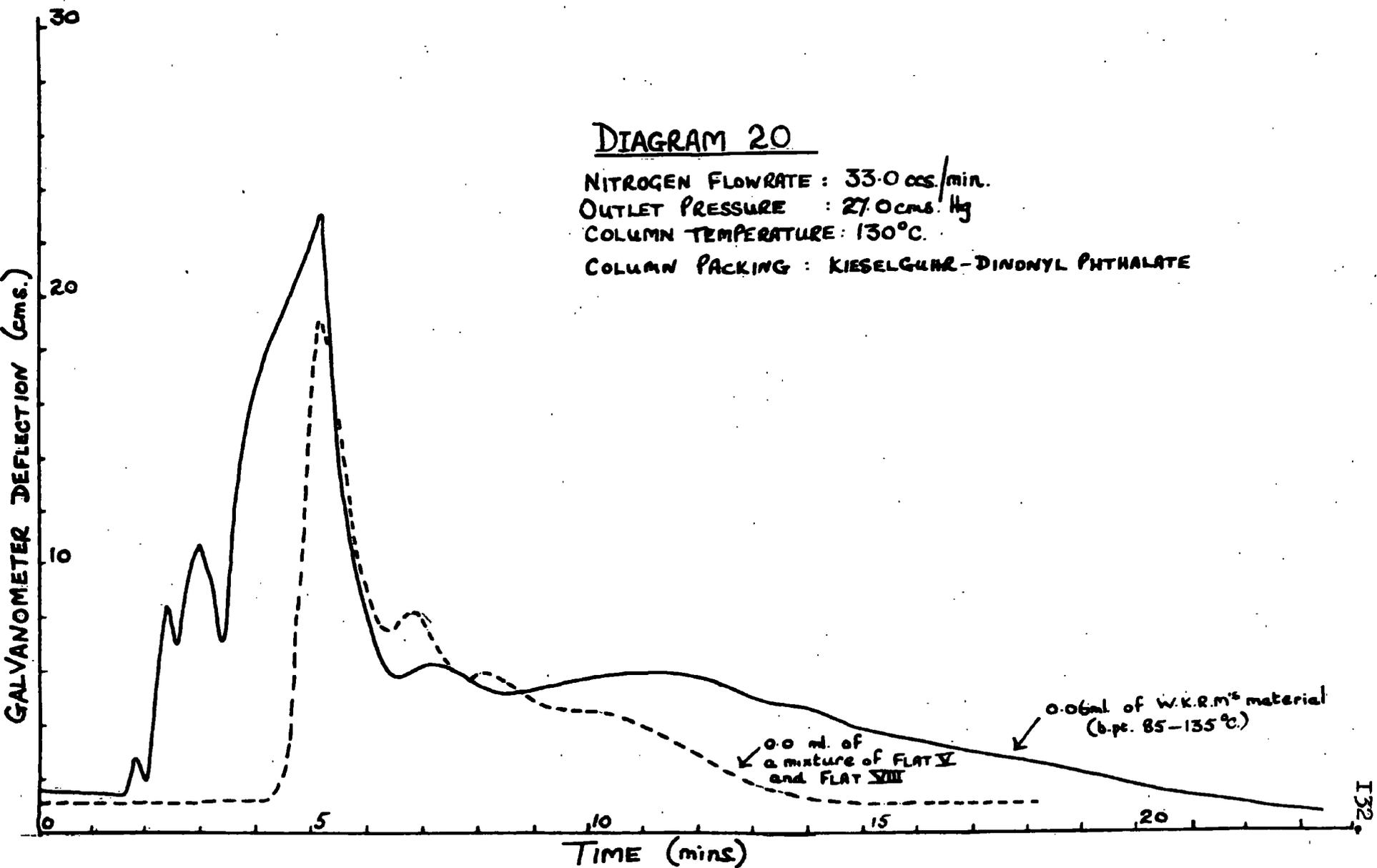
DIAGRAM 20

NITROGEN FLOWRATE : 33.0 ccs./min.

OUTLET PRESSURE : 27.0 cms. Hg

COLUMN TEMPERATURE : 130°C.

COLUMN PACKING : KIESELGUR-DINONYL PHTHALATE

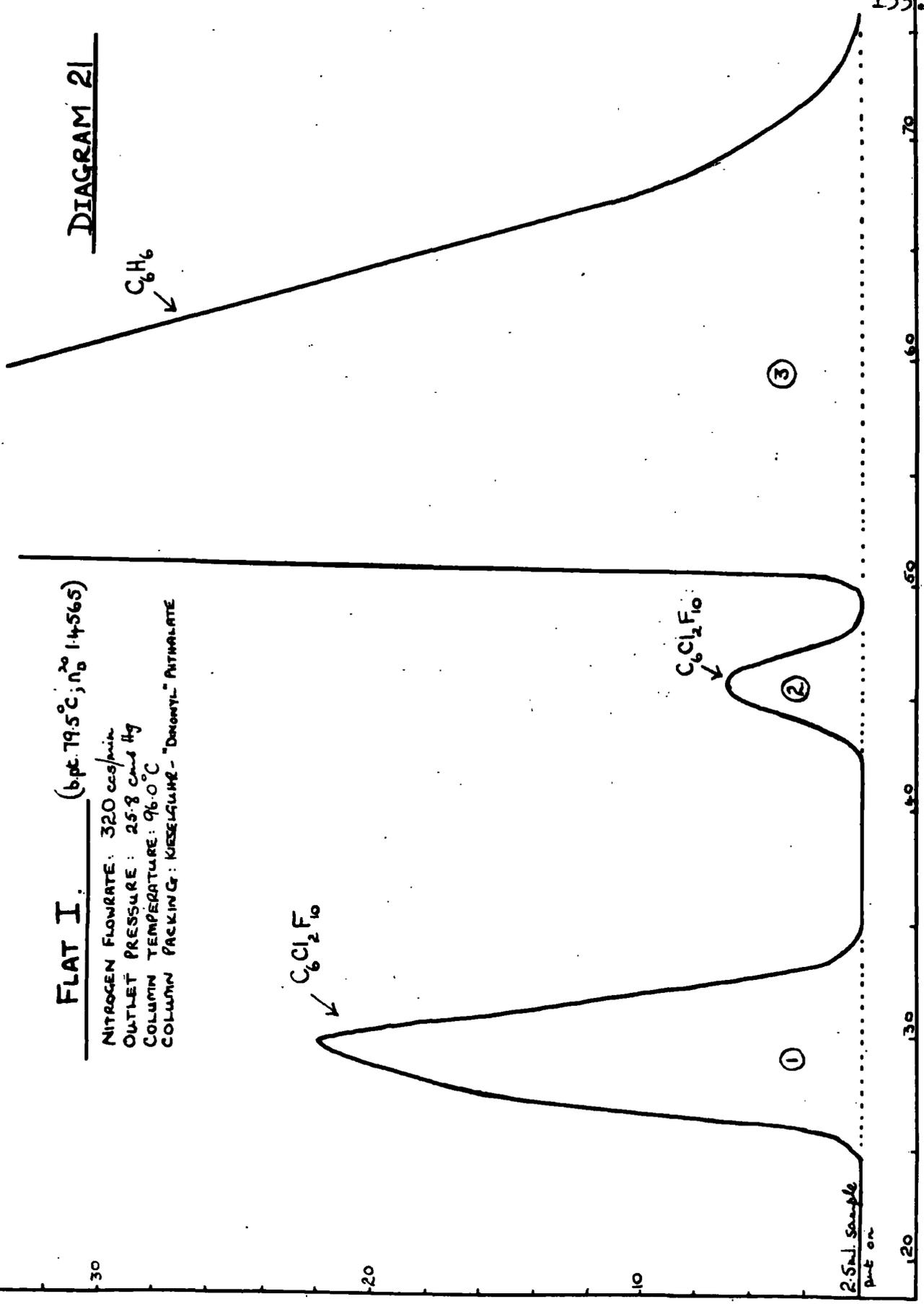


FLAT I. (b.pt. 79.5°C; n_D²⁰ 1.4565)

NITROGEN FLOWRATE: 320 ccg/min
 OUTLET PRESSURE: 25.8 cm Hg
 COLUMN TEMPERATURE: 96.0°C
 COLUMN PACKING: KIESELGUHR - "DINOMYL" ANTIALATE

DIAGRAM 21

GALVANOMETER DEFLECTION (CMS.)



TIME (mins)

FLAT III bpt 109-11 °C; No 1-3660

NITROGEN FLOWRATE: 250 ccs/min.

OUTLET PRESSURE: 24.0 cms.Hg

COLUMN TEMPERATURE: 105 °C

COLUMN PACKING: KIESELQUARTZ - DIMONYL PHTHALATE.

DIAGRAM 22

GALVANOMETER DEFLECTION (CMS)

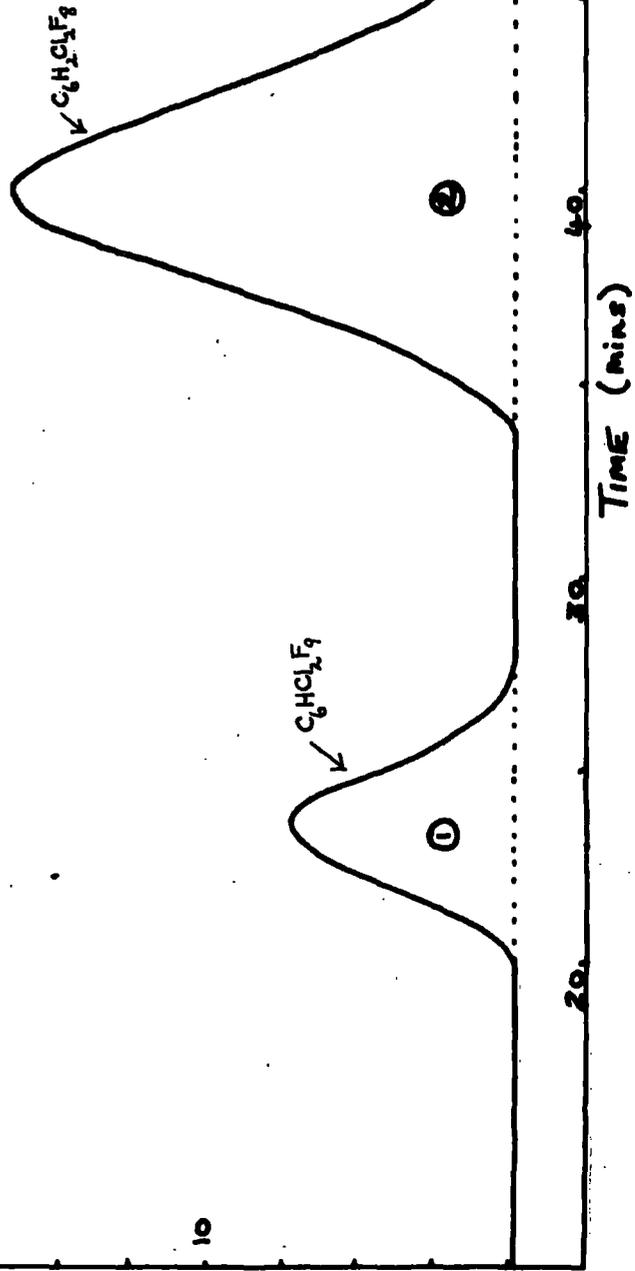
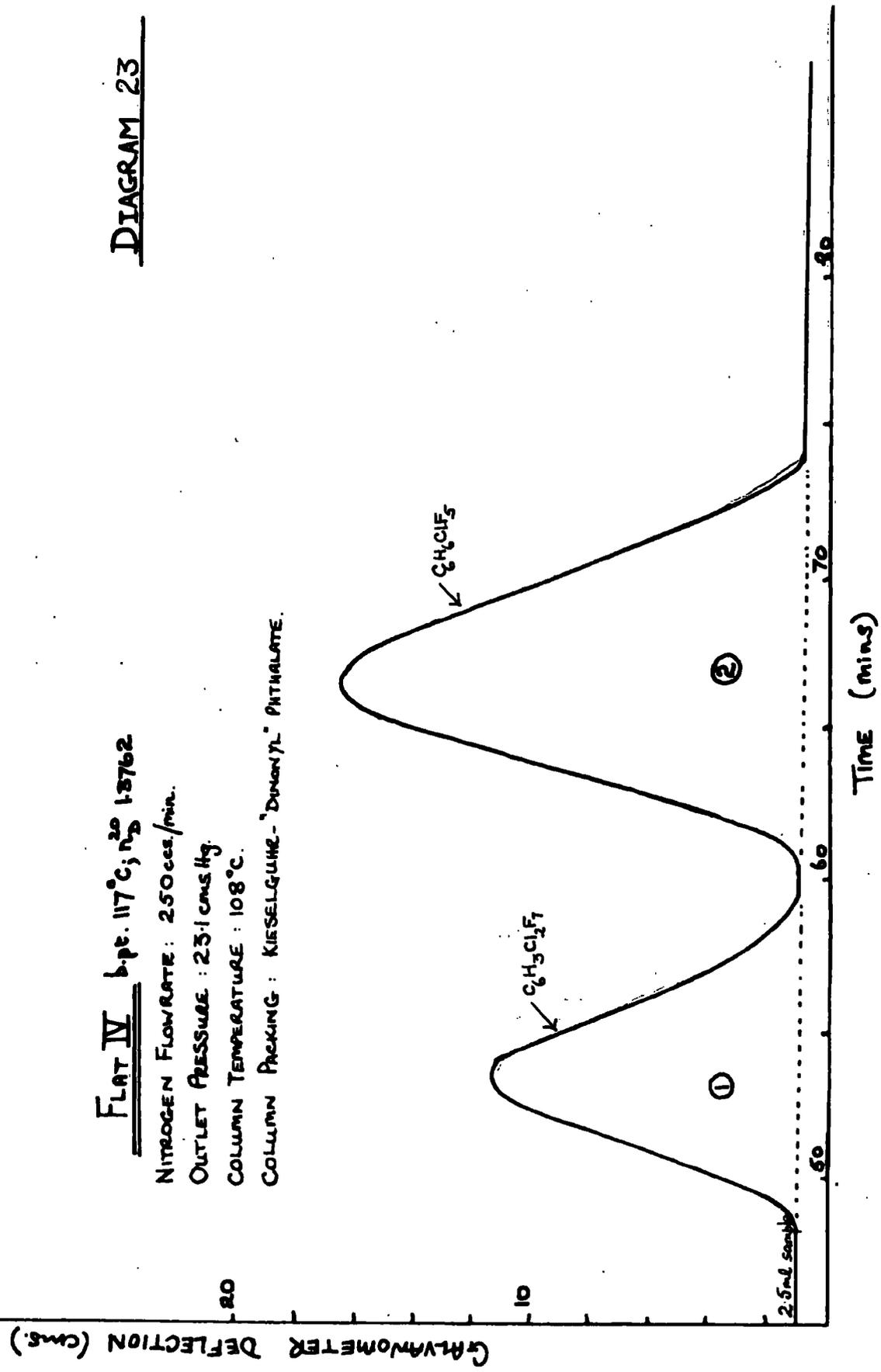


DIAGRAM 23

FLAT IV b.pt. 117°C; n_D^{20} 1.3762
 NITROGEN FLOWRATE: 250 cc./min.
 OUTLET PRESSURE: 23.1 cms Hg.
 COLUMN TEMPERATURE: 108°C.
 COLUMN PACKING: KIESELGUHR-"DIMONYL"-PHTHALATE.



FLAT II b.p. 81.0°C; n_D^{20} 1.4920

NITROGEN FLOWRATE: 258 ccs/min.

OUTLET PRESSURE: 20.0 cms. Hg.

COLUMN TEMPERATURE: 100.0°C.

COLUMN PACKING: KIESELGUHR-DINOMYL
PHTHALATE

DIAGRAM 24

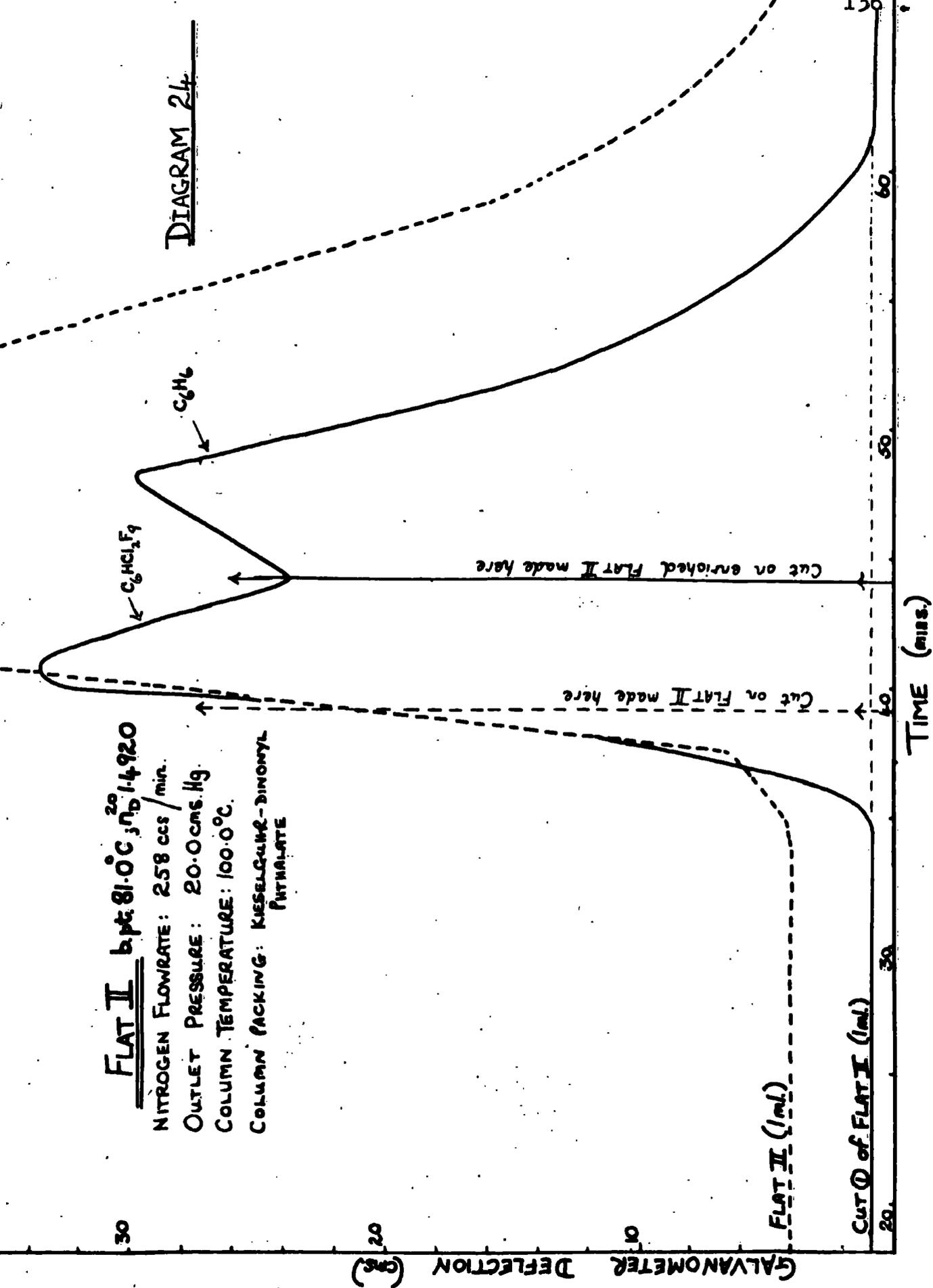


DIAGRAM 25

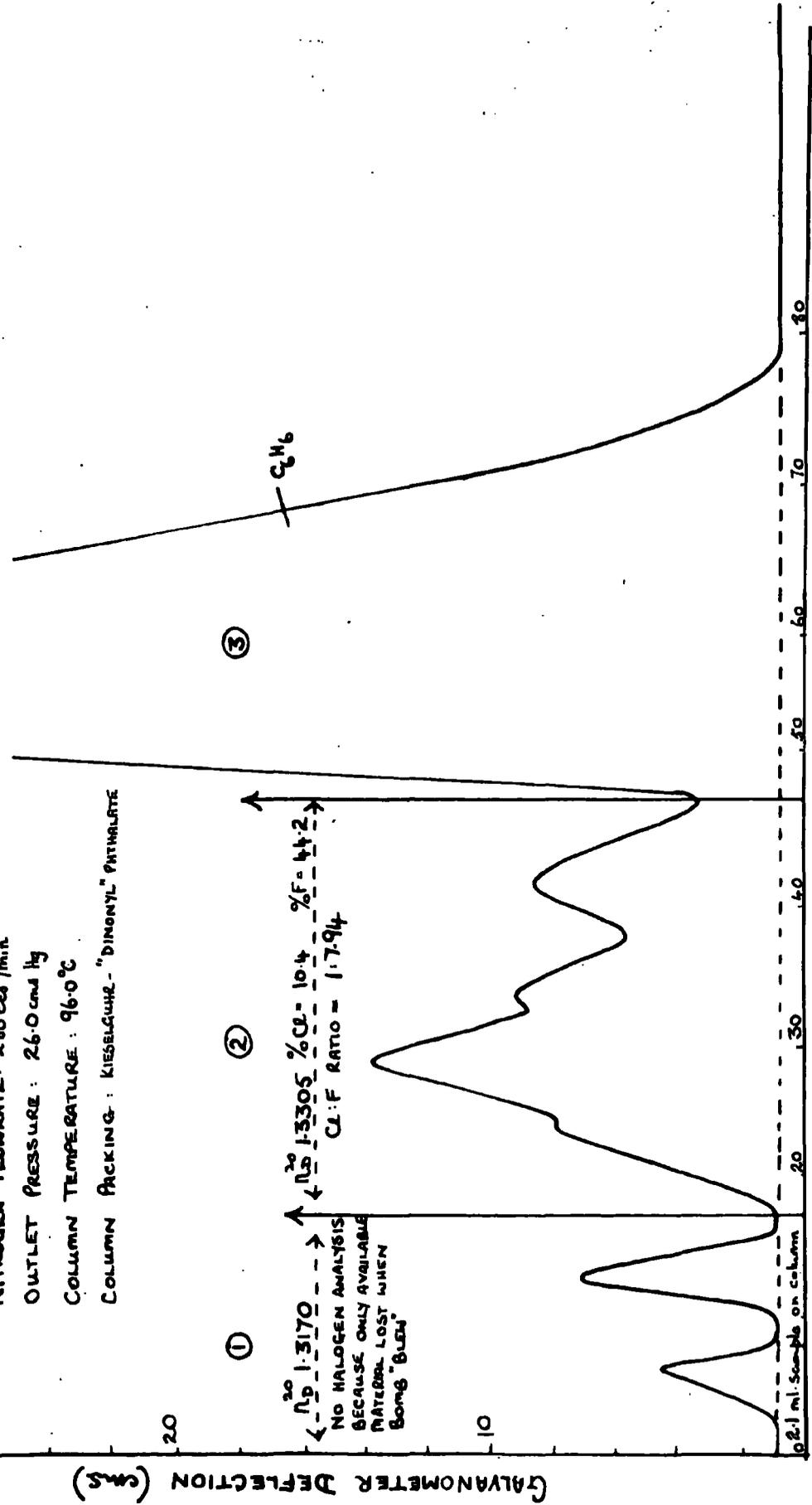
MATERIAL PRIOR TO FLAT I bpt. 58°C - 79°C ; n_D 1.358 - 1.456

NITROGEN FLOWRATE: 280 cc/min

OUTLET PRESSURE: 26.0 cm Hg

COLUMN TEMPERATURE: 96.0°C

COLUMN PACKING: KIESELGUHR - "BINONYL" PHTHALATE



FLAT VIII b.pt. 129.5°C; n_D^{20} 1.4350

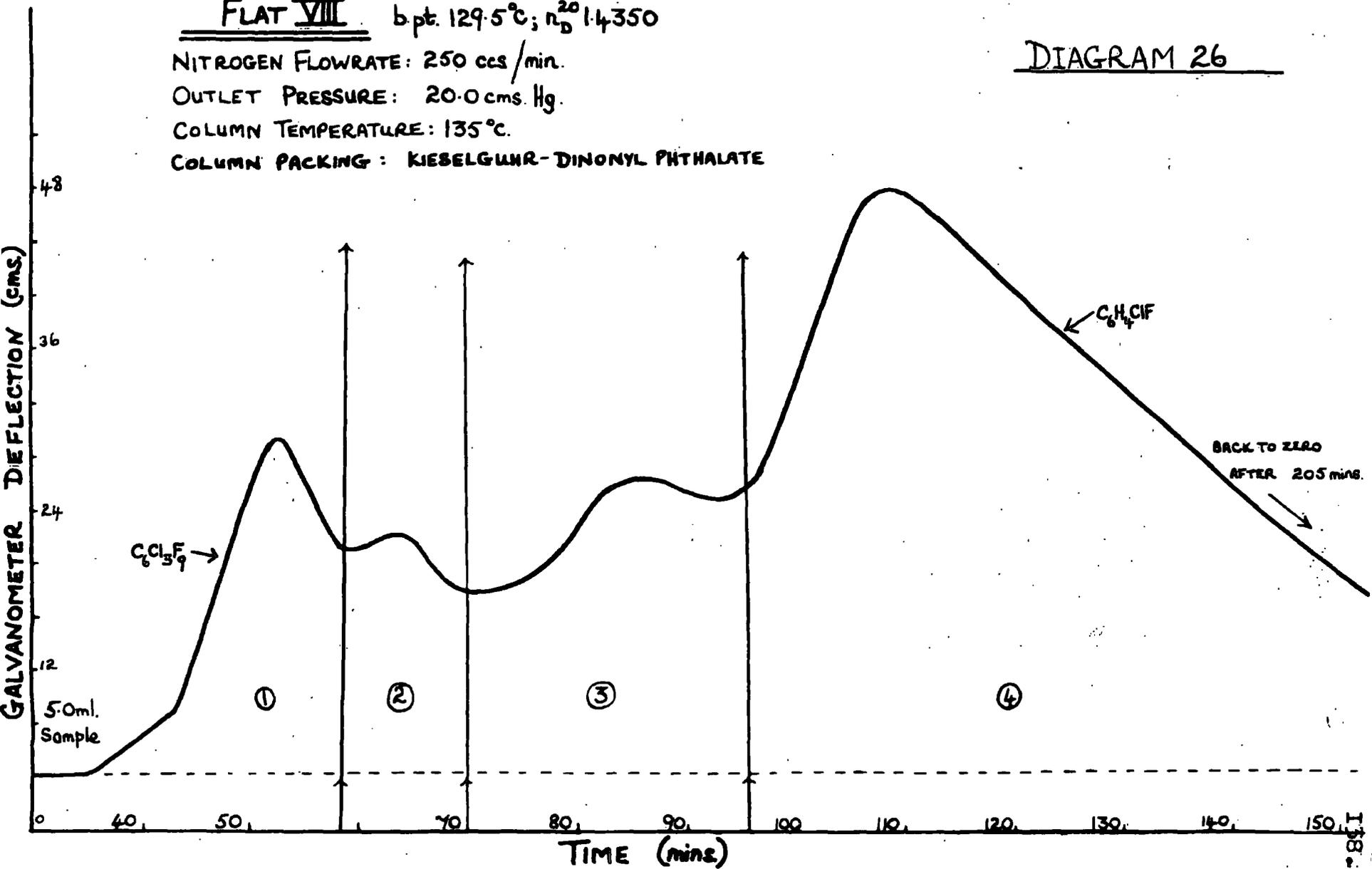
NITROGEN FLOWRATE: 250 ccs/min.

OUTLET PRESSURE: 20.0 cms. Hg.

COLUMN TEMPERATURE: 135°C.

COLUMN PACKING: KIESELGUHR-DINONYL PHTHALATE

DIAGRAM 26



FLAT VIII b.pt. 129.5°C; n_D^{20} 1.4350

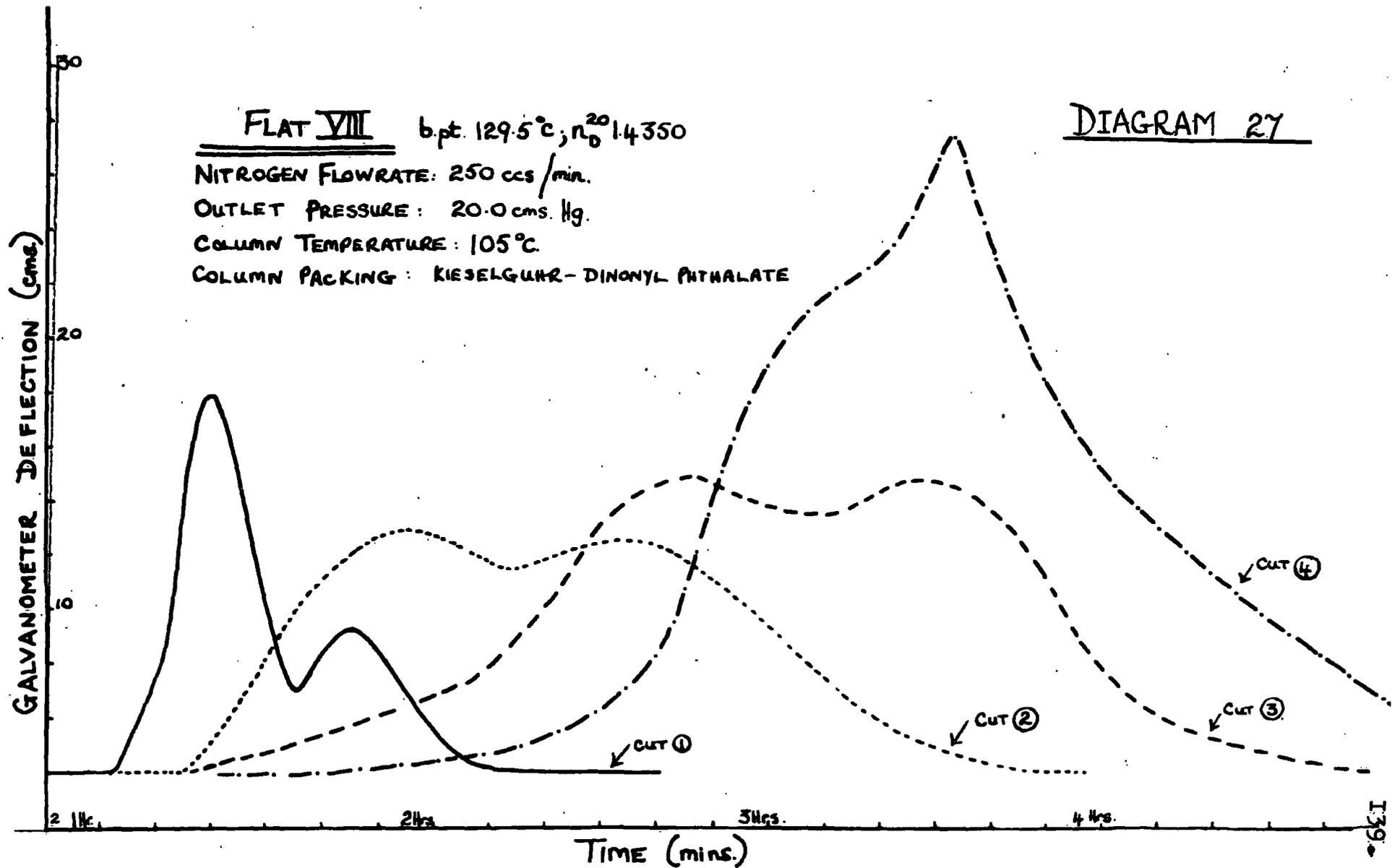
NITROGEN FLOWRATE: 250 ccs/min.

OUTLET PRESSURE: 20.0 cms. Hg.

COLUMN TEMPERATURE: 105°C.

COLUMN PACKING: KIESELGUHR-DINONYL PHTHALATE

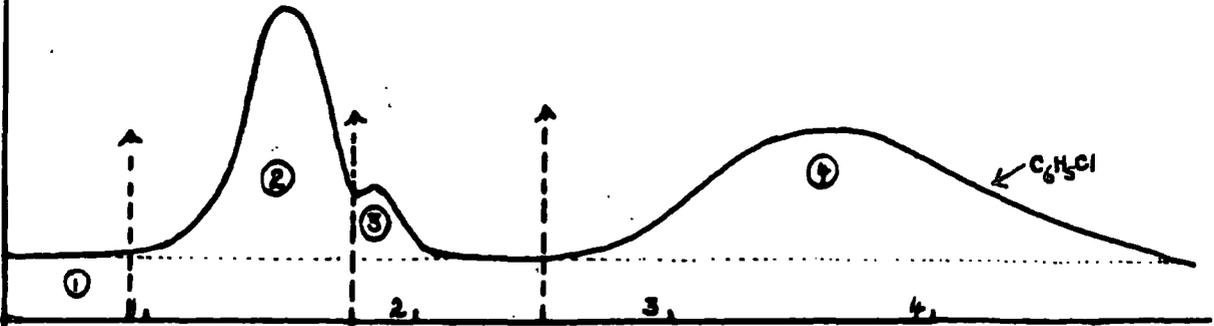
DIAGRAM 27



FLAT VI

b.pt. 124.0 °C; n_D^{20} 1.4087

DIAGRAM 28



FLAT VI

b.pt. 121.0 °C; n_D^{20} 1.3930

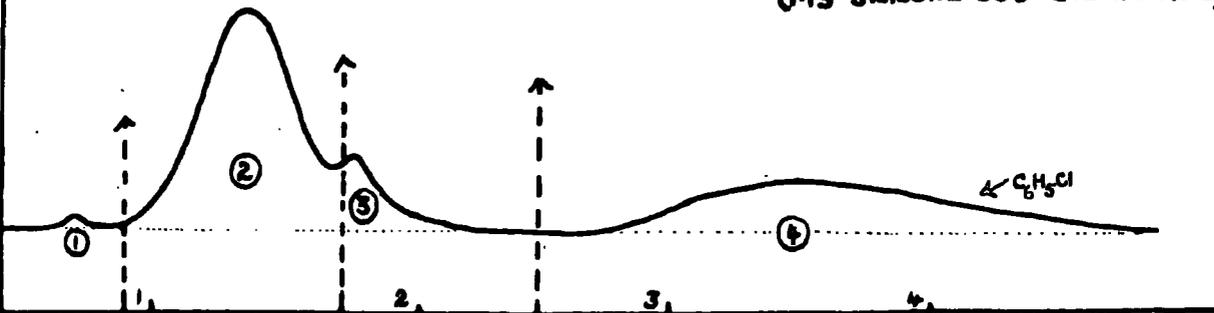
NITROGEN FLOWRATE : 250 ccs./min

OUTLET PRESSURE : 8.0 cms. Hg

COLUMN TEMPERATURE : 110 °C.

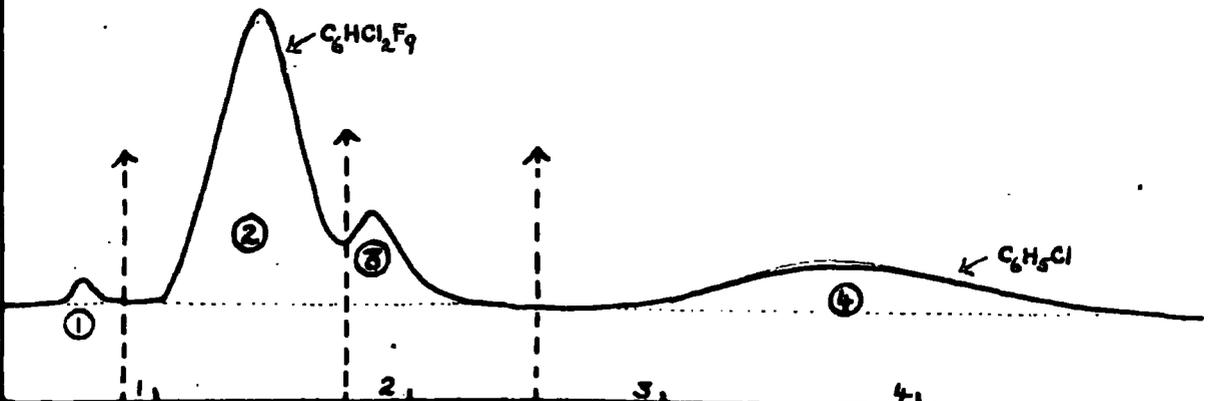
COLUMN PACKING : KIESELGUHR-
(MS SILICONE 550- STEARIC ACID)

GALVANOMETER DEFLECTION



FLAT V

b.pt. 118.0 °C; n_D^{20} 1.3830



TIME (Hrs.)

TABLE 10

The Analysis of Materials obtained by Gas-Chromatographic

Separation of the Distillation

Flats

Flat Number	Amount (gms.)	Peak Number	Amount (gms.)	Proposed Mol. Formula	B.Pt. (°C/764 mm.)	n _D ²⁰	% Cl		% F		Mol. wt.		Cl:F Ratio Found (atom)
							Calc.	Found	Calc.	Found	Calc.	Found	
I	68	1	6.0	C ₆ Cl ₂ F ₁₀	110.5 [*]	1.3385 ^{**}	21.32	21.3	57.06	57.0	333	340	1:5
		2	0.75	C ₆ Cl ₂ F ₁₀	-	1.3420	21.32	19.74	57.06	54.35			1:4.9
		3	60	C ₆ H ₆	80	1.5000	-	-	-	-	78	80	-
II	150	1	5.0	C ₆ HCl ₂ F ₉	-	1.4800	22.54	19.43	54.29	46.0	315	280	1:4.42
		2	135	C ₆ H ₆	-	1.4970	-	-	-	-	-	-	-
III	5	1	2	C ₆ HCl ₂ F ₉	110.0	1.3610	22.54	20.0	54.29	49.2	315	280	1:4.6
		2	3	C ₆ Cl ₂ F ₈ to C ₆ H ₂ Cl ₂ F ₈	108.0	1.3700	24.08	22.27	51.52	49.7	295		
								23.9		51.17	297	278	1:4.1
IV	17	1	6.0	C ₆ HCl ₂ F ₇ to C ₆ H ₃ Cl ₂ F ₇	114.0	1.3796	25.63	25.0	48.02	47.0	277	270	1:3.5
		2	11.0	C ₆ ClF ₅ to C ₆ H ₆ ClF ₅	114.5	1.3608	17.53	17.5	46.9	47.6	202.5	250	1:5.08
								17.03		45.55	208.5		

* B.Pt. at 747 mm. Hg.

** n_D^{25.5} measured because this material melted over the range 15-25°C.

(contd.)

The Analysis of Materials obtained by Gas-Chromatographic Separation of the Distillation Flats (continued)

Flat Number	Amount (gms.)	Peak Number	Amount (gms.)	Proposed Mol. Formula	B.Pt. (°C/764 mm.)	n _D ²⁰	% Cl		% F		Mol. wt.		Cl:F Ratio (atom)	Found
							Calc.	Found	Calc.	Found	Calc.	Found		
V	14	1	0.45	As for Peak 2 Flat IV	-	1.3607	-	-	-	-	-	-	-	-
		2	9.0	C ₆ HCl ₂ F ₉	122.7	1.3551	22.54	21.5	54.29	52.46	315	310	1:4.56	
		3	2.0	-	123.7	1.3770	-	12.4	-	36.9	-	240	1:5.55	
		4	1.0	-	129.0	1.5064	-	20.5	-	5.7	-	146	1:0.53	
VI	17	1	0.2	-	-	1.3606	This peak corresponds to peak 1 Flat V. -							
		2	11.0	C ₆ HCl ₂ F ₉	122.5	1.3551	22.54	22.0	54.29	52.0	315	310	1:4.42	
		3	4.0	-	123.7	1.3823	-	15.0	-	27.01	-	230	1:3.36	
		4	1.5	-	129.7	1.5060	-	27.6	-	9.3	-	204	1:0.6	
VII	9	1	No peak in Flat VII corresponding to peaks 1 of Flats V and VI											
		2	5.0	-	123.0	1.3615	-	23.65	-	48.2	-	270	1:3.81	
		3	1.0	-	123.5	1.3800	-	16.0	-	26.7	-	238	1:3.12	
		4	3.0	C ₆ H ₅ Cl	131.0	1.5168	31.62	29.8	-	3.7	112.5	123	1:0.23	
VIII	70	1	12.5	C ₆ Cl ₃ F ₉	128.5	1.3733	30.48	29.8	48.93	48.0	349.5	350	1:3.01	
		2	7.0	-	130.1	1.3863	-	23.08	-	39.0	-	276	1:3.16	
		3	19.5	-	129.6	1.4335	-	20.65	-	30.0	-	185	1:2.8	
		4	27.0	C ₆ H ₄ ClF	129.7	1.4920	15.02	15.0	28.06	28.0	130.5	138	1:1	

Chapter VI

- (i) Investigations into the presence of Double Bond Structures in the Compounds isolated by means of Gas Chromatography.
- (ii) De-hydrohalogenations and other Experiments.

Part (i)

Peak 3 flat VII appeared, from its analysis and physical constants, to consist mainly of monochlorobenzene; peak 4 flat VIII appeared to be a chlorofluorobenzene, the physical constants being close to those of the p-isomer. Attempts were made to prepare suitable derivatives and so prove this. The other peak materials were investigated for the presence of olefinic double bonds.

Qualitative tests for unsaturation were carried out on all the "peaks" listed in TABLE IO using the following reagents:- aqueous, acid (H_2SO_4), potassium permanganate (1.25 gms./litre), and a solution of bromine in chloroform (0.2 gms./50 mls.). Peak 2 flat III ($C_6H_xCl_2F_8$), and peak 2 flat VII ($C_6HCl_2F_9$) decolorised both reagents very slowly, but in all other cases the results were negative.

Quantitative detections were attempted, the reactions employed being hydrogenation, bromination, and the action of iodine monochloride, but the results were not conclusive and infra-red analyses had to be undertaken.

HYDROGENATIONS

Apparatus

The Towers' General Purpose Hydrogenator used, together with the modified hydrogenation chamber, which was designed to facilitate the removal and filtration of the reaction mixture, are shown in DIAGRAM 29 .

Catalyst

The catalyst used in all the experiments was a 5% palladium carbon prepared according to the instructions given by CHERONIS ("Technique of Organic Chemistry" Vol. VI, p. 240).

Solvent

The efficiencies of various organic solvents used in hydrogenations carried out at room temperature and atmospheric pressure fall into the following order (CHERONIS AND LEVIN, J. Chem. Ed., 1943, 20, 488):-

ethanol > 2-propanol > esters > ethers > hydrocarbons.

Moreover, 85% ethanol is more efficient than either 95% or absolute ethanol. Thus, 85% ethanol was used as a solvent in all the experiments.

Experimental Procedure

Approximately 30 mls. of solvent and 0.25 gms. of

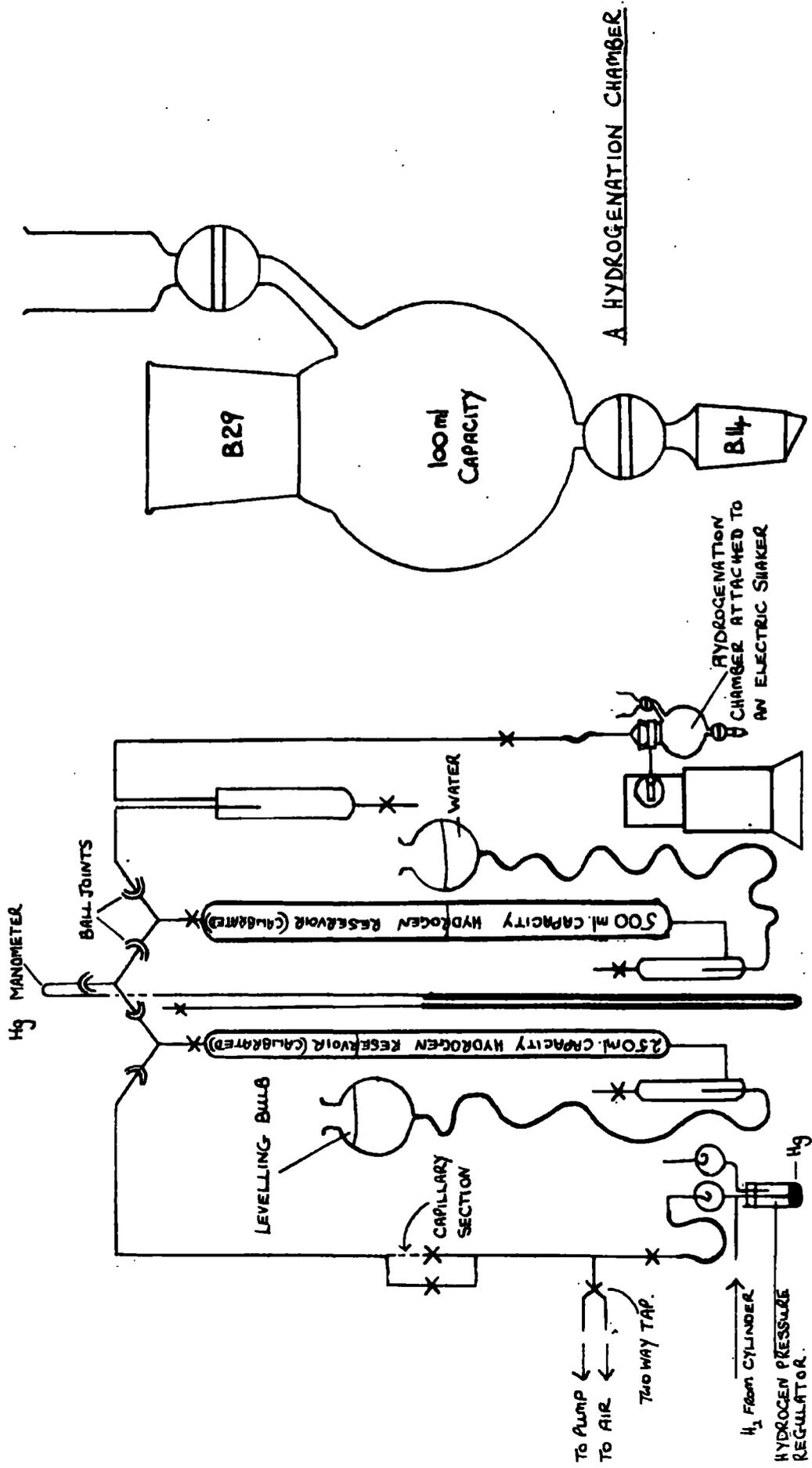


DIAGRAM 29 THE LAYOUT OF A TOWERS' GENERAL PURPOSE HYDROGENATOR

catalyst were placed in the hydrogenation chamber and the apparatus filled with hydrogen. After saturating the catalyst with hydrogen, the sample to be reduced (ca. 200-500 mgms.) was transferred quantitatively, using about 30 mls. of solvent, into the side-arm of the flask and allowed to run into the chamber under the influence of a slight reduced pressure effected either by lowering a water reservoir, or by means of the water pump attached to the apparatus. The shaker was then started, and the hydrogen introduced into the reaction chamber from the graduated tubes at a positive pressure of 1 cm. of mercury. When absorption of hydrogen had ceased the amount taken up was noted, the hydrogenation chamber removed, and the contents filtered through a Green's Number 401 paper under gravity. Filtration under suction was found to cause loss of any halogen hydracid present in the solution. The total halogen removed from the material was estimated by titrating the filtrate with standard (c.N/10) sodium hydroxide solution, using phenolphthalein as indicator, until the pink coloration at the end-point lasted for 30 seconds. One drop of N/100 nitric acid was then added and the chlorine present estimated by titration with standard (c.N/10) silver nitrate solution using dichloro-R-fluorescein as indicator.

The fluorine removed from the compound was estimated by difference, and the amount of olefinic double bond by calculating the amount of hydrogen required to replace the halogen removed and subtracting it from the amount of hydrogen absorbed during the reaction. As some of the compounds isolated from Chlorofluorination Run No. I could be de-hydrohalogenated by titrating them with N/10 alkali, blank hydrogenations were carried out in which no hydrogen and no catalyst were used. The compounds were simply dissolved in 60 mls. of solvent, the solution shaken in the apparatus for 20 minutes, then titrated as above. The results of these blank experiments are shown in TABLE 12. Corrections could then be applied to the actual hydrogenation experiments, and the results are given in TABLE 13. Also shown are details of the hydrogenations of flat III before separation, and flat XII which analysed to a pure compound. TABLE 11 gives details of hydrogenations carried out on known compounds.

A blank experiment was also carried out on the catalyst by placing 0.25 gms. in the apparatus with 60 mls. of solvent and saturating with hydrogen. The mixture was then filtered and the filtrate titrated as above. It was found that 0.00036 gm. equivalents of

TABLE II

The Hydrogenation of Known Compounds

(Catalyst: 5% Pd/C; solvent: 85% EtOH-H₂O)

Compound	Amount taken (gms.)	Solvent (mls.)	Catalyst (gms.)	H ₂ used up (mls. at N.T.P.)	Time taken (mins.)	% available Cl replaced	% available F replaced	% Double Bond saturated
<u>cyclohexene</u>	1.0448	100	0.3	284.5	12	-	-	99.6
1-chloro <u>cyclohexene</u>	0.8516	60	0.3	244.0	18	68.9	-	81.0
1,2,3,3-tetra- chloro-1,1-di- fluoropropene- (2)	1.5662	60	0.3	724.0	-	88.3	none	79.0
monochloro- benzene	0.1488	50	0.2	32.0	20	96.0	-	-
p-chlorofluoro- benzene	0.2306	50	0.2	40.0	20	90.0	-	-

TABLE 12

Blank Hydrogenations

(Solvent: 60 mls. of 85% EtOH)

Flat No.	Peak No.	Proposed Mol. Formula	Amt. taken (gms.)	Shaking Time (mins.)	% available Cl removed	% available F removed
I	1	$C_6Cl_2F_{10}$	0.1733	20	none	none
III	1	$C_6HCl_2F_9$	0.1904	20	negligible	3.68
	2	$C_6H_xCl_2F_8$	0.2308	20	1.8	2.97
IV	1	$C_6H_xCl_2F_7$	0.2284	20	5.4	2.2
	2	$C_6H_xClF_5$	0.1857	20	9.7	4.5
V	2	$C_6HCl_2F_9$	0.1281	20	16.4	6.5
VI	2	$C_6HCl_2F_9$	0.1519	20	10.6	5.0
VII	2	$C_6HCl_2F_9$	0.1537	20	14.2	2.8
VIII	1	$C_6Cl_3F_9$	0.1384	20	none	none
XII	-	$C_6H_xCl_2F_5$	0.1366	20	19.4	11.2
III	-	-	0.3551	20	0.4	3.0

TABLE 13

The Hydrogenations of "Peak" Materials
(Catalyst: 5% Pd/C; 85% EtOH - H₂O).

Flat No.	Peak No.	Proposed Mol. Formula	Amt. taken (gms.)	H ₂ used up (mls. at N.T.P)	Time taken (mins.)	% available Cl replaced	% available F replaced	% Double Bond present
I	1	C ₆ Cl ₂ F ₁₀	0.3222	12.0	30	36.5	negligible	negligible
III	1	C ₆ HCl ₂ F ₉	0.1615	13.6	6	48.0	negligible	negligible
	1	C ₆ HCl ₂ F ₉	0.3785	51.06	40	70.0	18.1	2.0
	2	C ₆ H _x Cl ₂ F ₈	0.5824	71.0	80	35.0	negligible	10.0
IV	1	C ₆ H _x Cl ₂ F ₇	0.2371	26.2	30	34.8	negligible	5.8
	2	C ₆ H _x ClF ₅	0.1669	22.5	30	24.3	3.1	negligible
V	2	C ₆ HCl ₂ F ₉	0.3594	11.2	20	20.2	1.3	5.0
	3	-	0.2216	12.0	30	39.4	5.2	-3.1 †
	4	-	0.1415	88.0	60	82.5	2.0	negligible †
VI	2	C ₆ HCl ₂ F ₉	0.2389	8.5	20	25.0	negligible	10.0
	3	-	0.2077	11.0	20	34.7	4.5	negligible †
	4	-	0.2598	44.5	30	80.3	negligible	negligible †

(contd.)

The Hydrogenations of "Peak" Materials (continued).

Flat No.	Peak No.	Proposed Mol. Formula	Amt. taken (gms.)	H ₂ used up (mls. at N.T.P.)	Time taken (mins.)	% available Cl replaced	% available F replaced	% Double Bond present
VII	2	C ₆ HCl ₂ F ₉	0.2182	16.5	30	28.2	3.0	15.5
	4	C ₆ H ₅ Cl	0.0982	17.6	20	93.0	-	6.0
VIII	1	C ₆ Cl ₃ F ₉	0.2083	16.0	20	29.3	4.2	negligible
	2	-	0.2085	24.1	20	27.5	1.0	negligible *
	3	-	0.1911	19.0	20	30.2	1.0	negligible *
	4	C ₆ H ₄ ClF	0.2407	40.0	20	83.2	none	negligible
XII	-	C ₆ H _x Cl ₂ F ₅	0.2717	23.5	20	20.0	8.7	10.0
III	-	C ₆ HCl ₂ F ₉	0.4813	50.5	100	40.5	7.8	6.3
		C ₆ H _x Cl ₂ F ₈						

* No correction applied for hydrolysis of starting material.

chlorine were present, which obviously originated from residual hydrochloric acid used in the preparation of the catalyst. A correction for this was applied to the results.

BROMINATIONS

Quantitative brominations of materials, which appeared from their analyses to be pure compounds (see TABLE (O)), were attempted by sealing the reactants in small glass bulbs and heating them in a furnace at 90°C. for a period of one week whilst irradiating them with ultra-violet light. After this time the bulbs were allowed to cool to room temperature, further cooled in an ethanol-"Drikold" mixture and then broken open under 10% potassium iodide solutions contained in polythene beakers. By titrating the liberated iodine with standard sodium thiosulphate solution the unreacted bromine was estimated. The results of the experiments are given in TABLE 14.

IODINE MONOCHLORIDE EXPERIMENTS

The materials which analysed to compounds were also treated with iodine monochloride in the following manner. About 150 mgms. of material and 200 mgms. of iodine monochloride were weighed into small (4 mm. internal diameter) Carius tubes, which were heated in a furnace at 120°C. for

24 hours. They were then allowed to cool to room temperature, and the unreacted iodine monochloride estimated by the method of CORNOG AND KARGES (J.A.C.S., 1932, 54, 1882). The tubes were cooled in an ethanol-"Drikold" mixture, opened, and excess of solid potassium thiocyanate added. They were then sealed by means of rubber teats and stood in an ice-water mixture for five hours, after which time they were broken open under distilled water contained in polythene beakers. The iodine which had been liberated was then extracted from the aqueous solution with carbon tetrachloride and titrated with standard sodium thiosulphate solution. From the titre, and a knowledge of the equation, the amounts of iodine



monochloride used up were calculated in terms of iodine. The results of the experiments are given in TABLE 15.

EXAMINATION OF PEAK 4. FLAT VIII.

The Nitration of Chlorobenzene (see HOFFMAN AND DAME, *ibid.*, 1919, 41, 1013).

A nitrating mixture consisting of 20 mls. of fuming nitric acid and 30 mls. of concentrated sulphuric acid was placed in a three-necked 100 ml. flask provided with a

TABLE 14Bromination Experiments

Flat No.	Peak No.	Proposed Mol. Formula	Amt. Taken (gms.)	Amt. Br ₂ Taken (gms.)	Amt. Br ₂ used up (gms.)	Amt. Br ₂ required to saturate one double bond or replace one H atom (gms.)
III	1	C ₆ HCl ₂ F ₉	0.1221	0.3050	0.0428	0.062
III	2	C ₆ H _x Cl ₂ F ₈	0.1085	0.2131	0.080	0.0588
IV	1	C ₆ H _x Cl ₂ F ₇	0.1568	0.2377	0.0469	0.0904
IV	2	C ₆ H _x ClF ₅	0.1104	0.2199	0.0464	0.0855
V	2	C ₆ HCl ₂ F ₉	0.2071	0.2399	0.0219	0.1054
VIII	1	C ₆ Cl ₃ F ₉	0.0905	0.2099	0.008	-

TABLE 15

Iodine Monochloride Experiments

Flat No.	Peak No.	Proposed Mol. formula	Amt. Taken (gms.)	Amt. ICl Taken (gms)	I equivalent to ICl Taken (gms.)	I used up (gms.)	Amount of ICl in term of gms. I for saturation of one double bond, or replacement of one H Atom.
III	1	$C_6HCl_2F_9$	0.1238	0.2876	0.2248	0.0452	0.050
III	2	$C_6H_xCl_2F_8$	0.1170	0.2520	0.1970	0.0730	0.050
IV	1	$C_6H_xCl_2F_7$	0.1891	0.4311	0.3369	0.0231	0.0867
IV	2	$C_6H_xClF_5$	0.0784	0.2564	0.2004	0.0727	0.0477
V	2	$C_6HCl_2F_9$	0.1363	0.4101	0.320	0.0267	0.0552
VIII	1	$C_6Cl_3F_9$	0.2853	0.6648	0.5196	0.009	-

Blank: 0.6559 gms ICl when treated with excess KCNS liberates, theoretically, 0.342 gms. of iodine. Amount found, 0.343 gms.

dropping funnel, reflux condenser and thermowell. From the dropping funnel was added 10 gms. of chlorobenzene, the operation taking one hour during which the temperature of the mixture rose to 45°C . The dropping funnel was then replaced by a stirrer, and the contents of the flask heated at 100°C . for two hours by means of an "Isomantle". The mixture was then cooled to c. 50°C ., and poured on to ice when the 2,4-dinitro compound separated out. Yield 17.5 gms. (96% of theoretical). On recrystallisation from absolute alcohol material was obtained with m.pt. 46°C . This was unchanged on further recrystallisation from methyl ether.

The Nitration of Peak 4 Flat VII Material

To 8 mls. of a similar nitrating mixture (see above) contained in a 25 ml. flask provided with a reflux condenser was added 0.54 gms. of peak 4 flat VII material (b.pt. 131°C ; n_{D}^{20} 1.5168). The mixture was heated at 100°C . for two hours with occasional shaking, cooled, and poured on to ice. Material separated, which, on recrystallisation from absolute alcohol, had m.pt. 45°C . and mixed m.pt. (with 2,4-dinitrochlorobenzene from above experiment) 45.5°C . It was taken and warmed for five minutes with 3-4 drops of aniline in a water bath. On

cooling 2:4-dinitrodiphenylamine was obtained as a bright red crystalline mass, m.pt. 155-155.5°C. after recrystallisation from rectified spirit.

Hydrogenation of Peak 4 Flat VII Material

The results for this experiment are given in TABLE 13, and can be compared with the results for an authentic specimen of chlorobenzene which are given in TABLE 11.

EXAMINATION OF PEAK 4 FLAT VIII

The Hydrolysis of p-Chlorofluorobenzene (see DE CRAUW,

Rec. trav. chim., 1931, 753).

70 gms. of p-chlorofluorobenzene were sealed up with 80 mls. of 3N sodium methylate in a Carius tube, and the mixture heated at 180°C. for a period of 15 hours. The reaction product was brown in colour, contained an appreciable amount of white sediment, and smelled strongly phenolic. It was washed into a distilling flask with water, the sediment dissolving, and about 60 mls. of methyl alcohol and water removed by distillation. The residue was acidified with 100 mls. of 3N hydrochloric acid and steam distilled. The distillate was extracted with ether, the extract dried over anhydrous magnesium sulphate and the ether removed by distillation. Yield

of crude p-chlorophenol 5.5 gms. (79% of theoretical).

Derivatives:- (i) A benzoyl derivative was prepared, m.pt. 92°C . after recrystallisation from methylated spirits (literature quotes 93°C .). (ii) With bromine in acetic acid p-chlorophenol is stated to give a 4-chloro-2:6-dibromophenol (HUNTER AND JOYCE, J.A.C.S., 1917, 39, 2640) m.pt. 92°C . The preparation of this derivative was carried out, and after several recrystallisations from an alcohol-water mixture, and a decolorisation with animal charcoal, material with m.pt. 90°C was obtained.

The Hydrolysis of Peak 4 Flat VIII Material

The above experiment was repeated on two batches of material from peak 4 flat VIII. (a) 10 gms. of material with b.pt. 130°C ., n_{D}^{20} 1.4920 were hydrolysed with 100 mls. of 3N sodium methylate at 185°C . for 20 hours and (b) 70 gms. of material with b.pt. 130°C ., n_{D}^{20} 1.4890 were hydrolysed with 80 mls. of 3N sodium methylate at 185°C . for 10 hours. In both cases the yield of product was small, and although the same phenolic smell was experienced as in the above experiment, it was accompanied by a hydrocarbon-like odour. The preparation of a benzoyl derivative was attempted but proved unsuccessful, the product being an oil which could not be persuaded to

solidify. On treatment of samples of the products from the hydrolyses with (i) ferric chloride in aqueous solution, a transient blue-purple colour was observed, (ii) ferric chloride in alcohol, a green coloration was obtained and (iii) with bromine water, a precipitate was obtained. No attempt was made to isolate a bromo derivative because the phenolic material was obviously a mixture, and only a small amount was available.

INFRA-RED ANALYSIS

(Quoted from the report of Dr. D.H. Whiffen.)

Apparatus

Two instruments were employed. One was a single-beam Grubb Parsons spectrometer (i), and the other a single-beam instrument, made in the workshops at Birmingham University, which incorporated a grating and had a greater resolving power. (ii).

Measurements

The materials were measured (i) in the region $1800-1500 \text{ cm}^{-1}$ in C. 0.3M solution in carbon tetrachloride. Experience of perfluoro-cyclohexenes and -cyclohexadienes and also hydro- derivatives indicates that the double bond absorption occurs in the range $1770-1630 \text{ cm}^{-1}$, and

that the exact frequencies depend on conjugation and environment. The intensity is normally 60% absorption under the above conditions with a 0.1 mm. rock salt cell, and always above 20% in the cases studied. The materials were also measured (ii) as pure liquids in the same 0.1 mm. cell from 2800-3200 cm^{-1} , which is the region characteristic of C-H stretching frequencies, the value c. 2980 cm^{-1} being found for hydroperfluoro-cyclohexanes. With the H atom attached to a double bond the frequency is likely to be rather higher, c. 3050 cm^{-1} .

Results

FLAT III PEAK 1 ($\text{C}_6\text{HCl}_2\text{F}_9$) (i) All absorption less than 10% (ii) Bands at 2881 cm^{-1} (medium), 2992 cm^{-1} (strong), and 3094 cm^{-1} (medium). Conclusion:- saturated and contains hydrogen.

FLAT III PEAK 2 ($\text{C}_6\text{H}_x\text{Cl}_2\text{F}_8$) (i) 30% absorption at 1695 cm^{-1} (ii) Bands at 2881 cm^{-1} (weak), 2984 cm^{-1} (medium), 3040 cm^{-1} (weak), and 3105 cm^{-1} (medium). Conclusion:- certainly contains hydrogen and probably some double bond; unexpectedly it would seem likely that some of the hydrogen is attached at the double bond. The intensities are:

consistent with a mixture.

FLAT IV PEAK 1 ($C_6H_xCl_2F_7$) (i) 15% absorption at 1695 cm.^{-1}
 (ii) Bands at 2868 cm.^{-1} (weak), 2984 cm.^{-1} (weak),
 and 3097 cm.^{-1} (strong). Conclusion:- much as for
 flat 3 peak 2 though the indications of unsaturation
 are weaker.

FLAT IV PEAK 2 ($C_6H_xClF_5$) (i) 10% absorption at 1695 cm.^{-1}
 (ii) Bands at 2975 cm.^{-1} (weak), 2984 cm.^{-1} (very strong),
 3036 cm.^{-1} (very weak), and 3090 cm.^{-1} (strong).

Conclusion:- almost all saturated, but may be a trace
 of unsaturation. Certainly contains more hydrogen than
 the other samples.

FLAT V PEAK 2 ($C_6HCl_2F_9$) (i) 10% absorption at 1695 cm.^{-1}
 (ii) Bands at 2875 cm.^{-1} (very weak), 2992 cm.^{-1}
 (strong), 343 cm.^{-1} (weak). Conclusion:- probably
 saturated.

FLAT VIII PEAK 1 ($C_6Cl_3F_9$) (i) All absorption less than
 10% (ii) Band at 2990 cm.^{-1} (very weak). Conclusion:-
 saturated and virtually free of hydrogen.

The interpretation of the bands near 2875 and 3110 cm.^{-1}
 is not clear. The most probable interpretation is that
 these are difference and summation tones respectively of
 the C-H stretching and a low frequency of c. 115 cm.^{-1}

This is supported by the fact that the former is always considerably the weaker. The compounds also showed rich spectra when measured as pure liquids in the 0.1 mm. cell from 1500-1800 cm.^{-1} , but there is no reason to doubt that these are summation bands and not of great interest.

FLAT VIII PEAK 3 (mixture) (i) 95% absorption at 1510 cm.^{-1} Conclusion:- essentially aromatic in nature.

FLAT VIII PEAK 4 ($\text{C}_6\text{H}_4\text{ClF}$) This material was measured from 700-1800 cm.^{-1} between sodium chloride plates. The spectra of the para isomer (NARASIMHAN, SABBAN AND NIELSEN, J. Chem. Physics, 1956, 24, 420) and the ortho isomer (NARASIMHAN AND NIELSEN, *ibid.*, p. 433) have been published and a comparison suggests that the para isomer is present to an appreciable extent (say 40%), and that there may well be some ortho (say 20%) although there remains some doubt on this point. There is certainly a further component or components with absorption bands at 701, 739, 775, 805 cm.^{-1} and elsewhere. Although 701 and 775 cm.^{-1} are about the expected positions for two strong bands of the meta isomer, the bands at 739 and 805 cm.^{-1} are even stronger and not altogether expected for this isomer. In the absence of a spectrum

of the meta isomer it is impossible to say whether this compound, a fourth unsuspected material, or both are present.

Part (ii)

Having obtained evidence for the presence of chlorobenzene and chlorofluorobenzene in the product from Chlorofluorination Run No. 1, it was decided to investigate by chemical means the possibility of fluorobenzene being present also. It would be expected to occur in peak 2 flat II material together with benzene and dichlorononafluorocyclohexane, but only in small amounts because gas-chromatographic analysis did not detect its presence.

THE NITRATION OF PEAK 2 FLAT II MATERIAL

100 gms. of peak 2 flat II material were slowly added to a mixture of 60 gms. of concentrated nitric acid and 60 gms. of concentrated sulphuric acid contained in a 250 ml. flask provided with a reflux condenser. The mixture was refluxed for 14 hours, cooled somewhat, and poured on to ice. The organic material which separated appeared to consist of a mixture of mono- and di-nitrated derivatives, and was separated from the aqueous layer.

a) The aqueous layer was continually extracted for 36 hours with ether, the ether extract dried over anhydrous magnesium sulphate and the ether removed by distillation.

The residue remaining consisted of nitrobenzene (b.pt. $211^{\circ}\text{C}.$). No fluoro-dibasic acid material was recovered.

b) The nitrated layer was dissolved in ether, the solution dried over anhydrous magnesium sulphate, and the ether removed by distillation. A further nitration was then carried out according to the instructions given by VOGEL ("Practical Organic Chemistry", p. 508) in order to completely di-nitrate the material. The solid product obtained was agitated with water at $60^{\circ}\text{C}.$, and the mixture filtered hot. By this means unchanged nitrobenzene, together with any 1-fluoro-2:4-dinitrobenzene (m.pt. $23^{\circ}\text{C}.$), was removed from the m-dinitrobenzene. Recrystallisation of the latter from rectified spirit afforded material with a m.pt. $90^{\circ}\text{C}.$, and a mixed m.pt. $90^{\circ}\text{C}.$ The material suspected to contain 1-fluoro-2:4-dinitrobenzene was boiled with 3N sodium hydroxide solution for 4 hours, the mixture cooled, acidified with hydrochloric acid, and then filtered to remove tar and carbonised material. These latter products were boiled with water, again filtered off, and the filtrate added to the main filtrate. A steam distillation of this aqueous solution was then carried out, and the distillate extracted with ether. The ether extract was dried with anhydrous

magnesium sulphate and the ether removed by distillation. A small amount of nitrobenzene only was recovered, no phenolic smell was observed and the residue did not react with aqueous or alcoholic ferric chloride or bromine water.

DE-HYDROHALOGENATIONS

These experiments were carried out as follows. Approximately 200 mgrms. of material was dissolved in 2 mls. of rectified spirit and 25 mls. of alcoholic potassium hydroxide (N) added. In most cases an immediate reaction occurred, solid potassium halides being precipitated, and the supernatant liquid becoming lemon yellow in colour. The mixture was shaken for half an hour, then made up to 100 mls. with distilled water when the precipitate dissolved up and organic material settled out of the solution. Analyses were carried out on the aqueous portion for chloride and fluoride by the method of cation-exchange (see CHAPTER VII). In the cases of peak 2 flat V and peak 1 flat VIII materials experiments were carried out in which the de-hydro-halogenation mixtures were refluxed before halogen analyses were carried out. The results are given in TABLE 16 .

TABLE 16

De-hydrohalogenation Experiments

(Materials shaken with 25 mls. of N. alcoholic KOH)

Flat No.	Flat NO.	Proposed Mol. Formula	Amt. Taken (gms.)	Conditions	% of Available Cl Removed	% of Available F Removed
I	1	$C_6Cl_2F_{10}$	0.2103	Room temp.	negligible	negligible
III	1	$C_6CHCl_2F_9$	0.0898	Room temp.	1.1	18.1
	2	$C_6H_xCl_2F_8$	0.1606	Room temp.	12.8	48.4
IV	1	$C_6H_xCl_2F_7$	0.1693	Room temp.	8.0	19.7
	2	$C_6H_xClF_5$	0.1638	Room temp.	19.5	36.3
V	2	$C_6HCl_2F_9$	0.1729	Room temp.	21.3	28.5
	2	$C_6H_xCl_2F_9$	0.1544	Refluxed for 6 hours	37.1	58.6
VIII	1	$C_6Cl_3F_9$	0.1422	Room temp.	negligible	negligible
	1	$C_6Cl_3F_9$	0.1806	Refluxed for 8 hours	45.3	51.0
XII	-	$C_6H_xCl_2F_5$	0.1146	Room temp.	23.2	24.0
III	-	mixture $C_6HCl_2F_9$ $C_6H_xCl_2F_8$	0.5208	Room temp.	0.00258 gms.	0.08584 gms.

THE OXIDATION OF FLAT III

5.417 gms. of material were heated at 105°C . with potassium permanganate (20 gms.) and water (80 mls.) for 6 hours in a flask provided with a reflux condenser. The reaction mixture was filtered, and the filtrate treated with sulphur dioxide until the excess of permanganate had been reduced, and then refiltered. The filtrate was acidified with concentrated sulphuric acid (10 mls.) and was then extracted continuously with ether for 24 hours. The ether extract was dried over anhydrous magnesium sulphate and distilled to remove ether. A residue of about 3 mls. remained which had a smell resembling that of trifluoroacetic acid. It was dissolved in a small amount of ether and the solution added to aniline in ether. A dianilinium salt was formed which was subsequently recrystallised from acetone. A m.pt. was not obtained because it started to decompose at 210°C . Analysis:- Found 5.7%; F 6.2%; equiv. (by titration with NaOH) 196; Cl:F ratio = 1:2.03. The molecular weight of the acid was, therefore, 206. This analysis does not fit any theoretical formula.

ANALYTICAL SECTION

A method was required whereby the chlorofluoro compounds obtained by the action of chlorine trifluoride on benzene in the vapour phase could be quickly and accurately analysed for halogen content. The method also had to be applicable to compounds containing, besides halogen, nitrogen and oxygen because in the elucidation of the structures of the compounds by chemical means derivatives containing these elements might be obtained (e.g. dianilinium salts of dicarboxylic acids). Such a method, which entirely eliminates all the failings of the hitherto known procedures, has been devised. It is both quick and accurate, and experienced analysts are not essential for its success.

Chapter VII

The Application of Cation Exchange Resins to the
Semi-Micro Determination of Chlorine, Fluorine and
Nitrogen in Organic Compounds.

Introduction

The determination of halogens in fluorine-containing organic compounds has always been tedious and difficult. In the case of fluorine, one is faced, after carrying out the sodium fusion in a nickel bomb such as that described by BELCHER AND TATLOW (*Analyst*, 1951, 76, 593), either with the awkward end-point of a thorium nitrate titration, or with the longer procedure of the lead chloro-fluoride process. As has been shown by BELCHER et al (*Mikrochim. Acta*, 1953, 3, 283; *Analyst*, 1952, 77, 602) both methods will give excellent results in the hands of experienced analysts especially since the possible error involved in seeing the colour change of the sodium alizarin sulphonate has been so much reduced by their colour comparison procedure. For the chlorine, direct argentometric titration of the chloride in a fusion solution using dichloro-R-fluorescein is, in my experience, impossible; other direct methods do not give sufficiently sharp end-points, and again recourse has to be made to longer indirect

methods such as those described by BELCHER, MACDONALD AND NUTTEN (Mikrochim. Acta, 1954, 4, 104), or BROWN AND MUSGRAVE (Anal. Chim. Acta, 1955, 12, 29). I have found, however, that the determination of these elements in organic compounds can be simplified considerably by making use of cation exchange resins which permit the determination of total halogen by alkalimetry. The resins also remove ions which are due to use of excess of sodium in the bomb and its subsequent neutralisation, and which interfere in the chloride estimation. SAMUELSON (Ion Exchangers in Analytical Chemistry, John Wiley and Sons, New York, 1953) has used cation exchange resins for the estimation of chloride, bromide and iodide, and OSBORN (Analyst, 1953, 78, 220) has mentioned their use for the estimation of fluoride, but both authors have simply taken solutions of the pure inorganic salts concerned and have not considered any of the difficulties which inevitably occur when the methods are applied to routine analysis of organic compounds in the laboratory. There are quite a number of these complications, and one point which must continually be borne in mind when using these resins is that any salt whatsoever will interfere since, on passing through the column, it will give rise to an acid.

The Development of the Method.

Polythene columns of the dimensions shown in DIAGRAM 31 have always been used for the exchange columns, containing about 20 gms. of Amberlite IR-120(H) as packing. However, when analyses are carried out on the semi-micro scale it is doubtful if polythene is really necessary since I found that the dilute hydrofluoric acid could be collected and titrated in glass flasks without introducing any error. Such an amount of resin, in the acid form, is equivalent to about 30 mls. of $N Na^+$ (or 150 mls. of a fusion solution which is generally 0.2N in Na^+) but the columns were regenerated after 70 mls. of fusion solution had been passed through them. This regeneration involves the addition to the column of 250 mls. of $N HCl$ which is then eluted with one litre of distilled water.

The actual columns were fabricated from polythene tubing by the method shown in DIAGRAM 30. The washer was cut from $\frac{1}{2}$ " polythene sheet by means of warm cork borers, then the outlet tube sealed into it by warming the parts gently over a small bunsen flame before pressing them together. The joint between this portion and the body of the column was made by a similar procedure..

The column was filled as follows:- A support of

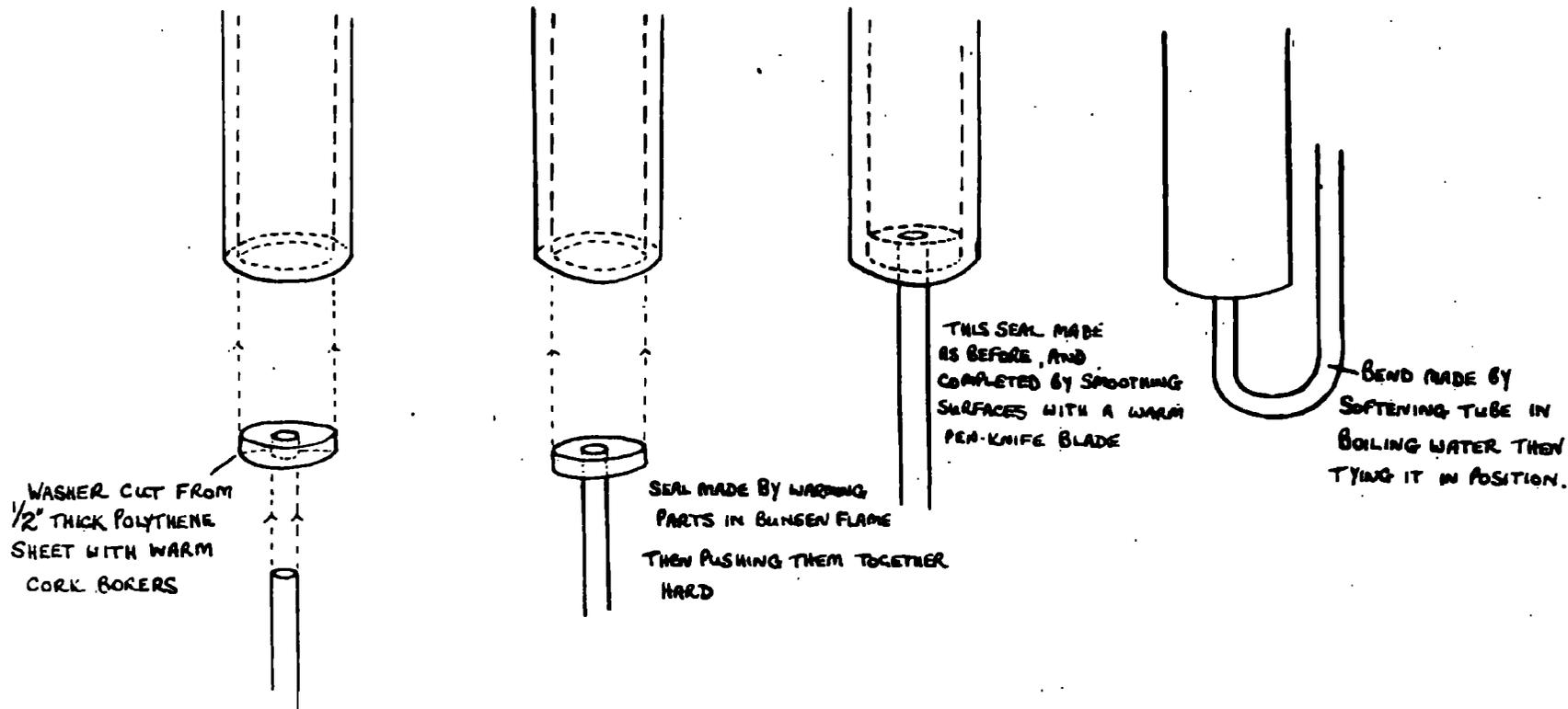


DIAGRAM 30 STAGES IN THE FABRICATION OF A POLYTHENE ION-EXCHANGE COLUMN.

polythene chips was placed in the column followed by resin (acid form), introduced by means of a spatula, until the support was covered to a depth of about 2". The remainder of the resin was then introduced in the form of a slurry with water. By this means the polythene chips were prevented from floating out of position.

The resin chosen for the work was Amberlite IR-120(H). This is a sulphonic acid type exchanger based on a polystyrene matrix containing some 10% of divinyl benzene. The resin is insoluble in water and any of the common organic solvents. It is quite stable at elevated temperatures (90°C or higher) and in strongly acid or alkaline media. It has a high exchange capacity, a good exchange rate and no great tendency to change volume on conversion from one form to another.

When 10 ml. aliquots of either 0.01N sodium chloride or 0.01N sodium fluoride were washed through the resin with 70 mls. of water from a dropping funnel and the resulting eluates titrated with 0.02N sodium hydroxide using Ma and Zuazaga's indicator (methyl red screened with bromocresol green, colour change r-g, through purple, at pH 5.1), the concentrations obtained for chloride and fluoride ions respectively were identical with those expected by theory (see TABLE 17A). In order to obtain reproducible results

with these dilute solutions, it was necessary to boil all the water used in preparing solutions to remove carbon dioxide, to use carbonate-free sodium hydroxide and to carry out blank runs on the distilled water to ensure its purity. On no account was water with a blank in excess of 0.03 mls. of sodium hydroxide employed. During a period when the only available distilled water had an exceptionally high blank a "Deminrolit" column was set up in order to purify it further before use. TABLE 17A also shows results obtained on solutions containing both \bar{Cl} and \bar{F} . In these determinations 20 ml. aliquots of a solution containing both ions were washed through the column and total halogen determined by titrating the washings with sodium hydroxide. A second aliquot was then put through, the same amount of sodium hydroxide added to it without using any indicator, then the solution evaporated down to about 15 mls., cooled, and titrated with 0.01N silver nitrate using dichloro-R-fluorescein as indicator. This titre gave a value for chloride content, which was subtracted from the total halogen content to give a value for fluoride.

Nevertheless, even when the precautions mentioned above were applied to the solutions obtained by fusing organic compounds containing either chlorine or fluorine with sodium, poor results, which were eventually traced to

two causes, were obtained. The first was due to water soluble salts in the filter papers used to separate the carbon residues. Various grades of filter paper were washed with 80 mls. of distilled water, the washings made up to 100 mls. and then 10 ml. aliquots washed through an ion exchange column. The acid present was equivalent to between 0.02 and 0.08 ml. of 0.02N NaOH depending on the grade of filter paper. This source of error was easily removed by using sintered glass funnels of No. 1 or No. 2 porosity.

TABLE 17A

The Estimation of \bar{Cl} and \bar{F} , both Separately and in Mixtures.

gms. F present	gms. F found (NaOH)	gms. Cl present	gms. Cl found (NaOH)	gms. Cl found ($AgNO_3$)
0.001849	0.001846	-	-	-
0.001849	0.001849	-	-	-
-	-	0.003625	0.003625	-
		0.003625	0.003630	0.003630
0.001849	0.001849	0.003625	-	0.003625
0.001849	0.001853	0.003625	-	0.003625

The second source of error lay in the method used to destroy the excess of sodium used in the fusion. Although

'pure alcohol when added to a synthetic fusion solution did not affect the eventual acid alkali or argentometric titrations (see TABLE 17A), when alcohol was used to destroy excess of sodium in an actual fusion high results were obtained. In a test run in which glucose was fused in the normal way, the excess of sodium was destroyed with alcohol and the fusion solution made up to 100 mls; a 10 ml. aliquot was equivalent to approximately 0.2 ml. of 0.02N NaOH.

TABLE 17B

<u>The Analysis of Synthetic Fusion Solutions Containing Cl,</u>				
<u>F, EtOH and made 0.2N w.r.t. NaOH.</u>				
<u>% EtOH present</u>	<u>gms. F present</u>	<u>gms. F found (NaOH)</u>	<u>gms. Cl present</u>	<u>gms. Cl found (AgNO₃).</u>
-	0.001479	0.001479	0.002903	0.002903
5	0.001479	0.001488	0.002903	0.002909
10	0.001479	0.001488	0.002903	0.002900
20	0.001479	0.001488	0.002903	0.002910
33	0.001479	0.001488	0.002903	-
40	0.001479	0.001488	0.002903	0.002908

An alternative method for destroying the sodium is described by BELCHER et al (loc. cit.) and involves packing the bomb with solid carbon dioxide and then adding water

carefully. This method results in the formation of a considerable amount of sodium carbonate, which has to be removed as carbon dioxide by boiling the acidified solution. Although this method is quite safe with the very dilute fluoride solutions obtained on the micro scale, experience has shown that on a larger (semi-micro) scale there may be a loss of up to two per cent of fluoride ion on boiling (ELVING, HORTON AND WILLARD, Fluorine Chemistry, Vol. II, Academic Press, and my own observations). The main fault with the method in this case is that the solid carbon dioxide contains non-volatile, soluble impurities which on passing through the resin are converted into acids, and cause results to be too high. Thus, after destroying some sodium in a nickel basin by this method, making up the solution to 100 mls., passing a 10 ml. aliquot through the resin, and then boiling off the carbon dioxide from the washings, the volume of 0.02N NaOH required could not be reduced below 0.06 ml. Therefore the apparatus shown in DIAGRAM 31 was devised for destroying the excess of sodium in an atmosphere of nitrogen at room temperature. Water is added from the dropper at the rate of about one drop every twenty seconds at first, but more quickly as the

sodium is destroyed. If the operation is carried out carefully no splashing occurs; this needs to be avoided since it results in attack on the glass by the concentrated alkali with slight buffering of the end-point in the acid-alkali titration. By this method the amount of carbon dioxide absorbed by the fusion solution is very small and is easily removed by bringing the washings from an elution to the boil and cooling immediately before adding indicator and titrating. The introduction of impurities is also avoided. When these precautions were taken, excellent results, which are shown in TABLE 21, were obtained.

When both chlorine and fluorine were present in the organic compound, the titration of the eluate with sodium hydroxide gave the equivalent of the total halogen present and an accurate method for the determination of chloride was necessary in order to be able to find the fluoride by difference. As has already been stated by BROWN AND MUSGRAVE (loc. cit.) it is impossible to take an aliquot of the solution from the sodium fusion, neutralize it with nitric acid and titrate with silver nitrate using dichloro-R-fluorescein as indicator, because the end-points are quite haphazard, presumably because of varying high

concentrations of nitrate ions from the neutralization. However, it was found that if an aliquot of the solution from the fusion was first put through the ion exchange column and then neutralized with the amount of alkali already known from the determination of total halogen, the dichloro-R-fluorescein indicator worked perfectly well, provided the solution was first evaporated down until it contained approximately 2 mgms. of chloride ion per 10 mls. of solution. This figure was chosen because the solution is then sufficiently concentrated to give a good colour change without the colloidal silver chloride coagulating before, or at, the end-point as it does when more concentrated solutions are used. The success of the method is simply due to the removal of excess alkali by the resin, with the result that the silver nitrate titration is carried out on a more or less pure solution of sodium halides, the only conditions under which adsorption indicators function properly.

An alternative procedure, and one which is better when solutions containing only small amounts of chloride ion (up to 1 mgm. per 10 mls.) are being titrated, is to neutralize the eluate from the ion exchange column with 0.02N. NaOH using methyl red screened with methylene blue

as indicator and then proceed directly to the determination of the chloride using mercuric oxycyanide as described by BELCHER, MACDONALD AND NUTTEN (loc. cit.). The application of this method to the cation exchange work was suggested by CUTHBERTSON, who had previously scaled the method up for semi-micro quantities. (See his Ph.D. thesis, 1956). Ma and Zuazaga's indicator can be used in this process but does not give such sharp end-points, and results tend to be slightly low.

It should perhaps be stated at this stage that successful attempts have been made by DeGEISO, RIEMAN AND LINDENBAUM (Anal. Chem., 1954, 26, 1840) to separate chloride, bromide and iodide ions on an anion exchange column. Similar methods would no doubt permit the separation of chloride and fluoride ions, but the procedure takes three hours which is too long for a routine analysis.

The cation exchange method can also be applied to organic compounds which contain nitrogen as well as chlorine and fluorine. As stated by BROWN AND MUSGRAVE (loc. cit.), the nitrogen cannot be determined as cyanide if oxygen is present in the compound, since a certain amount of cyanate is then formed. If no oxygen is present, the cyanide is determined by DENIGES' method (DENIGES, Compt. rend., 1893,

117, 1078), but both cyanide and cyanate must be removed before the halogens can be determined. The cyanide can be removed by treating an aliquot of the alkaline solution from the fusion with formaldehyde and allowing the mixture to stand for about 30 minutes when the cyanide is converted to hexamethylene tetramine. (As reported on by GRAHAM, J. Ass. Off. Agr. Chem., 1927, 10, 150.) The mixture can then be put through the ion exchange column where any sodium cyanate is converted to cyanic acid which immediately decomposes to ammonia and carbon dioxide. The ammonia is retained in the column and the carbon dioxide passes through in the solution. This is removed with the rest of the absorbed carbon dioxide when the washings are heated to the boiling point and then cooled before adding the indicator and titrating. Such treatment does not affect the fluoride estimation. Precautions in the removal of cyanide and carbon dioxide need only be taken when fluoride is present; if this is not so the solution containing chloride, cyanide and cyanate need simply be boiled, after passing through the column, until the hydrocyanic acid has been removed. TABLES 18, 19 & 20 show the results of analyses carried out on synthetic solutions in order to determine the effect on the titrations of destroying cyanide with 0.10N

formaldehyde solution. In TABLE 18 the efficiency of removal of cyanide was determined by means of alkalimetry after passing the solutions through the column. The blank on the potassium cyanide was carried out by passing a 5 ml. aliquot through the column then boiling off all hydrocyanic acid from the washings before titrating. In TABLE 19 the efficiency of removal of cyanide from solution was determined by means of a direct argentometric titration without passing the solutions through the column. The synthetic solutions were first neutralized to phenolphthalein with 0.02N NaOH, then one drop of M.A.R. 0.01N HNO₃ added before titrating with 0.01N AgNO₃ using dichloro-R-fluorescein as indicator. This was not an easy operation because troublesome frothing occurred which marred the end-points.

TABLE 20 shows results from analyses carried out on synthetic fusion solutions, from an examination of which it can be seen that, within the limits of experimental error, formaldehyde does remove cyanide from such a solution.

TABLE 21 shows that excellent results can be obtained when this method is applied to an actual fusion of an organic compound.

TABLE 18

0.01N KCN	0.10N HCHO	0.02N NaOH titre	NaOH titre adjusted for KCN & HCHO blanks
5 mls.	-	0.2 ml.	-
5 mls.	1 ml.	0.22 ml.	+ 0.004 ml.
5 mls.	2 mls.	0.23 ml.	- 0.002 ml.
5 mls.	3 mls.	0.25 ml.	+ 0.002 ml.
10 mls.	2 mls.	0.45 ml.	+ 0.018 ml.
15 mls.	3 mls.	0.65 ml.	+ 0.002 ml.
-	5 mls.	0.08 ml.	-

TABLE 19

0.01N NaCl	0.01N KCN	0.10N HCHO	0.01N AgNO ₃ titre
10 mls.	-	-	8.73 mls.
10 mls.	5 mls.	2 mls.	8.78 mls.
10 mls.	10 mls.	2 mls.	8.83 mls.
10 mls.	15 mls.	2 mls.	8.88 mls.

(It can be seen from the results that the KCN solution contained chloride equivalent to 0.05 mls. 0.01N AgNO₃ per 5 mls.)

TABLE 20

The Analysis of Synthetic Fusion Solutions Containing \bar{Cl} ,
 \bar{F} , \bar{CN} and made 0.2N w.r.t. NaOH

0.01N NaF	0.01N NaCl	0.01N KCN	0.10N HCHO	1.02N NaOH titre *	0.01N AgNO ₃ titre
10 mls.	10 mls.	-	-	8.25 mls.	10.8 mls.
10 mls.	10 mls.	5 mls.	1 ml.	8.24 mls.	-
10 mls.	10 mls.	5 mls.	2 mls.	8.27 mls.	-
10 mls.	10 mls.	5 mls.	3 mls.	8.3 mls.	-
10 mls.	10 mls.	5 mls.	HCN boil- ed off	-	10.84 mls.
10 mls.	10 mls.	5 mls.	HCN boil- ed off	-	10.83 mls.

* Titres adjusted for KCN and HCHO blanks (see TABLE 18).

Reagents

Sodium hydroxide solution. 0.02N.

Silver nitrate solution. 0.01N.

Mercuric oxycyanide solution. 20 g. of mercuric oxycyanide were shaken with 1 litre of distilled water and the solution neutralized approximately with 0.01N sulphuric acid using methyl red-methylene blue indicator, and filtered into a brown glass bottle.

Sodium chloride solution. 0.01N.

Sulphuric acid solution. 0.02N.

Ammonia solution. 6N.

Formaldehyde solution. 0.1M.

Indicators

Methyl red-methylene blue. 0.125 g. of methyl red was dissolved in 50 ml. of 90% ethyl alcohol; 0.083 g. of methylene blue was dissolved in 50 ml. of 90% alcohol. Equal parts were mixed immediately before use.

Methyl red-bromocresol green. 0.04 g. of methyl red and 0.06 g. of bromocresol blue were dissolved in 100 ml. of 95% alcohol.

Dichloro-R-fluorescein. 0.1 g. in 100 ml. of 70% alcohol.

EXPERIMENTAL PROCEDURES

Take a known weight of the organic compound containing about 10mg. of the elements to be determined, using a nickel weighing capsule if the compound is a liquid. Fuse with excess of sodium for 1-1½ hours at 600-700°C. in a nickel bomb. When cold, wash the outside of the bomb with distilled water and discard the washings. Remove the lid and wash the underside with a little water, allowing the washings to run into tube A, DIAGRAM 31. Now place the cup of the bomb in A, put on the lid B and pass a stream of nitrogen to displace the air. Add water, drop by drop, from the dropper

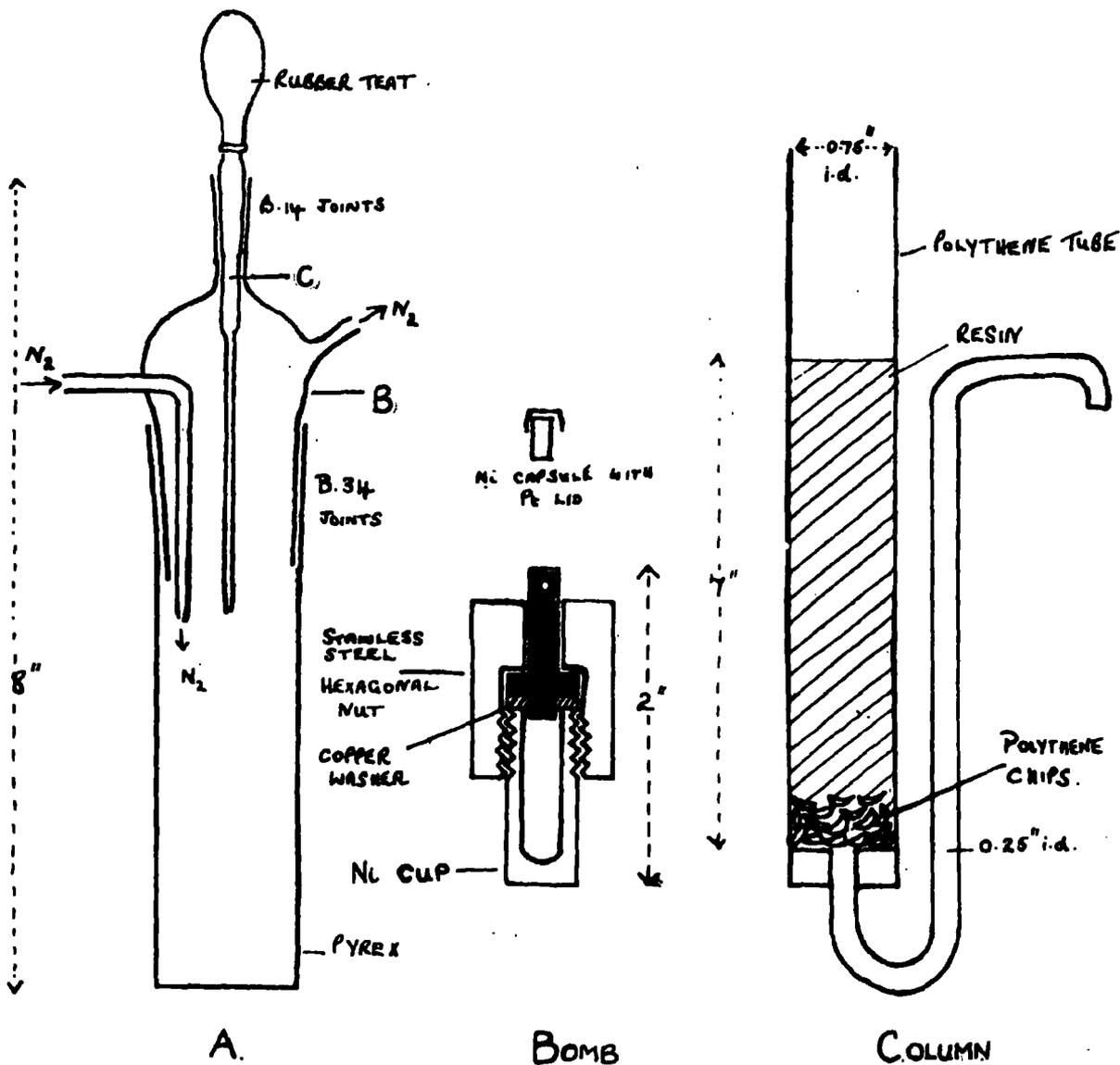


DIAGRAM 31

C, which is fitted with a rubber teat, taking care that no sodium splashes out onto the glass walls. When all of the sodium is destroyed, cover the nickel cup with water and heat A in a water bath to 50°C . for about two minutes so as to complete the extraction and coagulate the solid matter. Cool, filter, and wash quantitatively, using a funnel with a sintered glass filter plate of No. 1 or No. 2 porosity, into a 100 ml. standard flask.

If chlorine or fluorine is present alone.

Take an aliquot (10 ml.) of the fusion solution and run it from the pipette onto the Amberlite resin. Elute it with 70 ml. of boiled distilled water over a period of 10 minutes, collect all of the eluate, heat it to boiling point and cool immediately. Titrate the whole of this with standard 0.02N NaOH solution using methyl red screened with either bromocresol green or methylene blue as indicator (10 drops).

If chlorine and fluorine are present.

Proceed as above to determine the total halogen content, and then take a second aliquot, pass it through the column, neutralize with the previously determined volume of 0.02N NaOH, and then evaporate until the solution contains approximately 2 mg. of chloride per 10 ml. Titrate this

solution with 0.01N silver nitrate solution using ten drops of dichloro-R-fluorescein as indicator, the end-point being the disappearance of the green fluorescence with the appearance of a buff colour on the colloidal silver chloride.

Alternatively, after neutralization using methyl red screened with either methylene blue or bromocresol green as indicator, the chloride can be determined in the same aliquot using mercuric oxycyanide as described by BELCHER et al. Methyl red-methylene blue is the better indicator. If chlorine, fluorine and nitrogen are present.

If there is no oxygen in the compound and the cyanide is to be determined, this is done by DENIGES' method, an aliquot (25 ml.) of the fusion solution being treated with 6N ammonia solution (7 ml.) and 0.1N KI solution (2 drops), and titrated with silver nitrate solution to a permanent turbidity.

For the determination of chloride and fluoride, an aliquot (10 ml.) of the fusion solution is treated with 0.1M aqueous formaldehyde (3 ml.), allowed to stand at room temperature for 30 minutes to ensure complete reaction of the cyanide, and then washed through the ion exchange column and treated as before.

It is necessary to carry out a blank determination on the formaldehyde solution, since it contains an appreciable quantity of formic acid.

Since this work was published (BANKS, CUTHBERTSON AND MUSGRAVE, Anal. Chim. Acta., 1955, 13, 442) the work of EGER AND YARDEN (Bull. Research Council Israel, 1954, 4, 305) has appeared in the literature abstracts. (Am.C.A. 1955, 49, No. 19, 130181). These workers fused organic fluoro-compounds with sodium peroxide in a Parr bomb, then passed aliquots of the fusion solution through columns containing Amberlite IR-112 (H) and titrated the effluates with thorium nitrate using sodium alizarin sulphonate as indicator. Presumably they used the resin merely to "clean up" the fusion solution so that the composition of the solution to be titrated would be as close to that of a synthetic solution as possible. They missed the great opportunity of dispensing altogether with the thorium nitrate titration and its failings. They also estimated chloride and bromide in fusion solutions, but details of this are not given in the abstract. The work of ZENIN (Gidrokhim Materialy, 1954, 22, 115; Am.C.A., 1955, 49, No.21, 14568e) has also recently appeared, in the abstracts,

but here again alkalimetry was not employed in the determinations. Cation exchangers were used in the analysis of solutions for \bar{F} , the determination being carried out by (a) thorium nitrate titrations and (b) colorimetric procedures. Both of these were found unsatisfactory, so the fluosilicic acid method had to be reverted to.

TABLE 21

ANALYSES OF "KNOWN" ORGANIC COMPOUNDS.

Compound (g)	% Cl			% F		% N		Removal of Cyanide
	Calc.	Found		Calc.	Found	Calc.	Found	
		NaOH	AgNO ₃					
Benzene Hexachloride (0.08863) (0.05232)	73.2 73.2	73.2 73.3	73.2 73.5					
Chlorobenzene (0.03771) (0.05880) (0.05440)	31.55 31.55 31.55	31.5 31.5* 31.5	31.4 31.4	31.5 31.5*				
m-Chlorobenzoic acid (0.06709) (0.08194) (0.08492) (0.09473)	22.65 22.65 22.65 22.65	22.6 22.5 22.7 22.4 22.5*	22.6 22.5 22.6 22.4	22.6* 22.4 22.3* 22.2				
1,1-difluorocyclohexane (0.05909) (0.05859)				31.67 31.67	31.5 31.5			
p-chlorofluorobenzene (0.06490) (0.05640)	27.2 27.2		27.0 27.3	14.57 14.57	14.6 14.4			
p-chloronitrobenzene (0.12407) (0.09851) (0.10514)	22.54 22.54 22.54	22.5 22.4 22.5 22.4* 22.6 22.6*	22.5 22.3 22.4	21.9 22.5*				HCN boiled off HCN boiled off HCHO added HCN boiled off HCN boiled off HCHO added HCHO added
Anilinium trifluoroacetate (0.05310) (0.07057)				27.54 27.54	27.5 27.5* 27.8			HCHO added HCHO added HCHO added
Anilinium chloride (0.11464) (0.05221)	27.40 27.40	27.4 27.5 27.4* 27.5 27.4*	27.4 27.3	27.4 27.5*		10.81 10.81	10.7 10.7	HCN boiled off HCHO added HCN boiled off HCN boiled off HCHO added HCHO added
2-chloro-5-trifluoromethylacetoacetanilide (0.06069) (0.04759)	12.7 12.7		12.5 12.3	20.4 20.4	20.4 20.1			HCHO added HCHO added
Anilinium chloride + 1,1-difluorocyclohexane (0.02170) + (0.02972) (0.02143) + (0.02969)	27.40 27.40		27.2 27.3* 27.2	31.67 31.67	31.6 31.5* 31.5*	10.81 10.81	10.9 10.7	HCN boiled off for Cl ⁻ detn. HCHO added for NaOH titn.

APPENDIX

Chapter VII

The Development of a New Binary Test Mixture
for Evaluating Distillation Columns
at 50 mm. of Mercury.

It was necessary when choosing the type of column most suited to the task of separating the components of Chlorofluorination Run Number One by fractional distillation to compare the efficiencies of different types of column both at atmospheric pressure and under vacuum (see p. 34). Now although several workers have operated concentric-tube columns under reduced pressures (see CRAIG, Ind. Eng. Chem., Anal. Ed., 1937, 9, 441 and HALL AND PALKIN, Ind. Eng. Chem., 1942, 14, 807) no data has been given in the literature which will allow a direct quantitative comparison of the efficiencies of such columns when operated at different pressures. Thus, as the theory of distillation is not yet in a position to enable the effect of pressure on efficiency to be calculated quantitatively, although predictions can be made (see the discussion at the end of this chapter), it was necessary to test the concentric-tube columns under reduced pressure and so ensure that their efficiencies under vacuum were still superior to those of other types of column.

The first attempt to test the columns was made at 1 mm. pressure using the di-n-butyl azelate-di-n-butyl phthalate mixture of WILLIAMS (ibid., 1947, 39, 779).

At this pressure, however, it was found difficult to maintain steady boiling for long periods, and the values of efficiencies obtained varied between five and ten theoretical plates. This failure to obtain reproducible equilibrium conditions may have been due in part to the Cartesian diver type manostat being employed in the vacuum system as it is not reliable below 10 mm. pressure. Thus it was decided to test the columns in the region of 50 mm. where even boiling could be easily and simply maintained by means of a small internal pot heater of the type already described (DIAGRAM 13, and p. 92). However, since the mixtures (n-dodecane-cyclohexylcyclopentane and n-tridecane-dicyclohexyl) described by FELDMAN et al (ibid., 1949, 41, 1032) for use in this pressure range were not readily available and, in any case, only suitable for columns having up to twenty plates, and the o-dichlorobenzene-diethylbenzene mixture of BRAGG AND RICHARDS (ibid., 1942, 34, 1088) would have involved a difficult separation of o- and p- diethylbenzenes, it was decided to find a new test mixture the components of which could be obtained easily. After searching through lists of physical constants it was decided that a mixture of

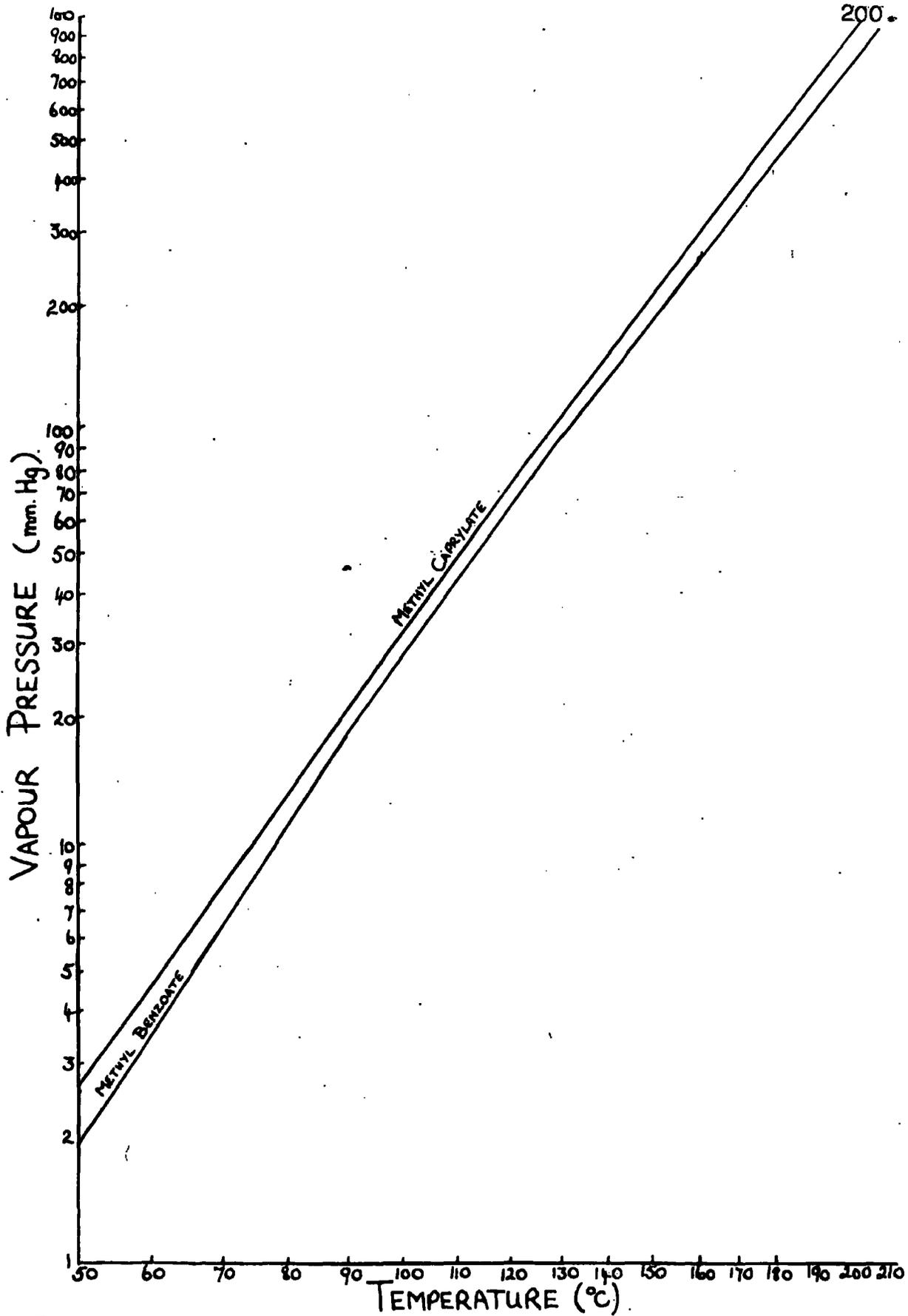


DIAGRAM 32

methyl benzoate and methyl caprylate ought to be suitable provided that they did not form a constant boiling mixture.

It was found that these two esters meet all the requirements listed by WILLIAMS (loc. cit.) for components of a test mixture which is to be used for evaluating low pressure distillation columns, except that they do not form ideal solutions. This, however, does not preclude the use of mixtures of the esters from efficiency tests, but merely limits the range of the mixture to about forty theoretical plates. Otherwise, they are close boiling (see DIAGRAM 32), have a large difference in refractive index (0.1 unit) which permits accurate analysis of mixtures by means of simple refractometry, are liquids at all ordinary temperatures, do not react chemically with each other, and are thermally stable.

EXPERIMENTAL

Materials Used

Commercial methyl benzoate was dried over anhydrous magnesium sulphate and then distilled under reduced

pressure through a concentric-tube column which had an efficiency of 60 plates at atmospheric pressure. The material used in all the experiments had the following physical constants:- b.pt. $112^{\circ}\text{C}/40\text{ mm.}$, n_{D}^{20} 1.5172.

Methyl caprylate, $\text{CH}_3(\text{CH}_2)_6\text{COOCH}_3$, was prepared in 91% yield from caprylic acid by the method of SAUER et al ("Organic Syntheses", Wiley and Sons, Inc., N.Y., 1955, Collective Vol. III, p. 605). The crude product was dried over anhydrous magnesium sulphate then distilled under reduced pressure as above to give material with the following physical constants:- b.pt. $115^{\circ}\text{C}/58\text{ mm.}$, n_{D}^{20} 1.4173.

Equilibrium Determinations

Mixtures of the two esters were weighed out, the refractive indices determined at $20 \pm 0.1^{\circ}\text{C}$ using an Abbé refractometer, and a refractive index-composition graph constructed from the data (DIAGRAM 33; TABLE 22). Vapour-liquid equilibrium determinations for mixtures of the two esters were then carried out at 50 mm. pressure by the method of WILLIAMS (loc. cit.), and using an apparatus which was a modification of his still (DIAGRAM 34). The main difference lies in the heating arrangements for the boiler; after trying several methods, including that of

TABLE 22Refractive Index-Composition Data for Methyl Benzoate-
Methyl Caprylate Mixtures

Mole % Methyl Caprylate	Refractive Index (n_D^{20})
0	1.5172
2.58	1.5131
7.26	1.5065
19.0	1.4923
13.26	1.4992
25.04	1.4849
31.44	1.4777
36.53	1.4725
39.7	1.4689
46.2	1.4625
50.5	1.4590
61.9	1.4473
66.6	1.4430
71.6	1.4387
84.0	1.4290
92.2	1.4230
100	1.4173

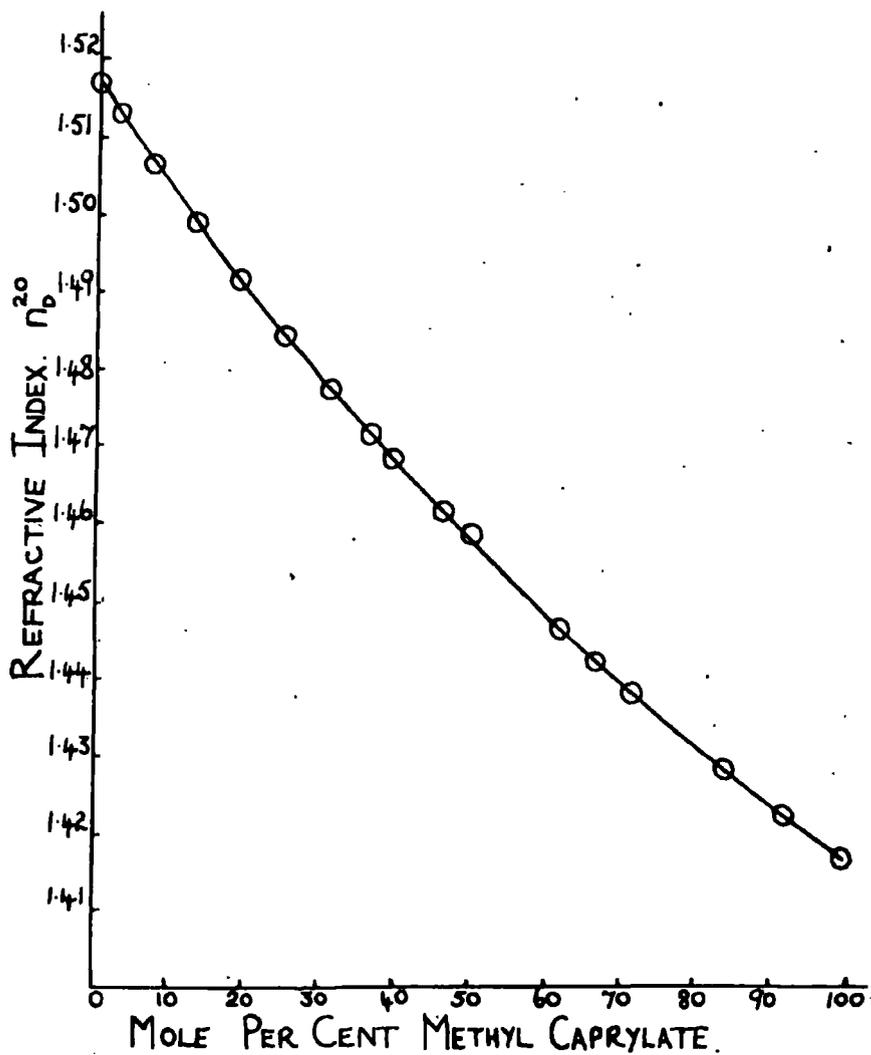
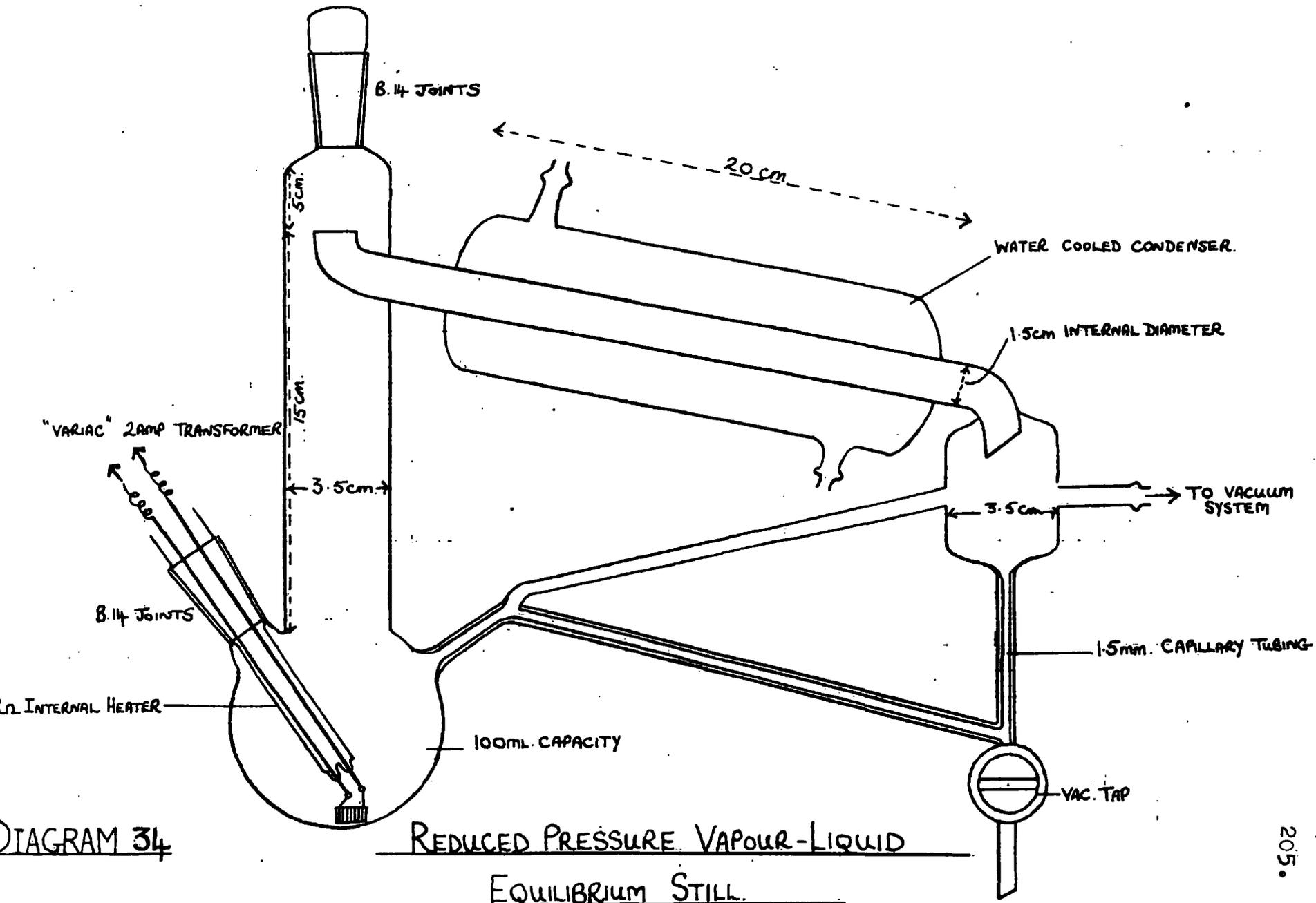


DIAGRAM 33 REFRACTIVE INDEX - COMPOSITION CURVE
FOR THE $C_6H_5COOCH_3 - CH_3(CH_2)_6COOCH_3$ MIXTURE.



Williams, it was found that the only reliable means of causing steady boiling was to supply the main amount of heat from an "Isomantle" and to have a small internal heater consisting of 12" of oxynichrome tape (24.8 ohms/yard) wound on a mica former. An electrically-heated brass oven body was employed to keep the walls of the still at a temperature of 130°C , i.e. about 15° above the boiling point of methyl benzoate at 50 mm., thus preventing condensation and fractionation. The heater was controlled by means of a Variac transformer. For each mixture of esters (60 mls.) the still was allowed six hours to attain equilibrium before samples of distillate and distilland were taken for analysis. The hold-up loop had a capacity of 1.5 mls., and the joints and tap were lubricated with manitol grease. The vacuum system to which the equilibrium still was connected has been described previously (DIAGRAM 14).

The vapour-liquid equilibrium data obtained is shown in TABLE 23. It can be seen from the variation in relative volatility that mixtures of the two esters do not form ideal solutions, and, therefore, when the mixture is used to evaluate a column a graphical method such as that of McCABE AND THIELE (Ind. Eng. Chem., 1925, 17, 605)

TABLE 23

Vapour-Liquid Equilibrium Data for the Methyl Benzoate-Methyl
Caprylate System at 50 mm. of Mercury

n_D^{20}		Mol. % Methyl Caprylate		Relative Volatility
Residue	Distillate	in Liquid	in Vapour	
1.5172	-	0	0	-
1.5142	1.5132	2.0	2.6	1.308
1.5045	1.5020	9.2	11.25	1.251
1.5034	1.5008	10.02	12.2	1.250
1.4968	1.4932	15.5	18.5	1.238
1.4893	1.4852	21.5	25.0	1.217
1.4823	1.4775	27.5	31.3	1.201
1.4765	1.4728	32.5	35.7	1.153
1.4711	1.4680	37.3	40.4	1.114
1.4670	1.4640	41.5	44.5	1.113
1.4626	1.4595	46.5	49.5	1.1128
1.4561	1.4542	52.5	54.8	1.09
1.4529	1.4510	56.0	58.1	1.09
1.4440	1.4428	65.5	67.0	1.07
1.4326	1.4320	79.2	80	1.051
1.4318	1.4312	80.2	80.8	1.039
1.4261	1.4258	87.2	87.5	1.017
1.4196	1.4196	96.6	96.6	1.00
1.4173	-	100	100	-

must be employed to calculate the number of theoretical plates. In order to facilitate this calculation, a graph of refractive index against theoretical plates was constructed in which the vertical scale has no absolute zero (DIAGRAMS ³⁵/₃₆). The plating of a column is found by subtracting the plate value corresponding to the refractive index of the distilland from that corresponding to the refractive index of the distillate when it has come to equilibrium.

Testing the Columns

This procedure has already been described in detail (p. 104) and details of the results obtained given in TABLE 6, p. 107. Quantitatively the efficiencies of the columns were reduced by 50% when operated at 50 mm., which shows that the concentric-tube type of column was much superior to other types of column for the problem in hand.

Distillation of a Known Mixture

In order to obtain some practice in the art of operating a continuous distillation under reduced pressure for a period of several days a 50-50 (vol:vol) mixture of aniline and p-cymene was fractionated at 178 mm. pressure. The distillation graph obtained (DIAGRAM 37)

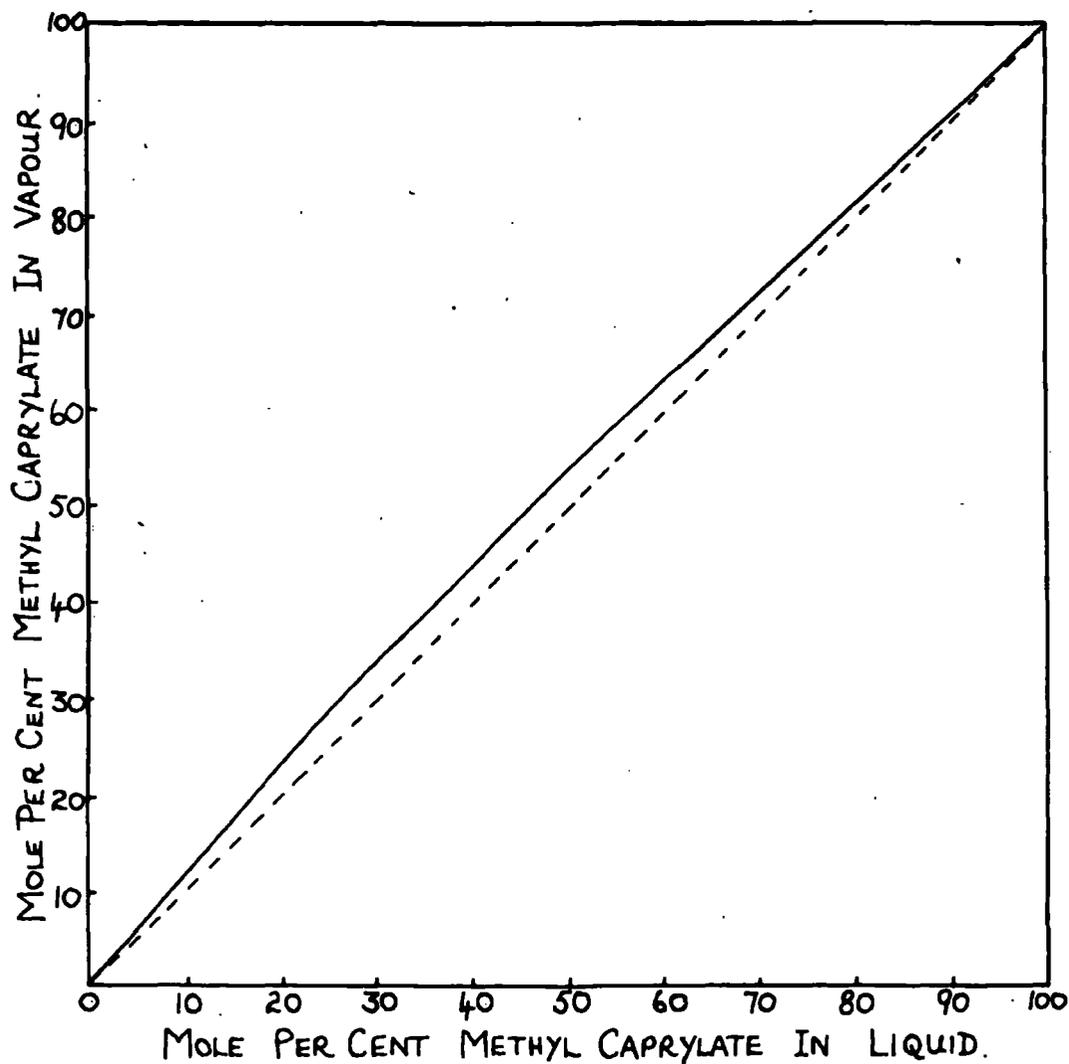


DIAGRAM 35 VAPOUR-LIQUID EQUILIBRIUM DIAGRAM FOR
THE $C_6H_5COOCH_3 - CH_3(CH_2)_6COOCH_3$ MIXTURE AT
50mm. Hg.

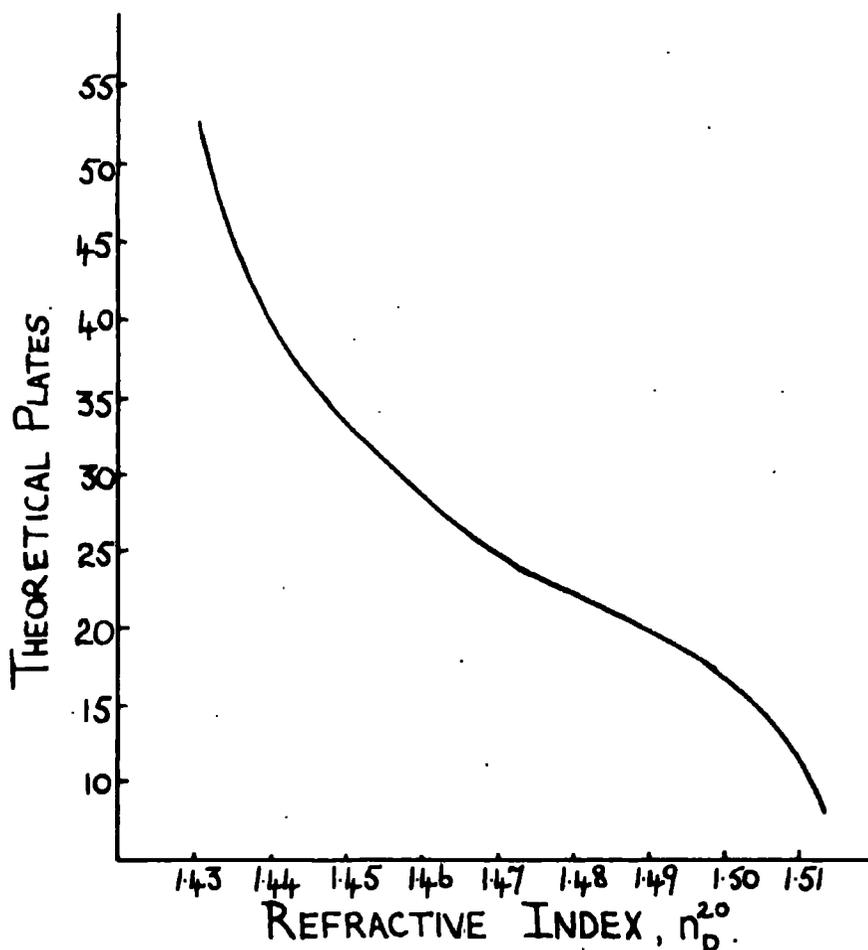


DIAGRAM 36 THEORETICAL PLATES - REFRACTIVE INDEX

GRAPH FOR THE ESTER TEST MIXTURE.

DISTILLATION CURVE FOR ANILINE - p-Cymene Mixture (50:50 mixture, vol. vol.)

COLUMN: 60-plate, concentric-tube

PRESSURE: 178 mm. Hg

TAKE-OFF RATE: 1.0 ml. per hour.

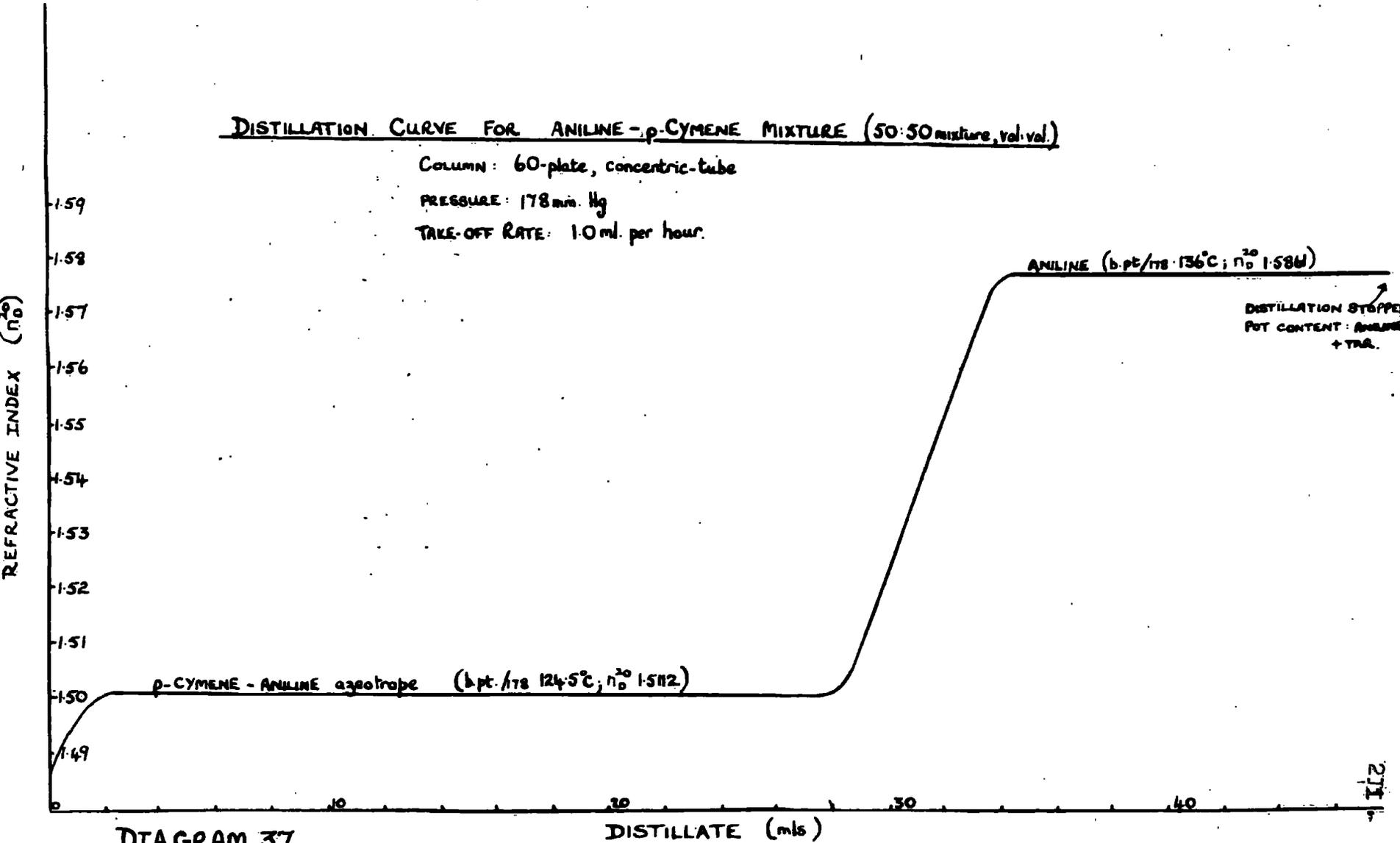


DIAGRAM 37

DISTILLATE (mls)

shows that an azeotrope containing some 96% p-cymene is formed at this pressure, but it is obvious from the theoretical shape of the graph that the distillation technique was excellent.

DISCUSSION

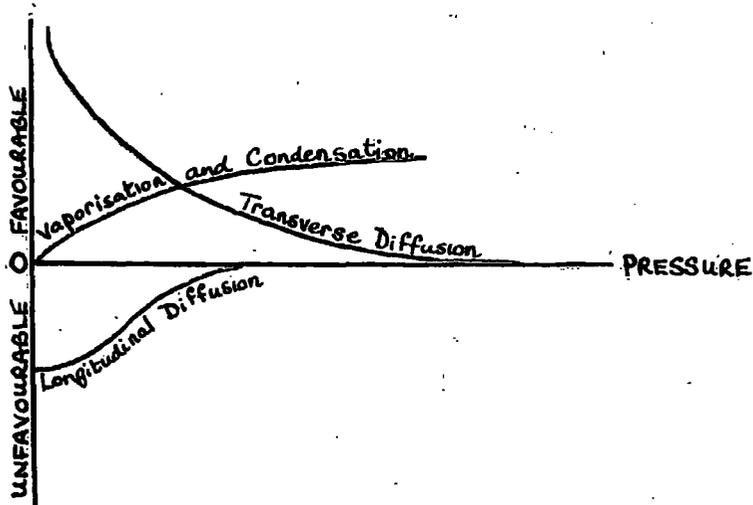
Although distillation is one of the most important tools used in organic chemistry workers in this field do not usually inquire very deeply into the theories behind it, especially where vacuum distillation is concerned. In this laboratory, however, it was noted that equations such as those of DOCKSEY AND MAY (J. Inst. Pet. Technologists, 1935, 35, 176) and WESTHAVER (Ind. Eng. Chem., 1942, 34, 126) indicate, on superficial examination, that H.E.T.P. is independent of pressure, whereas the bulk of the experimental evidence quoted in the literature shows that the efficiency of a distillation column decreases with a lowering of the operating pressure. Thus, although Docksey and May supported their predictions with results obtained from test runs carried out at different pressures on columns packed with Lessing rings using aniline-nitrobenzene mixtures, and BJORKMAN AND OLAVI (Svensk Kem. Tid., 1946, 6, 145) claim that the

efficiency of their spinning-band column remained constant over the pressure range 9-100 mm. of mercury, the weight of the evidence coincides with my own observations on concentric-tube columns already quoted. Especially to be noted is the work of FELDMAN et al (loc. cit.) who tested a Podbielniak column at different pressures with n-dodecane-cyclohexylcyclopentane test mixtures, because here the results do not suffer from any effects due to changing the compound type (see PETERS, Ind. Eng. Chem., 1922, 14, 476) or molecular weights (see CARSWELL, *ibid.*, 1926, 18, 294) of the components of the test mixture. An explanation of this discrepancy between theory and practice was sought and is set out briefly below.

If the derivations of the theoretical equations mentioned above are examined it can be seen that the original postulates describing equilibrium conditions contain only terms due to convection and diffusion processes in the vapour phase. If these physical processes were the only ones to be taken into consideration at all pressures, and the operating difficulties encountered in a low-pressure distillation overcome by careful choice of column and auxiliary equipment so that equilibrium could be established, then the efficiency of a column should remain constant.

As it does not, then there must be some other process, or processes, which contribute to the equilibrium state equations. BYRON, BOWMAN AND COULL (see Weissberger, "Technique of Organic Chemistry", Vol. IV, p. 85) have described the effect of one such process, namely the reduction in absolute vaporisation and condensation rates at low pressures, on the ease of establishment of equilibrium between phases by means of the following

graph:-



Relative importance of several factors:

in determining effect of pressure on

separation in fractionation

Other factors which might influence the equilibrium as pressure is decreased are disturbances in the stagnant layer of vapour in contact with liquid films. Whatever effects come in play, however, it is obvious that any

mathematical theory hoping to account for them will be a complicated one. This is unfortunate because distillation is already overburdened with elaborate mathematical treatments.

Having indicated the state of the theory it should be obvious that it was of the utmost importance to obtain the performance characteristics of the concentric-tube columns by testing them so that the maximum degree of separation when chlorofluorinated materials were distilled could be anticipated.

Chapter IX

A Note on the Benzene-Fluorobenzene System.

At the outset of the work on the vapour-phase chlorofluorination of benzene it was thought possible that one of the products of the reaction would be fluorobenzene by analogy with the liquid-phase work of ELLIS AND MUSGRAVE (J.C.S., 1950, 3608.). The problem of separating fluorobenzene from any unchanged benzene in the reaction mixture would therefore arise. RUFF AND KEIM (Z. anorg. allgem. Chem., 1931, 201, 245,) found that fluorobenzene present in the reaction mixture resulting from the action of iodine pentafluoride on benzene interdistilled with unchanged benzene when the mixture was fractionally distilled. Ellis and Musgrave at no time isolated a pure sample of fluorobenzene from their reaction mixtures, and stated that it formed a ternary azeotrope with unchanged benzene and carbon tetrachloride, the latter being the solvent in which the reaction was carried out. In both cases the lack of separation could have been due to the low efficiencies of the distillation columns used, which would account for an apparent azeotrope formation. Obviously, then, it was necessary to obtain a vapour-liquid equilibrium diagram for the benzene-fluorobenzene system, and so determine whether or not an azeotrope does exist. This was done and no evidence for azeotrope formation found.

Thus, assuming mixtures of benzene and fluorobenzene to form ideal solutions, it was calculated, using Fenske's equation (FENSKE, Ind. Eng. Chem., 1932, 24, 482) that the number of plates required to separate a mixture of benzene and fluorobenzene by fractional distillation into a distillate containing 99 mole per cent benzene and a residue containing 99 mole per cent fluorobenzene would be 66. Theoretically this meant that the concentric-tube distillation columns which were to be used for the fractionation of chlorofluorinated mixtures, and whose maximum plateage, i.e. at total reflux, was 60, would not separate benzene and fluorobenzene. As in all distillation calculations, which assume ideal conditions, the theoretical indications need to be checked in practice. This was done and DIAGRAM 38 gives details of the distillation graphs obtained for three mixtures which contained 85, 56 and 26 mole percent benzene respectively. No separation was effected, as indicated by theory. The graphs can be compared with the appropriate section of the distillation graph obtained for Chlorofluorination Run No. 1; no similarity exists.

In order to obtain further confirmation that fluorobenzene was not present in the reaction mixture from

Chlorofluorination Run No. One, analytical gas chromatograms for fluorobenzene and benzene-fluorobenzene mixtures were obtained, using apparatus and technique described in CHAPTER V, and compared with the chromatograms obtained for material distilled from the reaction mixture. These are shown in DIAGRAM 42 and indicate that benzene and fluorobenzene may be separated by this means if a large-scale column with a greater efficiency than the small analytical column is used.

EXPERIMENTAL

"Analar" benzene was dried over sodium wire, distilled from it using an ordinary Claisen flask arrangement, then redistilled through a 60-plate concentric-tube column. Fluorobenzene was dried over anhydrous magnesium sulphate, then distilled through a concentric-tube column. The physical constants of the materials so obtained, and used in all the experiments, were:-

C_6H_6 b.pt. at 759 mm. $80^\circ C$, n_D^{20} 1.5014. C_6H_5F b.pt. at 760 mm. $84^\circ C$, n_D^{20} 1.4653.

Known mixtures of benzene and fluorobenzene were:

weighed out, their refractive indices measured using an Abbé refractometer at $20^{\circ} \pm 0.1^{\circ}\text{C}$, and a graph of composition vs. refractive index constructed (DIAGRAM 39). This was then used to analyse unknown mixtures whose refractive index was known. Vapour-liquid equilibrium determinations were then carried out at atmospheric pressure using a very simple still of the Othmer type (DIAGRAM 40). No arrangement was made to keep the pressure inside the apparatus constant, but all the experiments were carried out on the same day during which the barometric height did not vary by more than 2 mm. The boiler was charged with 60 mls. of mixture and the still brought to equilibrium. This condition was determined by noting the temperature reading of the N.P.L. thermometer. When this reading had been constant for 30 minutes samples of distillate and distilland were taken and analysed. TABLE 25 gives details of the results, and DIAGRAM 41 shows the boiling point-composition diagram, and the vapour-liquid equilibrium diagram obtained from these. It is obvious that no azeotrope formation occurs.

TABLE 24

Refractive Index - Composition Data for
Benzene-Fluorobenzene Mixtures

n_D^{20}	Mole % Benzene
1.4653	-
1.4690	12.16
1.4720	20.80
1.4756	32.0
1.4818	50.01
1.4860	61.65
1.4900	72.33
1.4944	84.73
1.4970	91.65
1.5013	100.00

TABLE 25

Vapour-liquid Equilibrium Data for the
Benzene-Fluorobenzene System at Atmospheric Pressure

Atm. Pressure (mm. Hg)	Vapour Temp. (°C)	²⁰ n _D		Mole Fraction Benzene	
		Distilland	Distillate	Liquid	Vapour
753.8	79.35	1.5013	1.5013	1	1
754.2	79.45	1.5003	1.5006	0.97	0.98
754.2	79.77	1.4976	1.4982	0.90	0.92
754.2	79.8	1.4975	1.4981	0.895	0.91
755.5	80.83	1.4878	1.4889	0.63	0.66
755.5	80.99	1.4865	1.4880	0.59	0.63
755.5	81.2	1.4847	1.4862	0.54	0.57
754.0	82.1	1.4762	1.4785	0.31	0.37
753.8	82.42	1.4742	1.4755	0.25	0.29
754.2	82.87	1.4732	1.4740	0.22	0.24
753.8	83.5	1.4680	1.4690	0.09	0.11
753.8	84.0	1.4653	1.4653	-	-

THE DISTILLATION CURVES FOR THE FOLLOWING BENZENE-FLUOROBENZENE MIXTURES

(a) 85 MOLE % BENZENE (b) 56 MOLE % BENZENE (c) 26 MOLE % BENZENE.
 (CONCENTRIC-TUBE FRACTIONATING COLUMNS BEING USED).

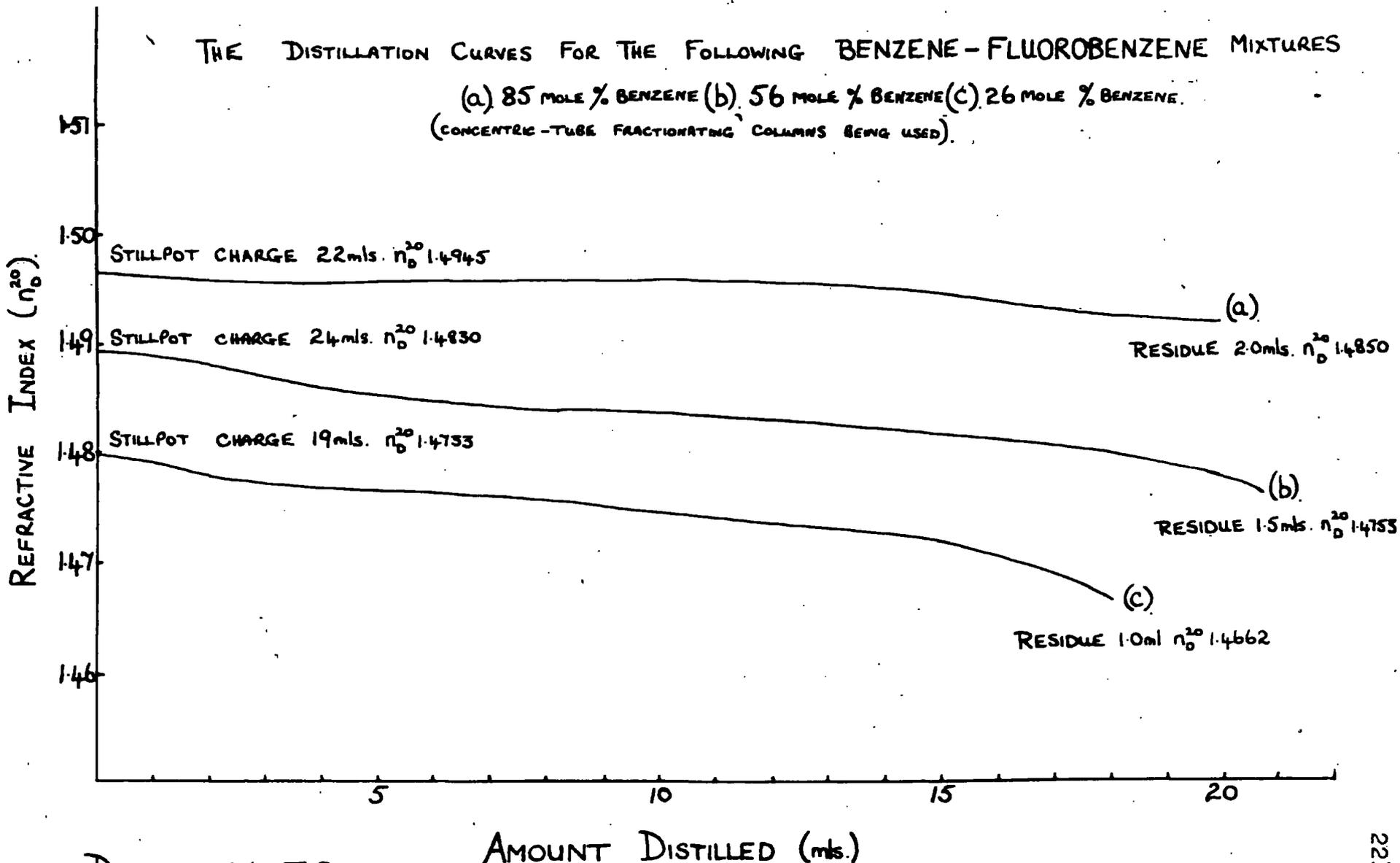


DIAGRAM 38

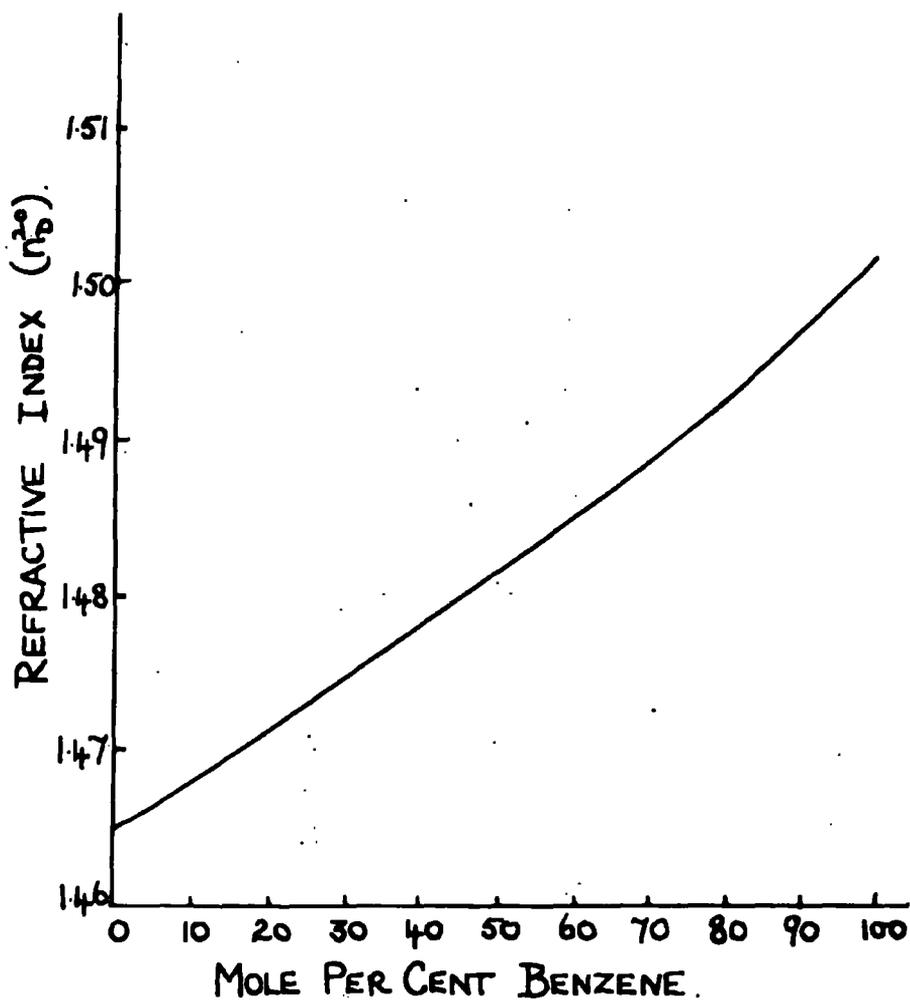


DIAGRAM 39 REFRACTIVE INDEX - COMPOSITION CURVE
FOR $C_6H_6 - C_6H_5F$ MIXTURES.

↑ TO THE ATMOSPHERE or
REDUCED PRESSURE SYSTEM.

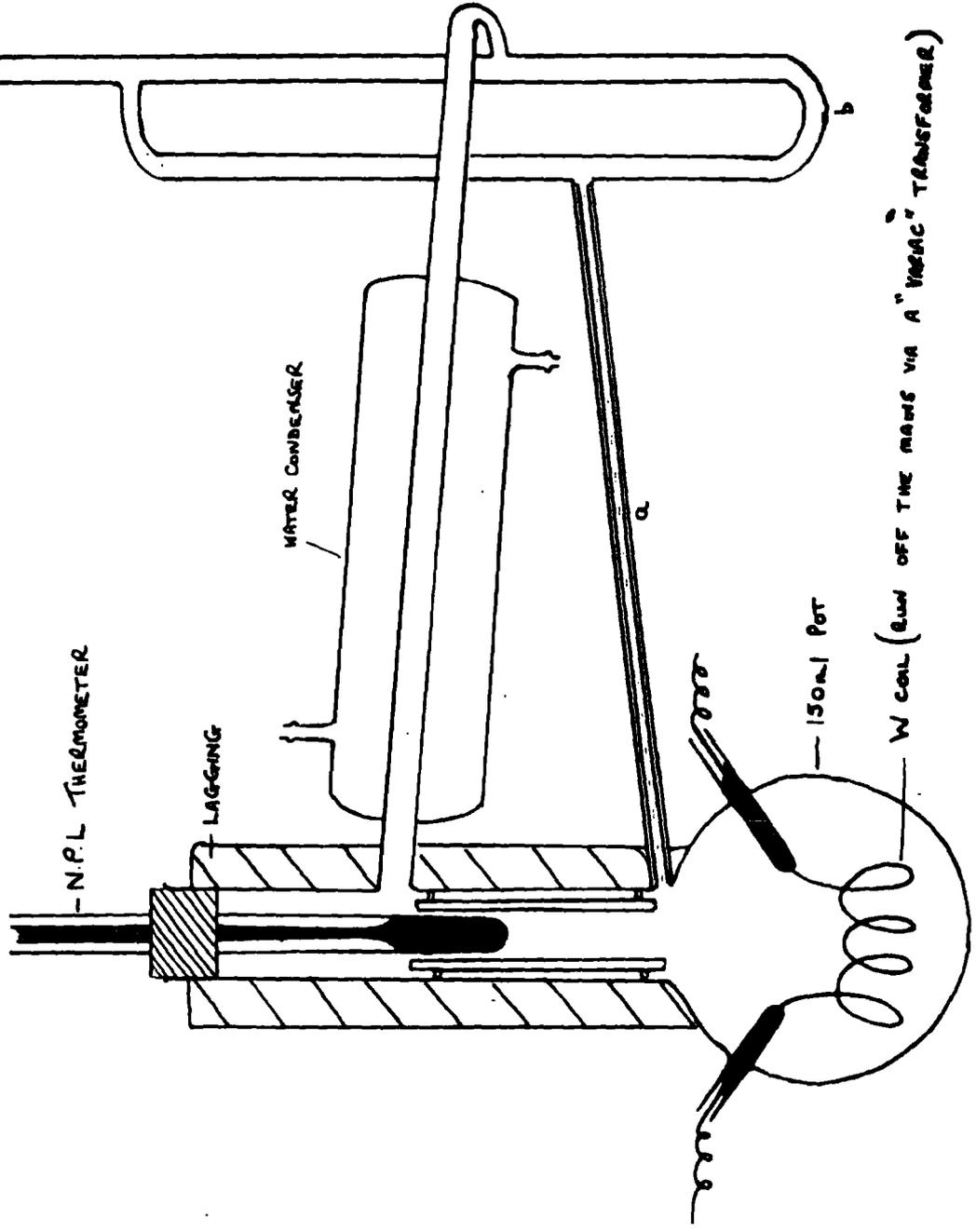


DIAGRAM 40 A SIMPLE VAPOUR-LIQUID EQUILIBRIUM STILL

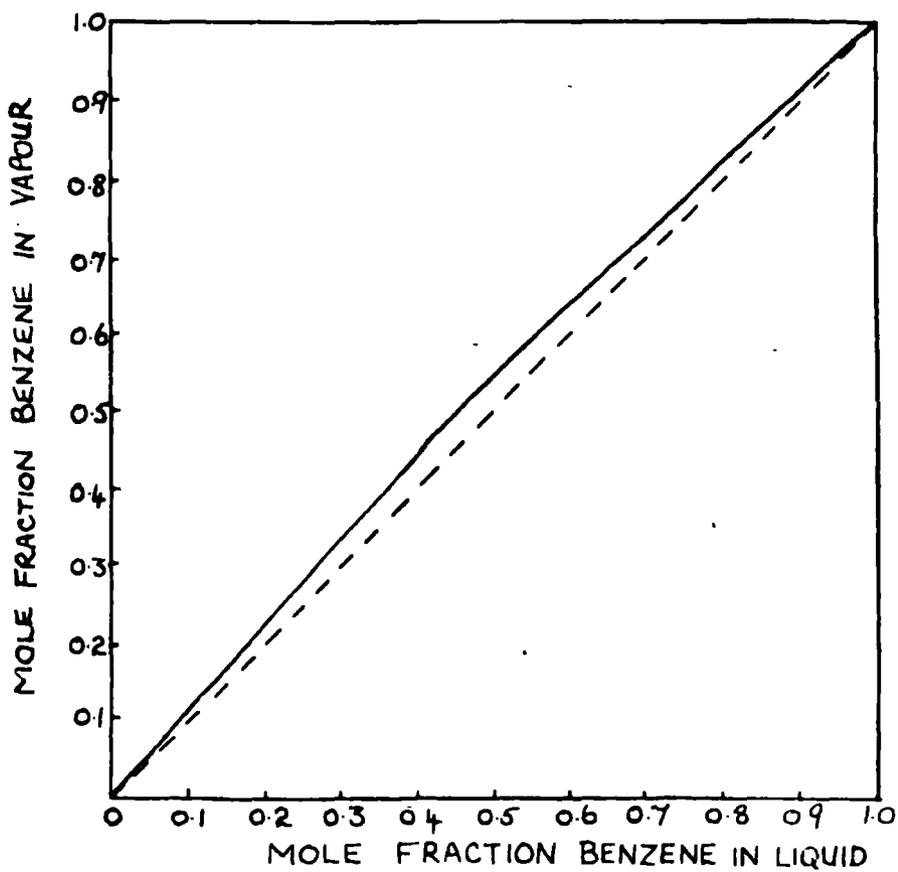
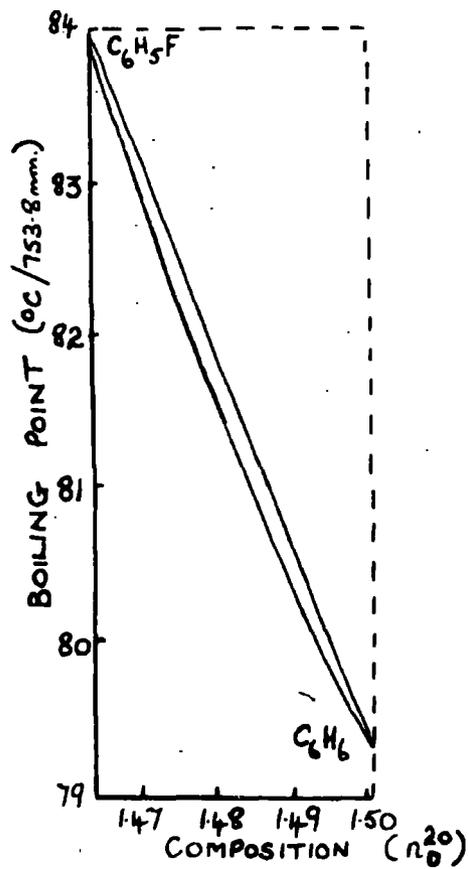


DIAGRAM 41

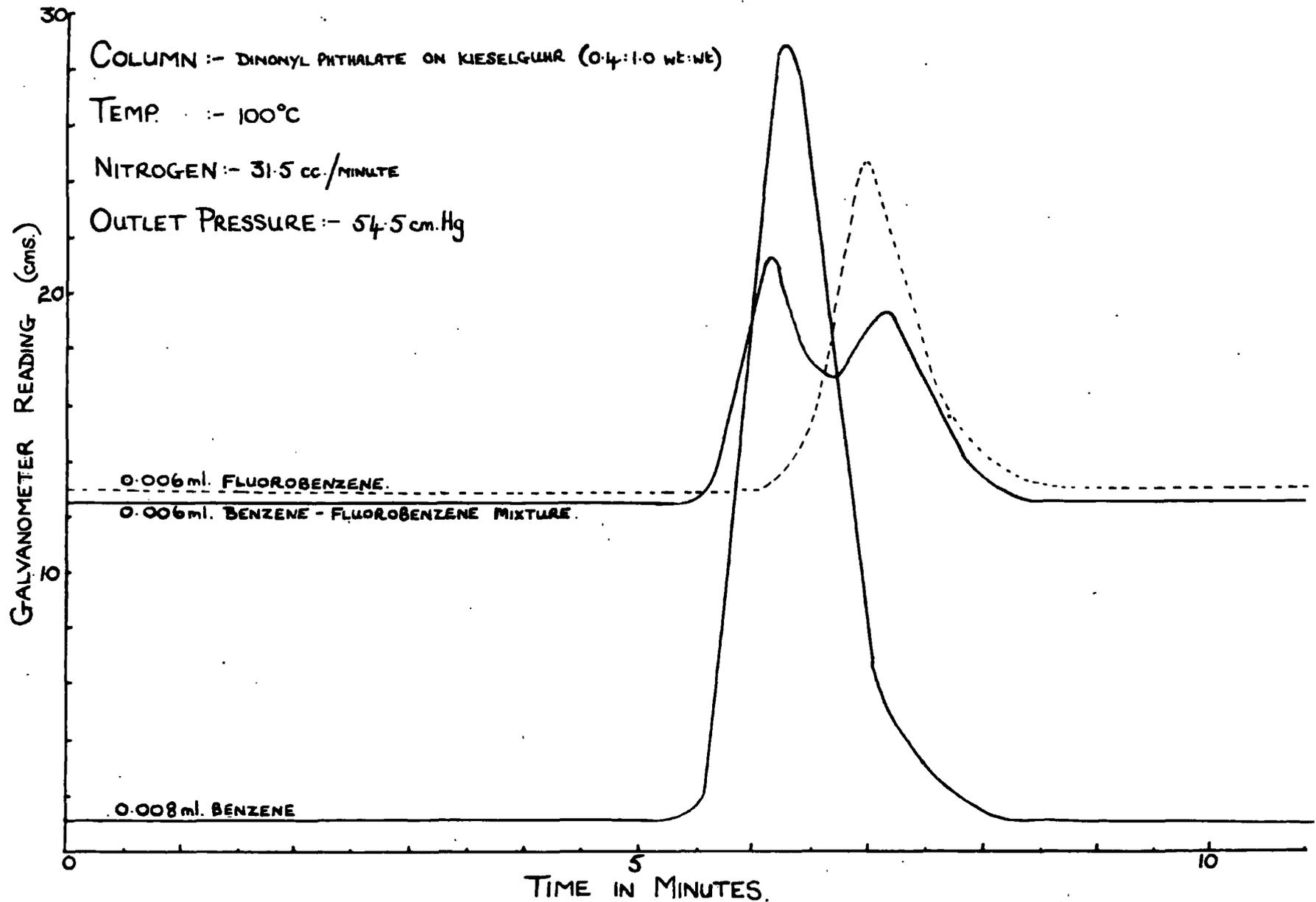


DIAGRAM 42 : ANALYTICAL GAS CHROMATOGRAMS FOR THE BENZENE-FLUOROBENZENE SYSTEM.

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