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Dragon Project Report

~~PRELIMINARY REPORT~~

MAST

A STUDY ON THE TRAPPING OF IODINE AT HIGH TEMPERATURES ON ACTIVATED CHARCOAL

by

R. O. LINGJAERDE
AND
L. PODO

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A STUDY ON THE TRAPPING OF IODINE
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ABSTRACT

An experiment is described for the testing of iodine retention characteristics of pure and metal coated/impregnated charcoal - in connection with the specification of internal fuel element trap filler material for the Dragon reactor.

The experimental set-up is briefly outlined and results obtained from runs using pure and 'treated' charcoal discussed. A theory for the mechanism of retention of iodine on pure charcoal at high temperatures is offered.

Pure coconut-based charcoal gives a satisfactory performance under simulating reactor conditions and is recommended to be used for the fuel element traps in the first fuel charge.

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A STUDY ON THE TRAPPING OF IODINE AT HIGH TEMPERATURES ON ACTIVATED CHARCOAL

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1. INTRODUCTION

Relatively early Dragon decided to incorporate a trap (consisting preferably of charcoal) located inside each fuel element in order to retain/delay volatile fission products carried in the purge stream, which had passed over the fuel elements.

The main advantages of this trap would be:

(i) To reduce fission product heat loading in parts of the externally situated purge stream purification plant.

(ii) To reduce deposition and possible blockage and/or corrosion (particularly by the halogens) in the purge pipe leading out of each fuel element.

The trap, an integral part of the fuel element, would be replaced with the latter.

In order to arrive at a specification for an effective trapping material to be used, an experiment was conducted simulating as closely as possible operating conditions anticipated for one internal trap. There are eight traps per fuel rod (constructed as shown in Fig. 1), seven rods per fuel element (Fig. 2).

A rig was erected (in principle similar to the one described in [1]), where purified helium carrying tagged iodine passed over charcoal contained in a test trap, and the time noted for the iodine to break through.

The experimental conditions/parameters chosen were:

(a) Correct flow of highly purified helium.

(b) Correct diameter of trap, but with varying depths.

(c) Trap temperature was varied, but the majority of tests were carried out at 450°C - assumed to be maximum operating temperature of the fuel element trap, taking into account fission product heating.

(d) Iodine was selected as a representative fission product, because its trapping efficiency on charcoal would be superseded by any other fission product (apart from the rare gases).

(e) To obtain results more rapidly, the iodine concentration in the helium was increased above that which could exist during actual operation (maximum value).

(f) Emphasis was put on testing pure coconut-based charcoal from the point of view of neutron economy, and knowing that this particular material generally has better retention characteristics than for example coal-based charcoal.

Metal coated and alkali metal 'impregnated' charcoals were also, however, tested.

2. DESCRIPTION OF THE EXPERIMENTAL SET-UP

2.1 General

The experimental rig is represented in Figs. 3 and 4. Helium passes through a purification plant (described below) and after its flow has been correctly adjusted, tagged iodine is injected into the stream at the desired partial pressure from a 'U' tube immersed in a refrigeration unit. The tagged iodine crystals contained in the 'U' tube have been generated as described below.

The helium stream containing iodine passes on to the test trap contained in a $\frac{1}{4}$ in. diameter glass tubing inserted in a furnace. The charcoal test trap, held in place by 'Fiberfrax' plugs, varied in depth from about $\frac{1}{2}$-6 in. for the different runs. As shown in Fig. 3, the build-up of activity on the test trap can be recorded during running by a scintillation counter. Prior to each run, the charcoal in the test bed was taken up to the desired temperature in the furnace and degassed by passing purified helium through it for about half an hour.

Iodine breaking through the test bed is collected in a trap down-stream of the furnace and recorded by a scintillation counter coupled to a multi-headed single channel analyser. A gas bubbler and a wet test meter completes the rig.

Three parallel rigs were in operation.

During operation, the refrigeration unit is kept at -20°C so as to give the iodine a partial pressure of $5 \cdot 10^{-6}$ atmospheres. The flow of helium is maintained at 69 cc/min (N.T.P.) which corresponds to the flow through one internal trap in the fuel element (based on a total passage of 7.84 g helium/s through all fuel elements). Assuming equilibrium between the iodine and the helium being established in the 'U' tube, a transport of approximately 0.2 mg/h of iodine is achieved.

2.2 The Helium Purification Plant

Diagrammatically, the purification unit is as shown in Fig. 5. A photograph of the completed rig is shown in Fig. 6. Helium is purified to 'reactor standard' by passing it through - in series - copper turnings at 400°C, copper oxide at 400°C, molecular sieve 5A at room temperature and activated charcoal at liquid nitrogen temperature.

Helium emerging from the purification unit was tested for some of its impurities. Results are shown in Table 1.

Table 1

Impurity	Concentration (vpm)	Method of Measurement (type of instrument used)
H_2O	1–2	Electrolytic water analyser
CO_2	not detectable (i.e., < 1)	Infra-red Gas Analyser
CO	not detectable (i.e., < 5)	Infra-red Gas Analyser
O_2	1	Herschmeter

Note: Levels of impurities recorded are only approximate because none of the instruments used are accurate at these low concentrations.

2.3 Generation of Iodine

Iodine can be generated from one of its salts in a variety of ways, some of which were tried in order to arrive at a convenient method to use in our particular set-up.

Sodium iodide was used as source of iodine and as oxidising agents potassium persulphate in concentrated sulphuric acid, potassium persulphate alone, potassium dichromate and sodium peroxide were tried. Potassium dichromate was found to be the only satisfactory one - giving an iodine yield of about 90% - and was used throughout. Potassium persulphate by itself and in concentrated sulphuric acid solution gave rise to sulphurous by-products (H_2S, SO_2, etc.), during generation which was difficult to completely remove and which poisoned the charcoal test trap (see Appendix 1).

Another method tried was to recover tagged iodine from a carbon tetrachloride solution (supplied by the Radiochemical Centre, Amersham). However, the process of distilling off the carbon tetrachloride must be carried out under vacuum in order to get a reasonable yield of iodine.

Iodine was generated in the rig prior to each run and the method eventually adopted was as follows.

A solution containing about 0.5 g of sodium iodide + approximately 10 mc I-131 (the latter supplied as a solution of iodide in weak sodium thiosulphate) was evaporated to dryness in the detachable iodine generation pot shown on Fig. 3. Then pure dry potassium dichromate was introduced and pure helium diverted through the generating pot and out to waste until the system was dry.

The mixture of iodide and dichromate was then heated and the iodine evolved trapped in the small 'U' tube, which is then kept at liquid nitrogen temperature.

Having completed the generation the small 'U' tube is warmed up, volatile by-products routed to waste and the pure iodine subsequently transferred to the 'U' tube contained in the refrigeration unit - the latter kept at liquid nitrogen temperature.

2.4 The Breakthrough Trap

The trap situated downstream of the furnace (see Fig. 3), where iodine breaking through the charcoal test bed is collected and recorded, is shown in Fig. 7 (dismantled) and in Fig. 8 (assembled).

The idea of using this type of trap for this experiment comes from AERE Harwell [2].

The trap consists of a charcoal impregnated filter paper backed by a millipore filter paper (type AA), clamped between two glass tubings. It is near to 100% efficient for collecting iodine escaping the test bed in one form or another.

A scintillation counter is positioned so that it 'views' the filter papers. The geometry of the set-up is good.

3. EXPERIMENTAL RESULTS

A series of runs were started using commercial, coconut-based, activated charcoal. Parameters varied for the different runs were charcoal mesh size, depth of test trap and trap temperature.

Results are given in Table 2. A system for rating the trap materials under test was adopted from General Atomic [1].

"The capacity of a particular material for delaying fission products are measured in terms of "Reactor Equivalent Delay" (in days). These "RED" values give an indication of how long a particular fission product atom entering one of the high temperature fuel element traps can be expected to remain (neglecting the decay factor). In the case of I-131, the most abundant iodine fission product, the half-life is only 8.1 days. Thus, a delay of ten half-lives or 81 days would result in a decrease in iodine activity by a factor of 2^{10} or 1024. This long delay (equivalent to a "RED" value of 81) would, therefore, reduce the iodine concentration leaving the trap to less than 0.1% of its original value."

Table 2

Showing Results from Runs using Uncoated Coconut-Based Charcoal
(Ultrasorb SC II British Carbo Norit Ltd.)

Charcoal Mesh Size	Length of Test Trap (in)	Iodine Breakthrough in Test Trap after (h)	Temperature (°C)	RED Value* (days)	Approximate Amount of Iodine Escaping Test Trap During Running (%)	Remarks
25/36	0.65	151	450	58	1	
10/24	0.65	135	450	52	1	
18/52	0.65	130	450	50	1	
18/52	0.5	Undefined	450	Undefined	>10	Undefined breakthrough due to channelling
10/24	1	290	450	70	1	
10/24	3	>310	450		< 1	Slight leakage after 180 h running - stopped after 310 h
10/24	6	>310	450		0	Stopped after 310 h
10/24	1	114	500	29	1	
10/24	1	51	600	13	1	
10/24	1	<24	700	<6	1	
10/24	2	-	450	-	Large and continuous leakage	Sample acid washed. Free from alkali metals

* RED values calculated on basis of 8 traps per fuel rod, each trap 6 in. long and $\frac{1}{4}$ in. in diameter.

In one of the runs reported in Table 2, the iodine product breaking through the high temperature charcoal trap had condensed in the cooler portion (rough internal surface of the glass) of the rig prior to reaching the breakthrough trap. A white crystalline substance was observed, which on chemical analysis revealed the presence of potassium, sodium and iodine + other metallic impurities in trace quantities. Further examination showed potassium iodide to be the main compound present, suggesting that a reaction had taken place between the entering iodine and the potassium impurities in the charcoal. The significance of this will be discussed later.

Results from runs using silver and copper coated, coconut-based charcoal are presented in Table 3.

Two of the samples were obtained from General Atomic, two from British Carbo Norit Ltd.

The silver coated samples from General Atomic were prepared [1] by reducing silver - from a solution of silver acetate - directly on to the charcoal. Ammonia is employed to reduce the reaction rate by complexing most of the silver ions and to achieve a more tightly adherent coating. A similar process was used by British Carbo Norit Ltd.

The copper coated material (also from General Atomic) was prepared by soaking charcoal in a saturated copper nitrate solution, drying the product, reduce first to the oxide by baking at about 300°C and finally reduce to the copper by heating to 500°C in a stream of hydrogen.

Both copper and silver seem to be present as surface deposits only and BET measurements have indicated no apparent decrease in the surface area of the activated charcoal [1] which for the latter is in the order of $1 \cdot 10^3\ m^2/g$.

Table 4 gives results from runs using potassium, sodium and barium impregnated, coconut-based, charcoal. These were prepared so as to attempt increasing the "chemical reactivity" of the internal traps (see paragraph 4) and were made by soaking charcoal in solutions of potassium hydroxide, sodium hydroxide and barium carbonate/barium hydroxide at various concentrations. After the soaking process, the charcoal was dried in an oven at about 100°C.

In one of the runs reported in Table 4, (at temperature 700°C), again a crystalline deposit formed downstream of the trap. This deposit on analysis revealed the presence of I^-, K^+, Na^+, CO_3^{--} and OH^- but it was not established definitely in which form iodine appeared.

4. DISCUSSION AND CONCLUSION

When we set out to do the iodine trapping experiment described, our object was primarily to find a filler material for the Dragon fuel element internal trap which could delay the I-131 released to the purge stream in excess of five half-lives, operating the trap at a maximum temperature in the region of 400-500°C [3]. The material to be used also had to have a low neutron cross section, because of the location of the trap in the reactor core.

Pure coconut-based charcoal complies with these specifications and will

Table 3

Showing Results from Runs Using Metal Coated Coconut-Based Charcoal

Charcoal Mesh Size	Metallic Coating	Length of Test Trap (in)	Iodine Breakthrough in Test Trap After (h)	Temp. (°C)	RED Value* (days)	Approximate Amount of Iodine Escaping Test Trap During Running (%)	Remarks
10/24	20 w/o Ag	0.5	384	450	193	0	Sample from British Carbo Norit Ltd.
10/24	37 w/o Ag	0.5	400	450	200	0	Sample from General Atomic
10/24	5 w/o Ag	1	232	450	58	0	Sample from British Carbo Norit Ltd.
10/24	43 w/o Cu	0.5	168	450	84	0	Sample from General Atomic

*RED values calculated on basis of 8 trap per fuel rod, each trap 6 in. long and $\frac{1}{4}$ in. in diameter.

Table 4

Showing Results from Runs Using Alkali Metal Impregnated Coconut-Based Charcoal

(Ultrasorb SC II, British Carbo Norit Ltd.)

Charcoal Mesh Size: 10/24

Impregnant	Length of Test Trap (in)	Iodine Breakthrough in Test Trap after (h)	Temperature °C	RED Value* (days)	Approximate Amounts of Iodine Escaping Test Trap During Running (%)	Remarks
KOH (5.8 w/o K)	0.5	400	450	200	0	
KOH (11.6 w/o K)	0.5	>766	450	–	0	Stopped after 766 h running
KOH (17.1 w/o K)	0.5	>766	450	–	0	Stopped after 766 h running
NaOH (4.1 w/o Na)	0.5	>330	450	–	0	Stopped after 330 h running
KOH (11.6 w/o K)	3	>552	600	–	0	Stopped after 552 h running
KOH (17.1 w/o K)	3	>552	700	–	0	Deposit in Rig Downstream of Trap. Stopped after 552 h running
$BaCO_3/Ba(OH)_2$ (2.1 w/o Ba)	1	240	450	60	0	

* RED values calculated on basis of 8 trap per fuel rod, each trap 6 in. long and $\frac{1}{4}$ in. in diameter.

now be used for the fuel element traps in the first charge.* The delay the charcoal will offer for iodine under conditions prevailing, will most probably exceed five half-lives (as demonstrated in the H.T.G.C. Pluto Loops) even for the trap situated in the middle fuel rod, which is about half the length of the traps in the outer six.

The mechanism of retention of the iodine on pure charcoal - at high temperatures - is undoubtedly one of chemisorption, where the alkali metal impurities plays the role of chemical getters. The charcoal acting as a chromatographic column for the iodides formed. This conclusion is drawn from the following facts:

(a) Potassium iodide was the main compound present in the breakthrough product from one of the trap runs.

(b) Potassium is the predominant 'active' metal impurity in commercial coconut-based charcoal (see Appendix 2).

(c) If coconut-based charcoal with a very low alkali metal impurity content is used (acid washed charcoal - last run reported in Table 2), iodine is hardly retained at all.

In Table 2, it can also be seen that the shallower the test trap, the more readily iodine escapes during running, accounted for by a 'chemical' channelling - part of the inflowing iodine fails to find a metal getter.

The retention of the iodine in the fuel elements during reactor operation is also likely to be aided by a possible reaction between the iodine and the fission product caesium. Any caesium iodide formed - if any reaches the internal trap - will be even more strongly adsorbed on the charcoal than potassium iodide (it is less volatile).

One way of improving the retention characteristics of pure charcoal is to deposit metals forming low volatile iodides,(e.g., silver and copper) on it. This has been demonstrated and discussed in [1] and confirmed by ourselves. 'RED' values for our trap arrangement in the order of 200 days can be achieved using for example 37 w/o silver coated material.

However, the total amount of silver thus to be introduced into the Dragon reactor core (bottom reflector) is appreciable and raises problems as to its effect on the neutron economy.

By far the best retention characteristics were demonstrated by coconut-based charcoal impregnated with potassium hydroxide or sodium hydroxide - as shown in Table 4 - at temperatures even as high as about 600°C. The material prepared has the additional advantage of having a low neutron cross section.

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*The mesh size of the charcoal granules will be 10 x 24 and it has been proposed to support the trap with "Fiberfrax" which is an aluminium-silicate fibre, temperature and radiation resistant.

The retention of iodine seems to increase with increasing amount of hydroxide deposited. However, 'RED' values were not obtained for most of the runs due to interruption of the experiment when values in excess of 200 were obtained.

This rather unexpected high performance of the hydroxide impregnated charcoal was surprising and it seems difficult to offer a satisfactory explanation for the mechanism of retention in this case. The rather long delay for the iodine (in one form or another) to break through the test trap may suggest not a simple potassium (sodium) iodide formation on the trap but the formation of another stable, but less volatile form of iodine.

Time did not unfortunately permit us, however, to carry this experiment any further in order to probe more into the theoretical aspects of the retention mechanism.

5. ACKNOWLEDGMENT

The authors wish to thank Dr. de Bruijn for his interest and support and Miss D. Bartlett for her help in carrying out the experimental work.

6. REFERENCES

[1] R. M. Watkins, D. D. Busch, and L. R. Zumwalt. "High Temperature Fission Product Trap Study for Gas Cooled Reactors." June, 1961. GA-1990.

[2] V. J. Emerson. AERE Harwell. Private Communication.

[3] S. B. Hosegood. Dragon Project. Private Communication.

SULPHUR POISONING

When persulphate - alone or in a sulphuric acid solution - is used for liberating iodine from an iodide, certain sulphurous by-products are generated simultaneously (SO_2 and H_2S mainly).

These compounds (even trace quantities) prevents iodine from being sorbed on charcoal at high temperatures. The reason probably being that the sulphurous compounds react preferentially to the iodine with the alkali metal impurities (essential chemical getters for the iodine to be retained on charcoal at high temperatures).

This poisoning effect should, however, not be embarrassing during operation pending the reactor graphite having been properly degassed before start-up. It is well known that graphites in the initial degassing process can release fairly large quantities of SO_2, H_2S and CS_2. SO_2 up to 600°C and H_2S + CS_2 up to 1400°C.

APPENDIX 2

The following quantities of metal impurities were found in a sample of Ultrasorb SC II (British Carbo Norit Ltd.) submitted to chemical analysis. (Results expressed in percentage by weight):

Ash	3.1
Fe	0.14
Na	0.08
K	0.87
Mg	0.03
Mn	0.01
Si	0.6*
Al	0.06
Ca	0.06

* A large proportion of the Si found was present as angular flint-like pieces, some over 1 mm^3 size.

FIG. 1. FISSION PRODUCT TRAP
Constituent Parts of "Fluted Barrel" Design

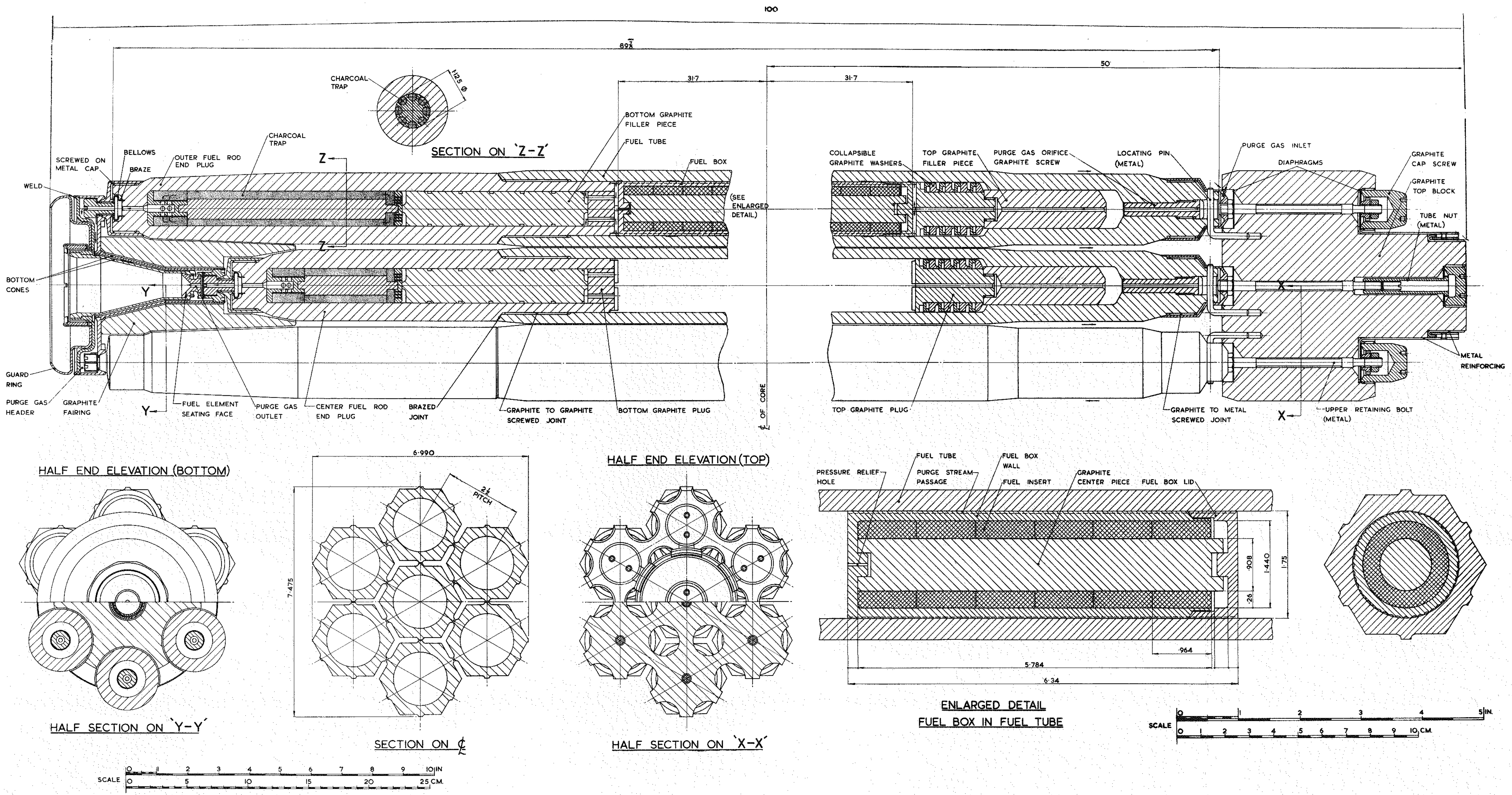

FIG. 2. DRAGON FUEL ELEMENT ASSEMBLY MARK IX

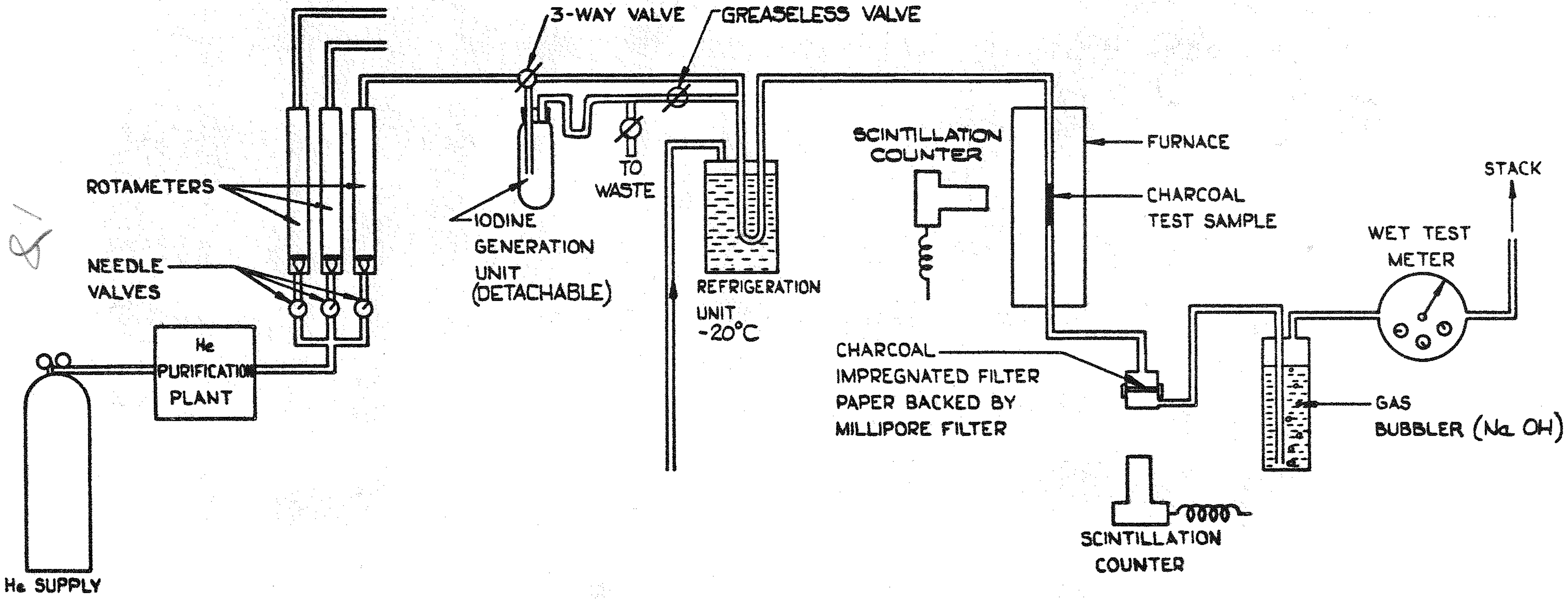

FIG. 3 DIAGRAM OF APPARATUS TO STUDY FISSION PRODUCT TRAPPING ONE OF THREE PARALLEL RIGS.

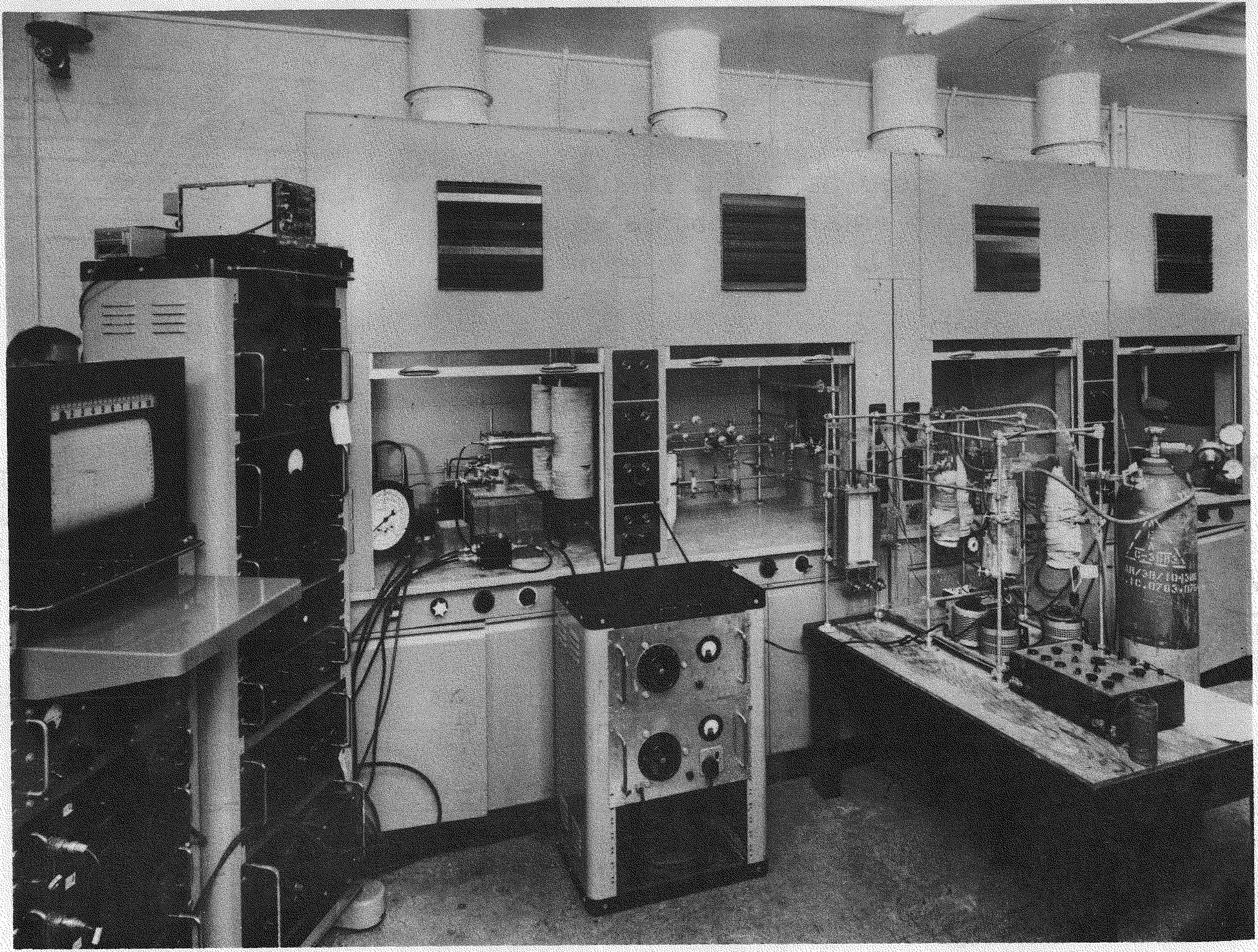

FIG. 4. PHOTOGRAPH OF APPARATUS TO STUDY FISSION PRODUCT TRAPPING.
TWO PARALLEL RIGS SHOWN WITH PART OF LEAD SHIELDING REMOVED

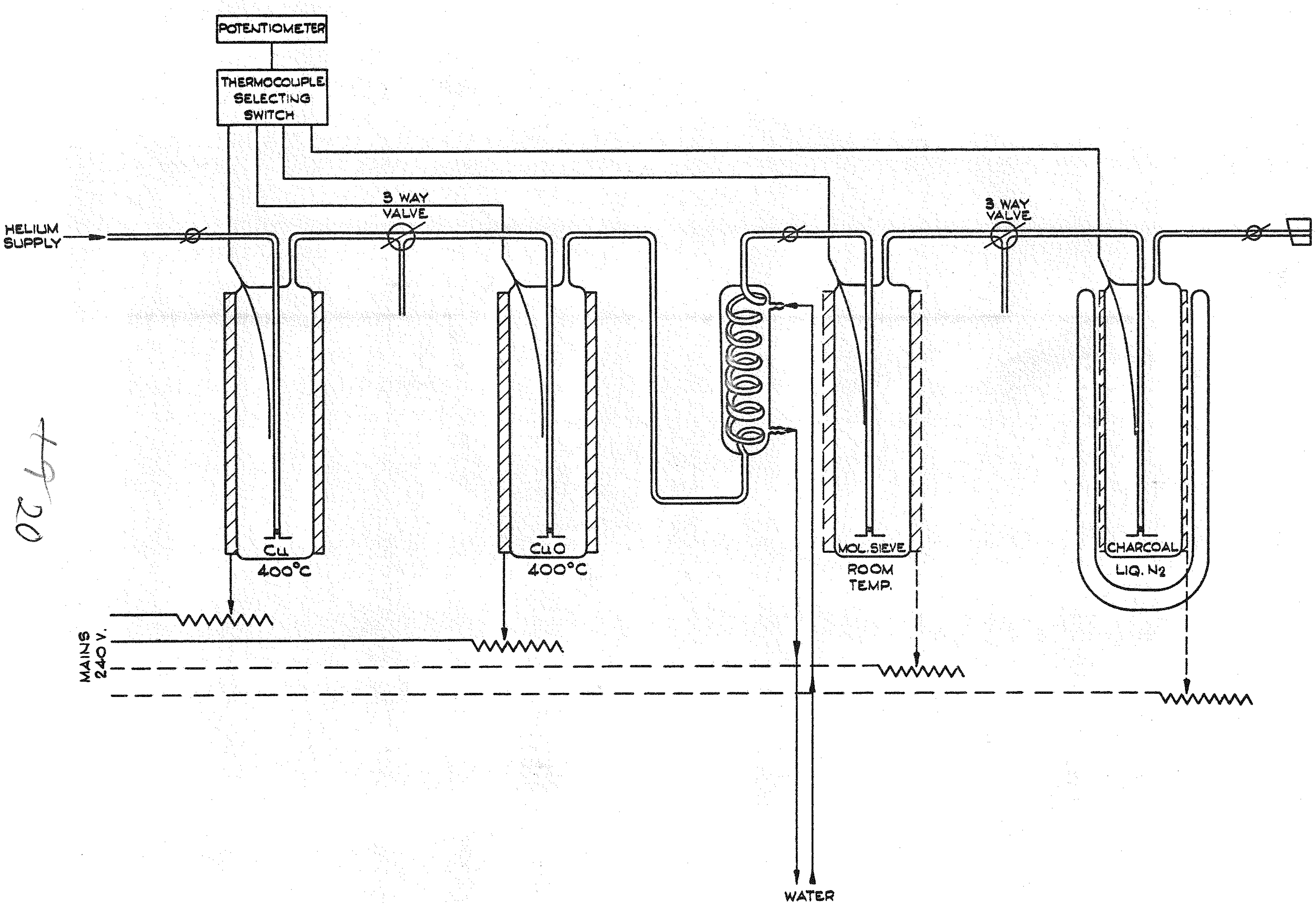

FIG. 5 HELIUM PURIFICATION PLANT LABORATORY SCALE

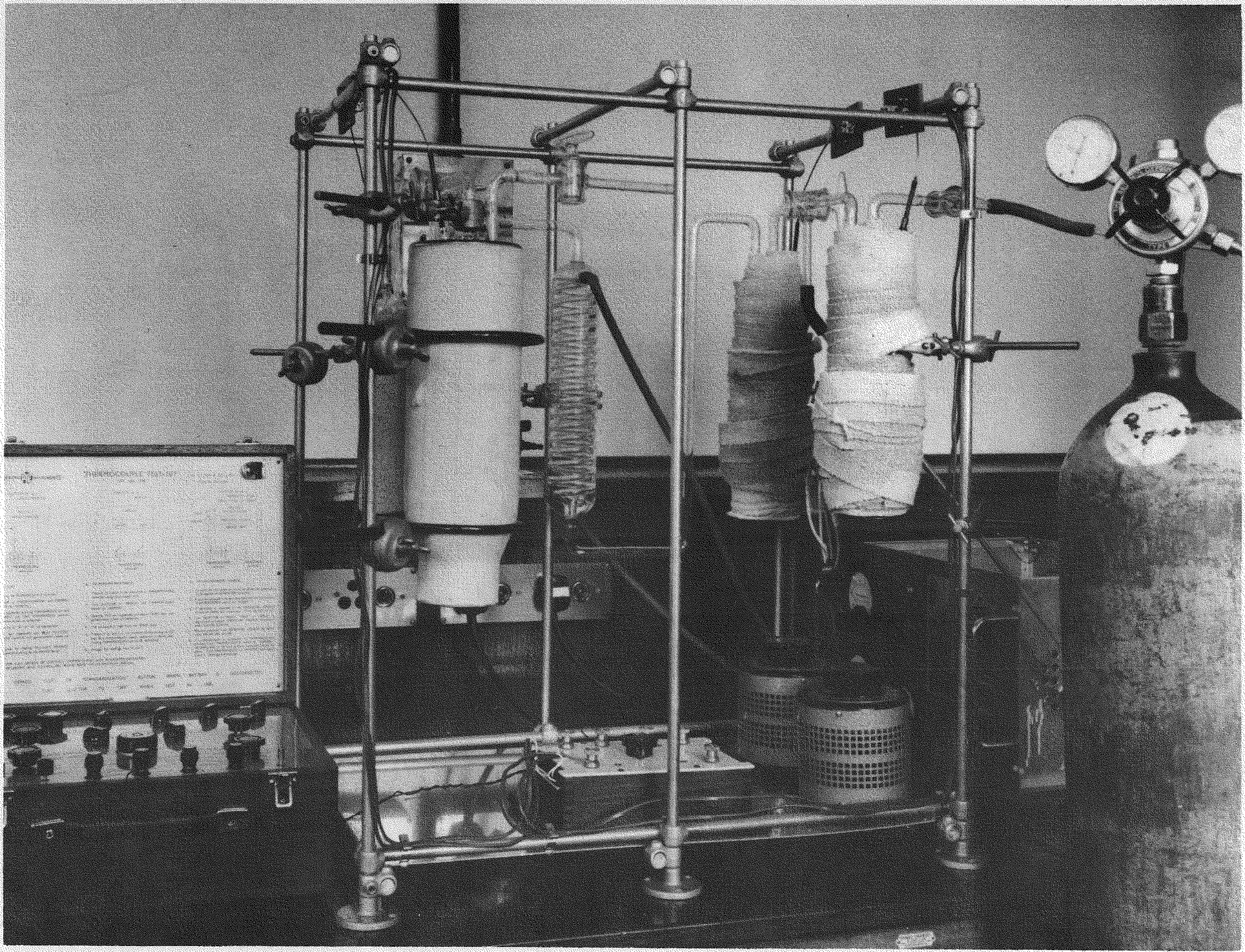

FIG. 6. HELIUM PURIFICATION PLANT LABORATORY SCALE

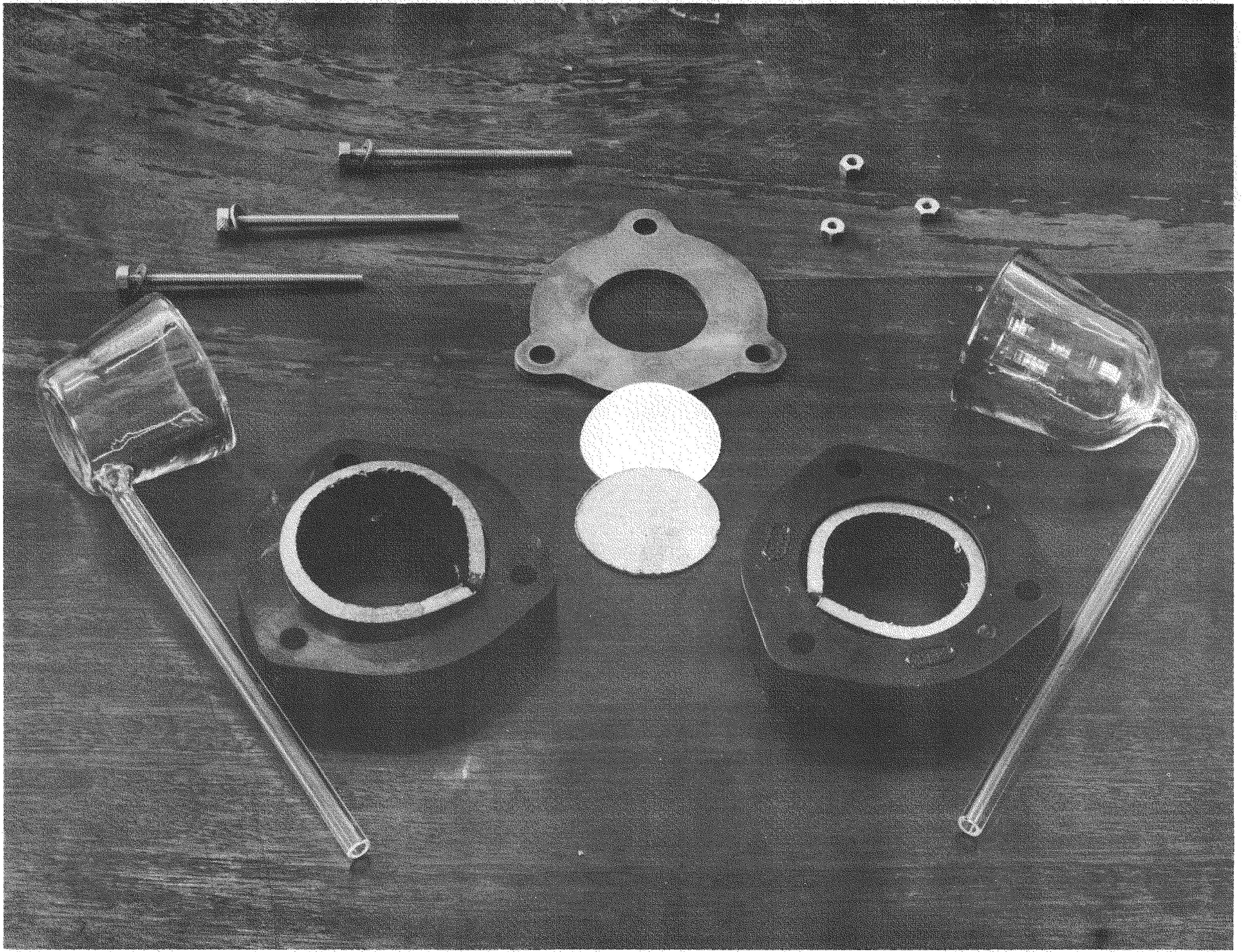

FIG. 7. THE BREAK-THROUGH TRAP DISMANTLED

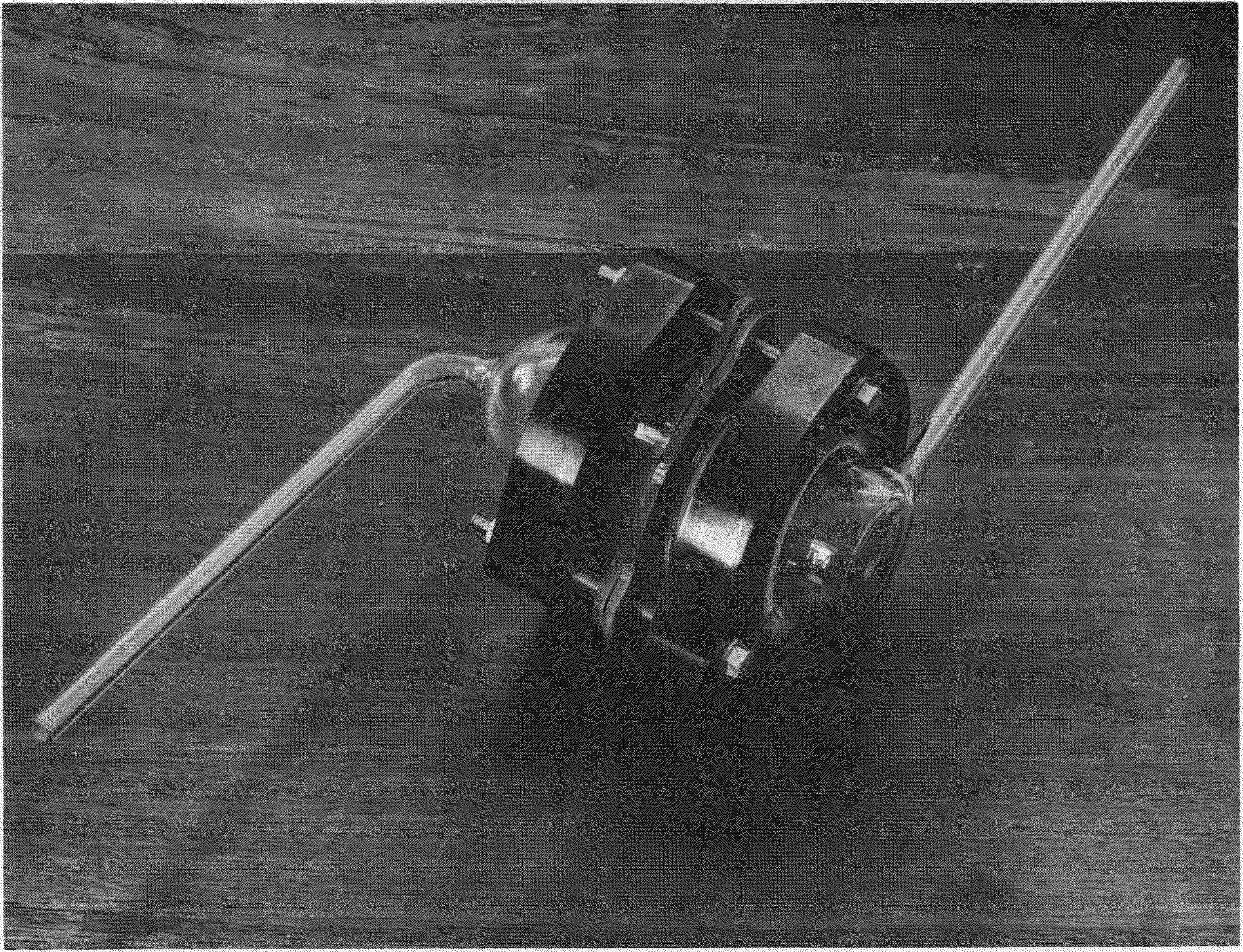

FIG. 8. THE BREAK-THROUGH TRAP ASSEMBLED