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ROYAL AIRCRAFT ESTABLISHMENT

FARNBOROUGH, HANTS

TECHNICAL NOTE No: CHEM.1321
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L4 **COPOLYMERS OF
FLUORONITROSOALKANES
AND FLUOROALKENES
PART II. THE PREPARATION OF
PERFLUORONITROSOMETHANE**

by

L5 P.S.FITT and J. VEITCH

L6 **OCTOBER, 1957**

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1. Perfluronitrosomethane—
Preparations.

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SUBJECT: Copolymers of Fluoronitrosoalkanes and Fluoroalkanes
Part II. The Preparation of Perfluoronitrosomethane (U)

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ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH

Copolymers of fluoronitrosoalkanes and fluoroalkenes

Part II

The preparation of perfluoronitrosomethane

by

P.S. Fitt and J. Veitch

R.A.E. Ref: Chem/826/6/PSF/JV

SUMMARY

A comparison of the methods of Haszeldine and Mrs. Mason for the preparation of perfluoronitrosomethane is made in this note. Details of its preparation by an adaption of Mrs. Mason's method are given.

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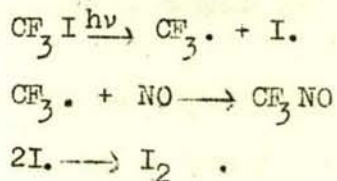
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1 Introduction

Perfluoronitrosomethane was required for the study of its copolymerisation with tetrafluoroethylene, which is now being undertaken in the Chemistry Department. Only one satisfactory method is available for the preparation of perfluoronitroso compounds¹, and a controversy has been in progress in the literature over the best conditions for the reaction.

The method, first described in 1953 by both Miss Banus (now Mrs. Mason)^{2,3} and Haszeldine⁴, involves the irradiation of mixtures of perfluoriodomethane and nitric oxide with ultraviolet light. Perfluoriodo compounds have an absorption band in the region 2670-2710 Å⁵, so that both workers were able to use mercury-discharge lamps, giving light of 2537 Å wavelength, as their sources of irradiation. When irradiated with ultraviolet light, perfluoriodomethane undergoes homolytic fission to trifluoromethyl and iodine radicals; the former react with the nitric oxide to give perfluoronitrosomethane, whilst the iodine radicals combine to form iodine molecules:



Perfluoriodomethane is prepared by the action of iodine on the silver salt of trifluoroacetic acid, the well known Hunsdiecker reaction^{6,7}. The nitric oxide may be made by standard methods.

A comparison of the two literature methods for the preparation of perfluoronitrosomethane, and a discussion of the method used at the R.A.E., are given below.

2 Comparison of the methods of Haszeldine and Mrs. Mason

I.C.I. Ltd. Plastics Division, used the method of Barr and Haszeldine^{1,8,9} for the preparation of CF_3NO , but after discussions with the I.C.I. workers¹⁰ and with Mrs. Mason¹¹, and a careful study of the relevant literature, it was decided that better results would be obtained using an adaptation of Mrs. Mason's method^{2,3,12}.

Barr and Haszeldine mixed perfluoromethyl iodide with a large excess of nitric oxide in a twenty-litre flask containing a large quantity of mercury. The contents of the flask were irradiated for 20-25 hours with a centrally-placed Hanovia ultraviolet light, with an output of 7 watts¹³, while the flask was shaken slowly to disturb the mercury surface. Mercury was considered necessary to remove iodine and dinitrogen tetroxide produced in the reaction. After the period of irradiation was complete, oxygen was admitted to the flask to oxidise the excess of nitric oxide to dinitrogen tetroxide, and the gases were bubbled through 30% sodium hydroxide solution to remove iodine and acidic by-products. The gaseous mixture was fractionated in vacuo to give the nitroso compound and unchanged perfluoriodomethane. The yield of nitroso compound was about 40% (based on the amount of iodide taken).

Mrs. Mason mixed equal amounts of nitric oxide and iodo compound in a 500 c.c. cylindrical reaction vessel, which was surrounded by a spiral cold mercury-discharge lamp (output ca. 25 watts). The quantities of the reactants were adjusted so that the initial pressure in the reaction vessel was just below atmospheric. The mixture was irradiated for 10-15 minutes, unreacted nitric oxide was pumped off at -196°C, and the gases were washed with alkali before fractionation. This method was claimed to give

approximately twice the yield obtained by Barr and Haszeldine. Mrs. Mason has shown that the yield obtained by her method is unaffected by the presence or absence of mercury. She has also pointed out^{3,11} that it is not necessary to oxidise the small amount of unreacted nitric oxide, because it can easily be pumped away from the products at the temperature of liquid nitrogen.

Mrs. Mason used a more powerful source than the Cambridge workers, and her technique is therefore more in line with the recommended photochemical practice¹⁴ of using a high intensity source unless the reaction is of the chain type.

3 R.A.E. method

It was decided that Mrs. Mason's method would be more satisfactory than Barr and Haszeldine's for the following reasons:-

(1) The reaction time was shorter for the production of comparable amounts of CF_3NO , so that any danger of decomposing the product by over-irradiation was minimised.

(2) The yield was reported to be much better.

(3) The product was claimed to be more pure.

The reaction vessel had to be larger than Mrs. Mason's, so that more material could be prepared per run, and her arrangement of a cylindrical chamber surrounded by a spiral lamp could not conveniently be used. Instead, a large annular vessel with a centrally placed ultraviolet source was designed (Figs.2 and 7), and it was decided that the lamp should be the most powerful consistent with a reasonably long operational life. The path for the radiation could be kept fairly short in an annular vessel, one advantage of such a design. A large gas-handling manifold (Figs.1,5 and 6) and a low-temperature still (Figs.3,4,5 and 8) were also constructed, the latter to a design supplied by I.C.I. Ltd., Plastics Division.

The argon-filled cold mercury-discharge lamp was made from a ten-foot length of Vycor glass tubing (13 mm. O.D.; 1 mm. wall thickness). This particular glass was chosen for its excellent transmission (80%) of light of wavelength greater than 2400 Å, and its complete lack of transmission at wavelengths below 2000 Å. In addition to radiation of 2537 Å wavelength and a small amount of visible light, cold mercury-discharge lamps produce some light of 1850 Å. The latter, which would destroy the perfluoronitrosomethane, was eliminated by the Vycor glass, and the lamp gave substantially pure 2537 Å radiation. Electrodes were fitted to the lamp by Hanovia Ltd.

Equal amounts of perfluoroiodomethane and nitric oxide were admitted to the reaction vessel (Figs.2 and 7), the amounts being chosen so that the pressure in the vessel at the beginning of the reaction was slightly below atmospheric. The mixture was then irradiated, and the progress of the reaction was followed by a mercury manometer. When no further fall in pressure was observed (ca. 90% theoretical in $1\frac{1}{2}$ - 2 hours), the gases were transferred to a 20 l storage bulb (Fig.1); the process was repeated several times, and the crude products were combined. Unreacted nitric oxide was pumped away from the crude perfluoronitrosomethane at -196°C (liquid nitrogen) and the product was purified by distillation. The average yield of purified perfluoronitrosomethane was 80% of theoretical (b.p. of CF_3NO : -86.6°C ¹⁵).

The iodine produced in the reaction was deposited on the walls of the reaction vessel, which was designed so that it could be dismantled for cleaning.

4 Experimental

Information about the design of the vacuum line and the handling of gases was obtained from standard works of reference^{16,17,18}.

4.1 Preparation of perfluoriodomethane

Perfluoriodomethane was prepared as described by Haszeldine⁷.

4.2 Preparation of nitric oxide

Nitric oxide was prepared by the method of Inorganic Syntheses¹⁹, and the crude material was dried (P_2O_5) and purified by repeated fractionation.

4.3 Preparation of perfluoronitrosomethane (The capital letters in the text refer to Fig.1)

Equal volumes of nitric oxide and perfluoriodomethane, the amounts being chosen so that the pressure in R at the beginning of the reaction was ca. 70 cm., were condensed into T_1 , with tap 2 shut; with taps 1 and 3 shut and tap 2 open, the mixture was then allowed to enter the reaction vessel R. Tap 2 was closed, and the mercury-discharge lamp turned on: after a few minutes, a steady fall in pressure could be observed on the reaction vessel manometer, and iodine was deposited on the walls of R. The fall in pressure stopped after $1\frac{1}{2}$ - 2 hours, depending on the size of the charge, and the crude blue product was transferred through the line of traps to one of the storage bulbs (B). A further charge was then admitted to the reaction vessel, and the process repeated until a mole of crude product had been prepared.

Unreacted nitric oxide was pumped off at $-196^\circ C$, and fractionation of the residue gave pure perfluoronitrosomethane (80% yield).

4.4 Operation of low-temperature still (See Fig.3)

The still is first evacuated to 10^{-4} mm. of mercury, when the levels of mercury in the limbs of the manometer (P) is that indicated by X.

The Dewar flask (J) is filled with liquid nitrogen, Relay 2 is turned on, and the pre-cooling switch (Fig.4) is closed, so that the heater (I_1) operates continuously and the liquid nitrogen vent valve (K) is closed: liquid nitrogen is forced into the condenser (C) by the rise in pressure in the vacuum flask (J). The nitrogen outlet (F) from the condenser is kept closed, and nitrogen, forced through the small holes (D) round the top of the condenser, flows freely out of the bottom of the jacket, through the space round the still-pot (H). Tap T_1 to the vacuum-line is opened, and the distilland condensed into H; T_1 is then closed, F is opened, and the pre-cooling switch is turned off (Relay 2 still switched on).

Relay 1 (Fig.4), and the still-pot heater (I_2) are switched on, and the rate-valve (M) is set to a convenient rate of flow, which must be determined by trial and error. When the distilland begins to boil, vapour passes out of the top of the column and is stopped by the magnetic take-off valve (L): the pressure in the system rises, and the level of mercury in the manometer (P) falls until the mercury surface in the open limb reaches the first probe (R and Fig.4). The circuit through Relay 1 (Fig.4) is then complete, the take-off valve (L) opens, and gas flows into the vacuum-line at a rate determined by the rate-valve setting; the latter is chosen so that the pressure in the system continues to rise until the surface in the open limb reaches the upper probe (S), completing the circuit through Relay 2. The nitrogen vent-valve (K) is then closed,

the heater L_1 is turned on, liquid nitrogen is forced into the condenser and escapes as a gas through F, and the flow of distillate is checked. The level of mercury rises in the closed manometer limb, and so falls away from the probes in the open limb, breaking the circuits; the escape of gas into the vacuum-line then stops. This process is repeated, so that steady distillation takes place, and the temperature of the gases leaving the column is measured by a chromel thermocouple placed in E.

5 Conclusions

Perfluoronitrosomethane has been prepared in excellent yield by an adaptation of Mrs. Mason's method, which is considered by the authors to be superior to Haszeldine's method.

Acknowledgements

Grateful acknowledgement is made to I.C.I. Ltd. Plastics Division, for their advice and for permission to publish drawings of their low-temperature still, and to Hanovia Ltd., Bath Road, Slough, for fitting electrodes to the mercury-discharge lamp.

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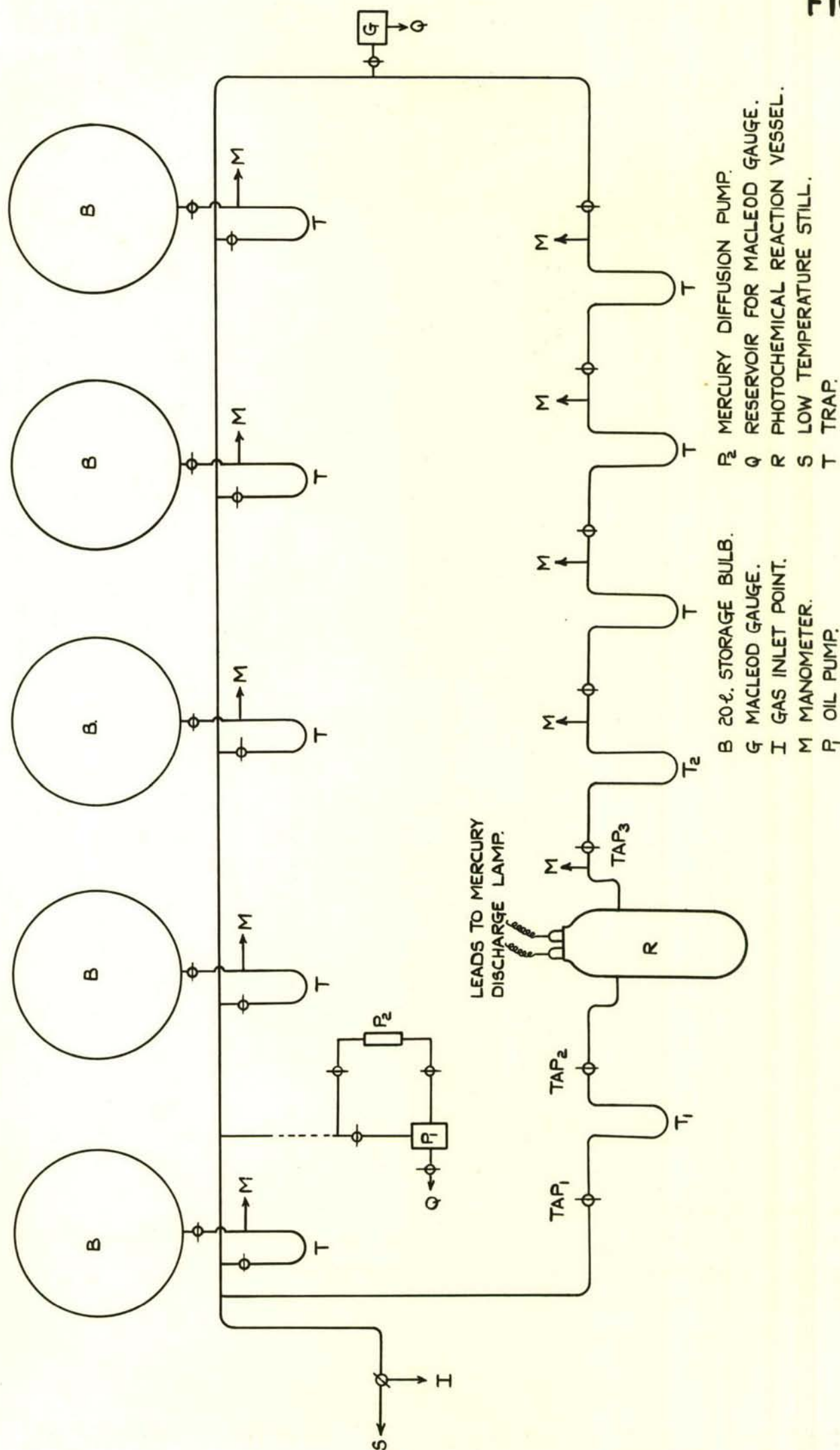
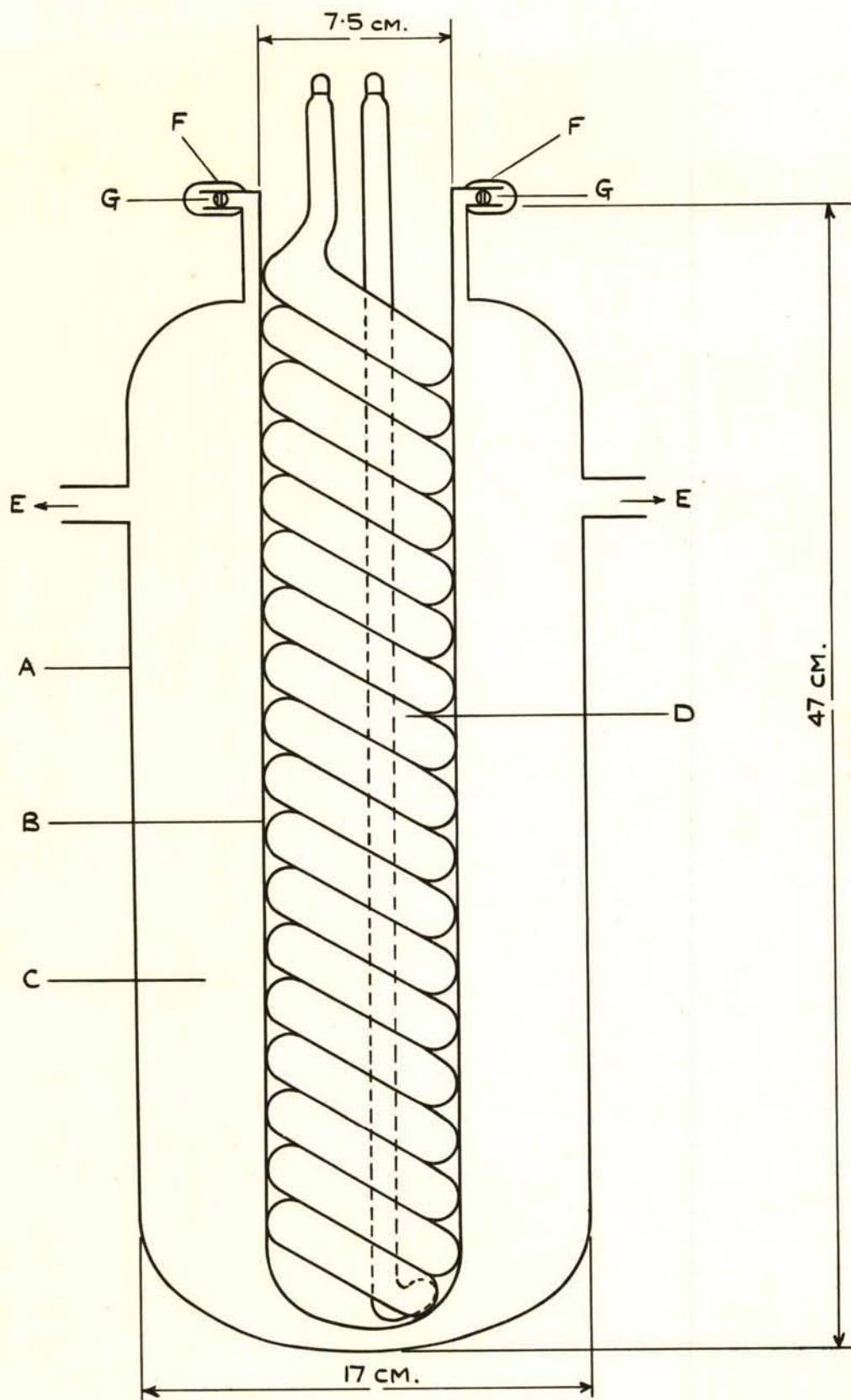


FIG. I. LINE DIAGRAM OF THE VACUUM MANIFOLD.



- | | |
|---|--------------------------------|
| A PYREX OUTER VESSEL. | E VACUUM-LINE. |
| B SILICA INNER TUBE. | F SEALING COMPOUND (APIEZON Q) |
| C 6-l. ANNULAR SPACE. | G POLYTHENE RING. |
| D MERCURY DISCHARGE LAMP
(MADE FROM VYCOR SPIRAL). | |

FIG.2. LINE DIAGRAM OF PHOTOCHEMICAL REACTION VESSEL.

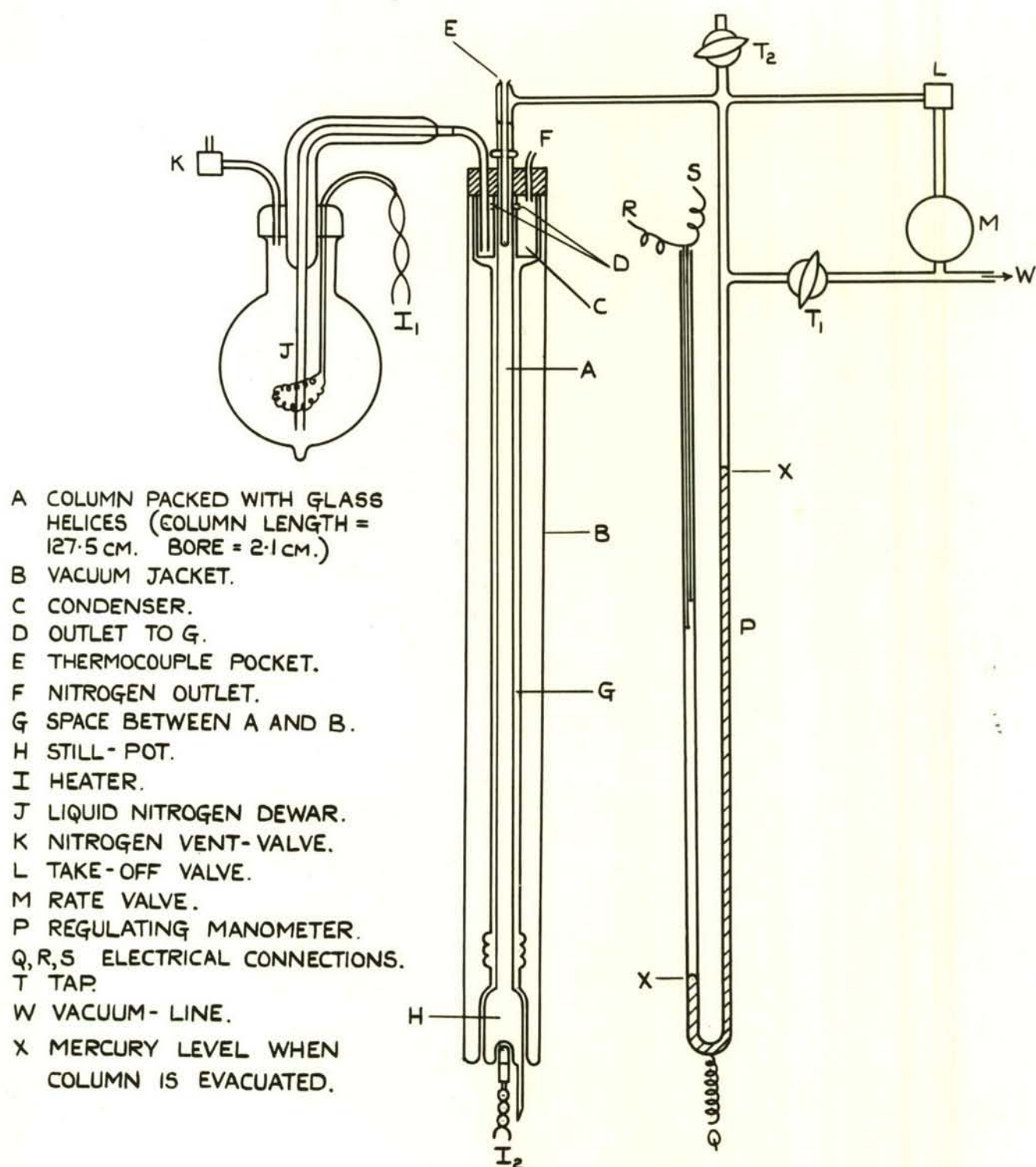


FIG. 3. LINE DIAGRAM OF LOW-TEMPERATURE
STILL.

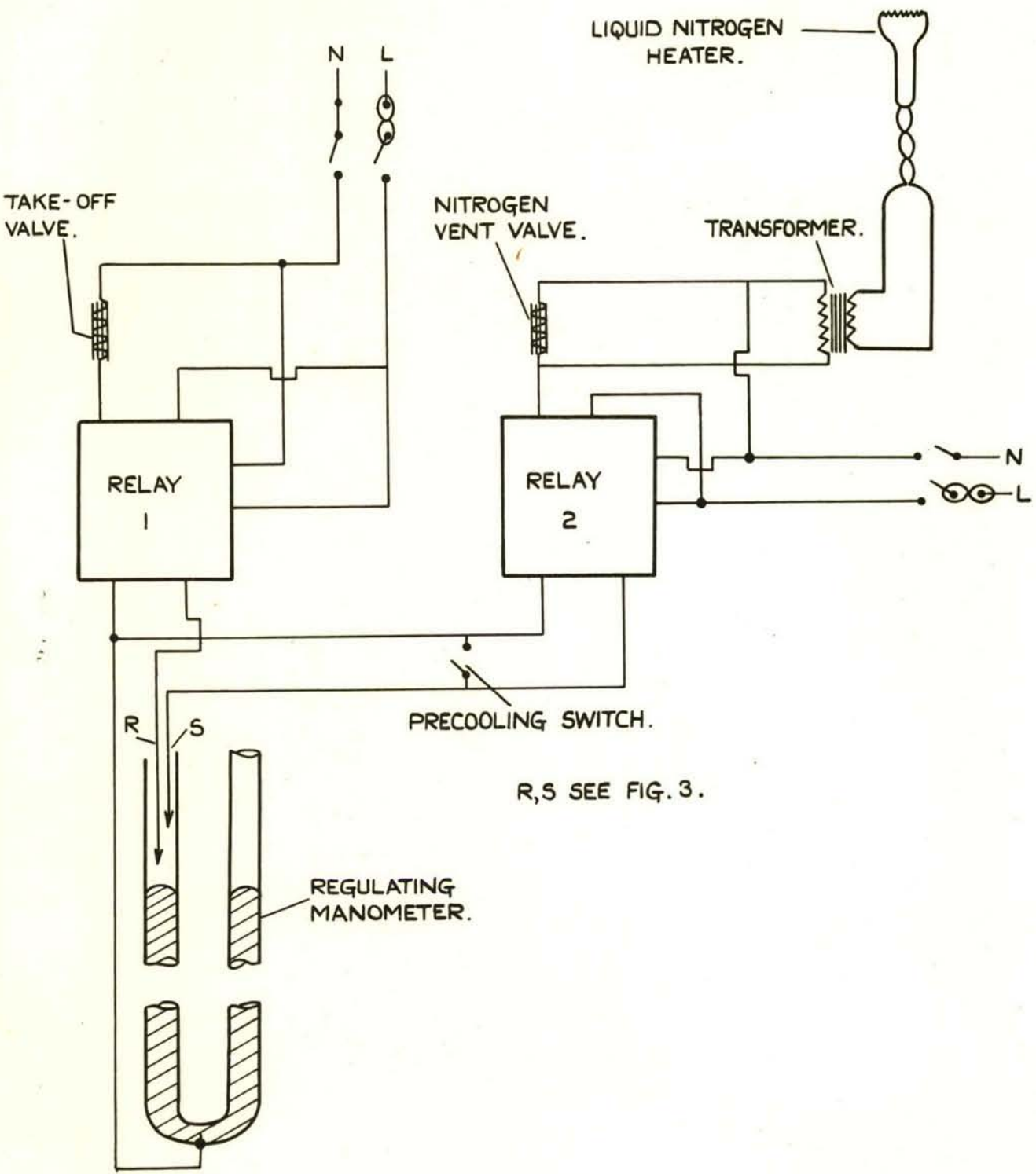


FIG. 4. ELECTRICAL CIRCUIT FOR LOW-TEMPERATURE STILL.

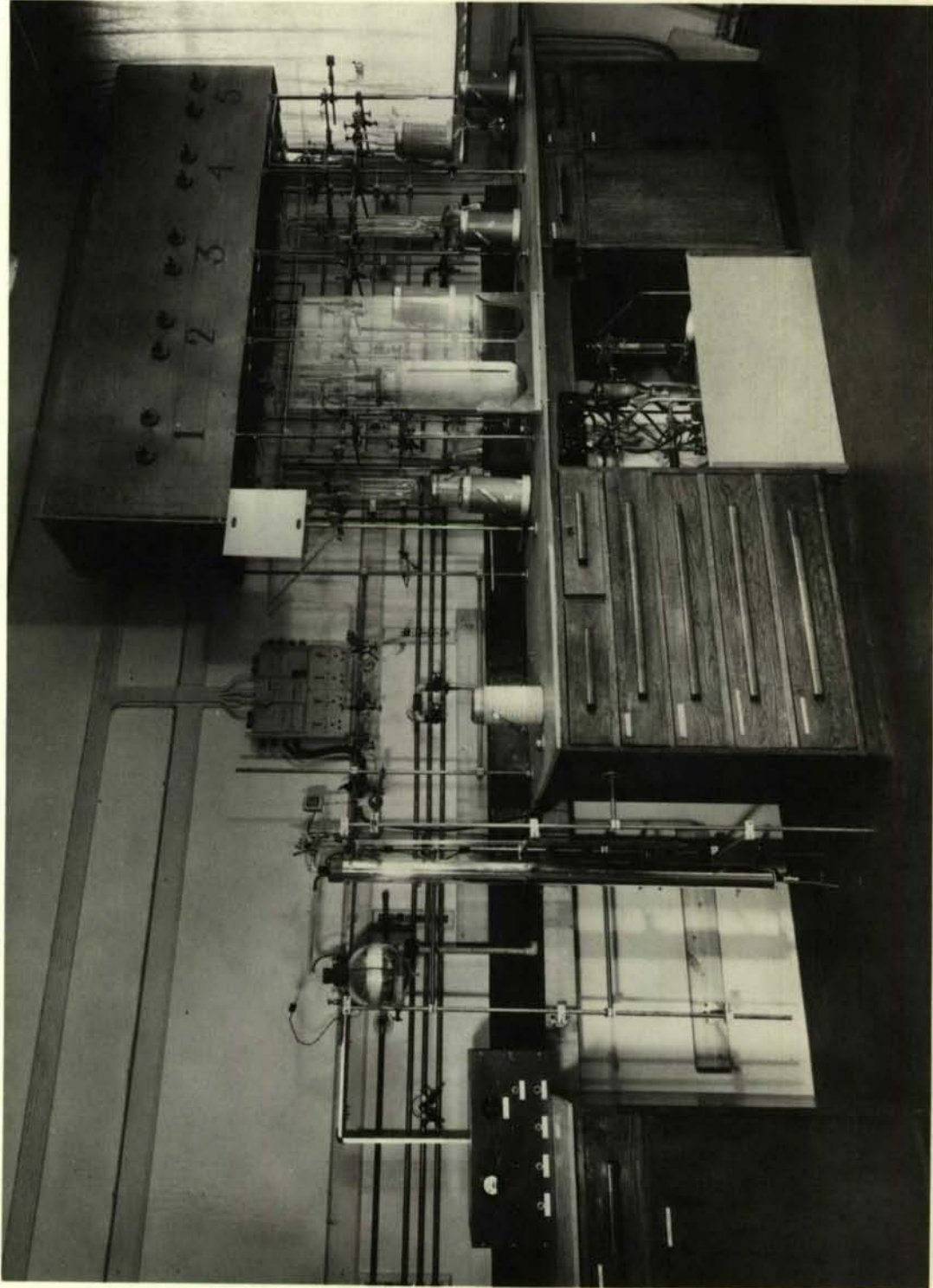


FIG.5. GENERAL VIEW OF VACUUM-MANIFOLD AND LOW TEMPERATURE STILL

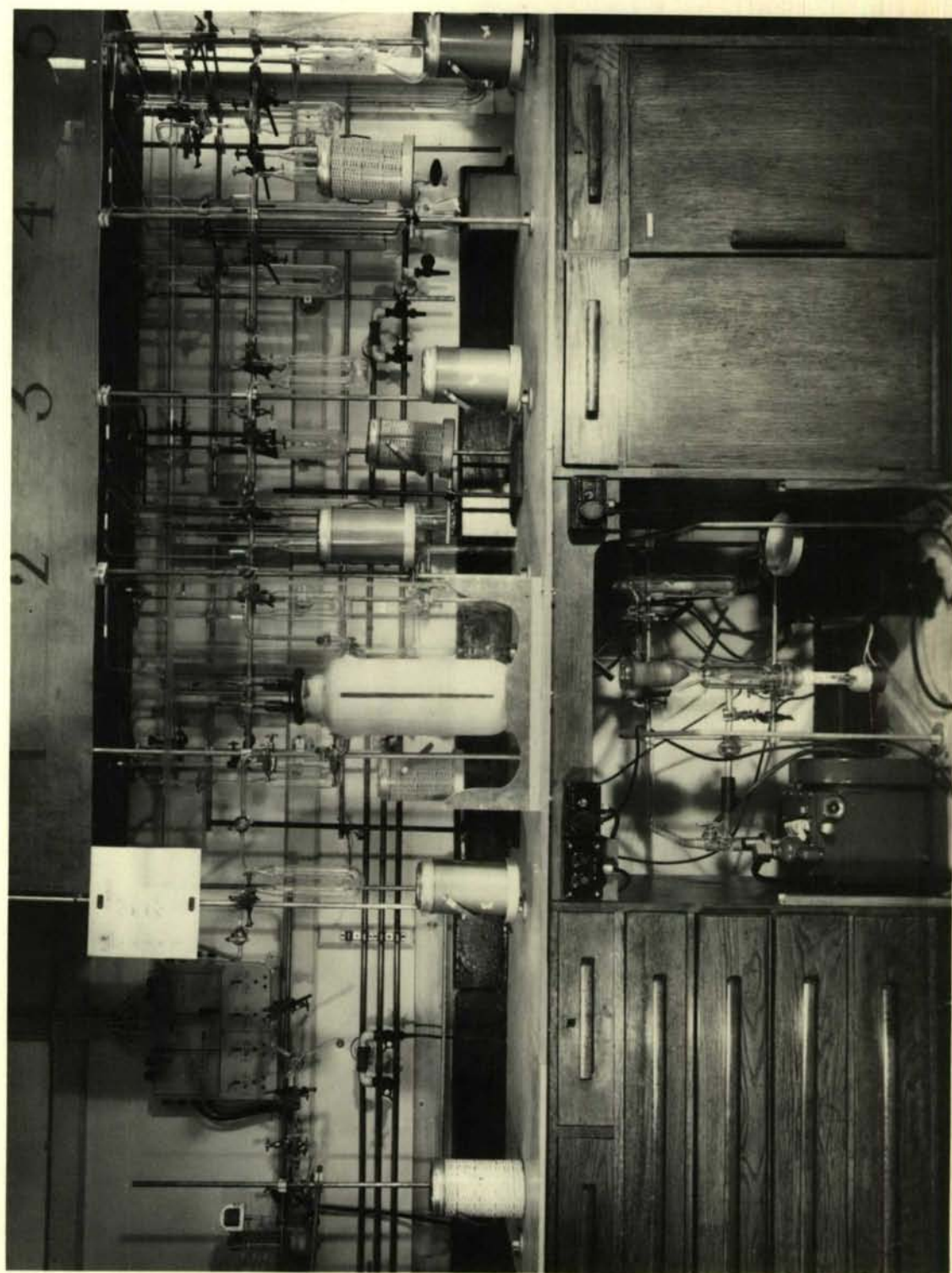


FIG.6. VACUUM-MANIFOLD

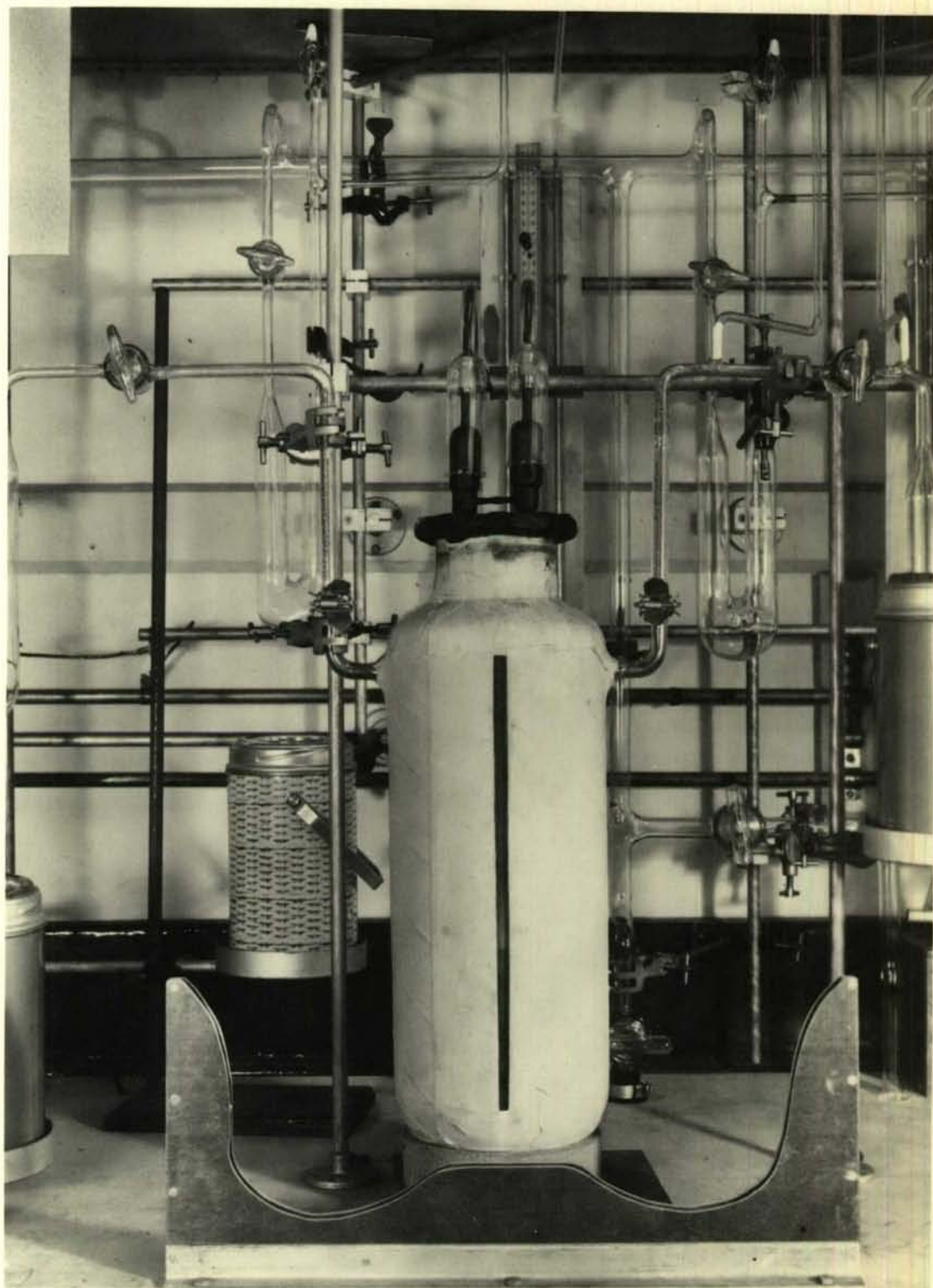


FIG.7. PHOTOCHEMICAL REACTION-VESSEL

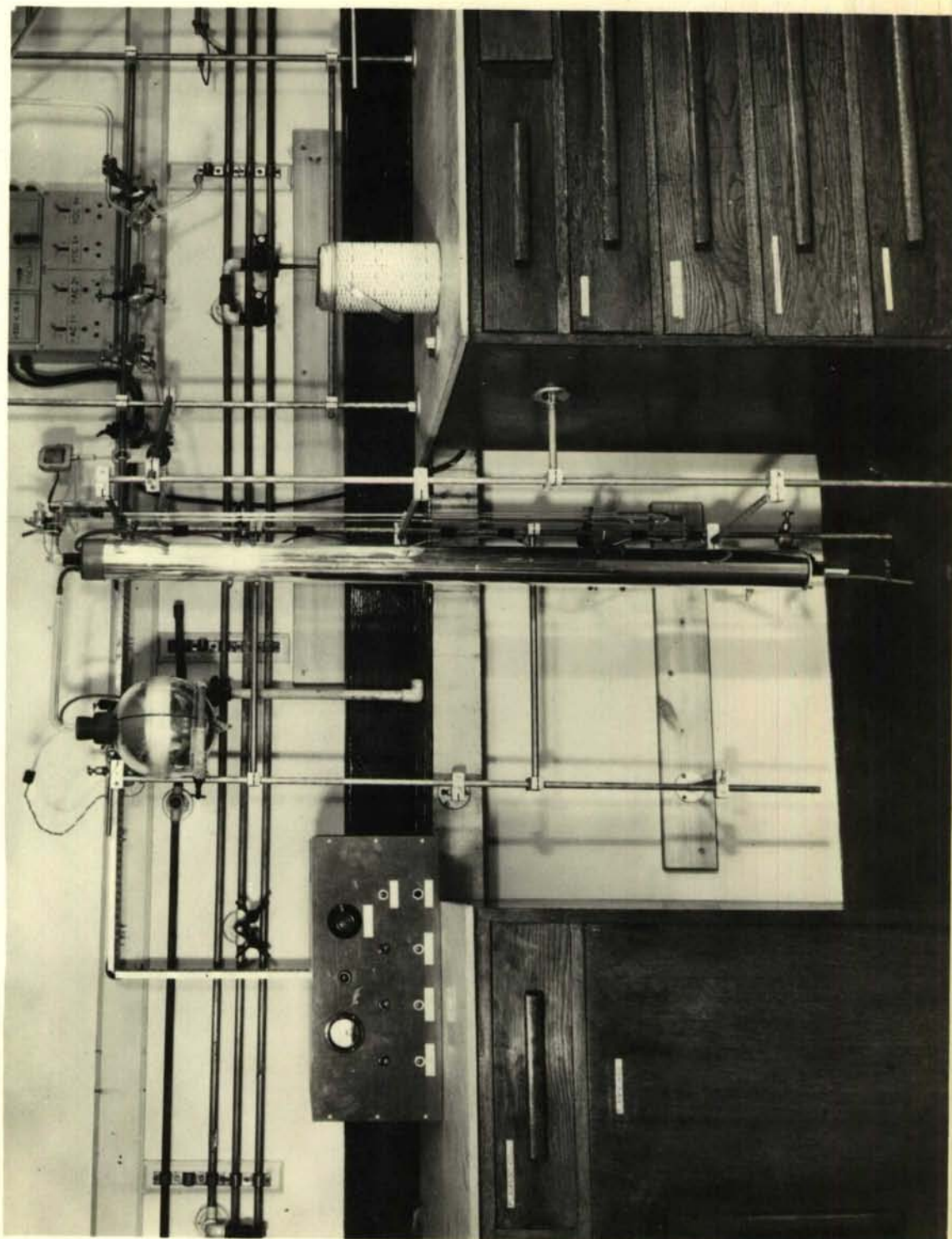


FIG.8. LOW TEMPERATURE STILL