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THE SYNTHESIS OF DEUTERO-POLYTHENE

by

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CHEMISTRY

ABSTRACT

The small-scale preparation of deutero-polythene, starting from deuterium oxide and calcium carbide, was investigated. The procedure adopted gives about 60% yields of deutero-polythene having a melting point of 120 to 130°C and a density of 1.02 to 1.05. The ethylene-d_4 gave appreciably greater yields and polymerized at lower temperatures than ethylene-H_4.

ACKNOWLEDGMENT

The author wishes to thank John C. Potts and John D. Rogers of Group CMR-9 for advice and aid in designing, constructing, and testing the high pressure equipment.

THE SYNTHESIS OF DEUTERO-POLYTHENE

Introduction

The high temperature polymerization of ethylene is an oxygen catalyzed chain reaction, and the final product contains appreciable amounts of oxygen attached to terminal carbon atoms.

The problem of synthesizing deutero-polythene may be divided into two phases: (1) the preparation of deutero-ethylene; (2) the polymerization of deutero-ethylene.

The synthesis of deutero-ethylene may be accomplished by two methods: (1) the catalytic reduction of deutero-acetylene with deuterium, or (2) the chemical reduction of deutero-acetylene with chromous chloride.

Catalytic reduction of deutero-acetylene with deuterium appeared the most attractive method because of its simplicity. Fourteen experiments were tried in which the kind of catalyst, method of preparation, and temperature of reduction were varied. This approach was unsuccessful, the chief products being polymers and reduction products other than ethylene. Since this work was completed, similar results were reported by Douglas and Rabinovitch[1] in an article which appeared recently in the current literature.

The chromous chloride reduction of deutero-acetylene is much more complicated and involves the following steps:

1. Preparation of deutero-acetylene
2. Preparation of DCl
3. Preparation of $CrCl_2$ in D_2O solution
4. Reduction of C_2D_2 to C_2D_4 with $CrCl_2$ in D_2O
5. Purification of C_2D_4

These steps in the synthesis of deutero-polythene will be discussed in order.

The synthesis of acetylene from calcium carbide and water takes place according to the following equation:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

In practice the amount of C_2H_2 generated actually amounts to 82 to 85% of the theoretical quantity. In addition, the gas so formed contains small amounts of higher hydrocarbons as well as traces of arsenic, phosphorous, and sulfur containing compounds.[2]

All commercial calcium carbide contains a surface coating of calcium hydroxide due to reaction with the moisture of the air, and this coating should be removed in order to prevent H-D exchange and consequent dilution of deuterium.

For the first experiments the lumps of calcium carbide were carefully brushed with a stiff brush, then broken up into small particles before charging into the acetylene generator. In the later experiments the calcium carbide was heated to 500 to 600°C while in a vacuum before introduction into the generator. Calcium hydroxide becomes anhydrous at 580°C and thus any possibility of H-D exchange is removed.

The preparation of a solution of chromous chloride in deuterium oxide required first the preparation of deuterium chloride, and the dissolution of chromium in the deutero-chloric acid, followed by the reduction of the mixture of chromous and chromic chlorides to the chromous state with amalgamated zinc in a large Jones Reductor. The reduction with the zinc is necessary because a mixture of chromous and chromic salts is always formed when chromium is dissolved in acids, even when the reaction is conducted in an inert atmosphere.

The deuterium chloride was made by the hydrolysis of sulfuryl chloride with D_2O, followed by distillation with sodium chloride.

Since appreciable quantities of deuterium are formed during the dissolution of the chromium in the acid, the gas generated was passed over hot copper oxide, and the deuterium was recovered as the oxide.

Reduction of acetylene with the chromous chloride was first observed by Berthelot[3] who noted that chromous sulfate produced a transient precipitate with acetylene. The solid quickly redissolved to yield a gas which was identified as ethylene. This reaction has since been used for reducing small quantities of acetylene to ethylene.

The polymerization of ethylene is an oxygen catalyzed high pressure reaction. The general conditions for the reaction are outlined in a patent[4] and may be easily summarized. The products obtained at 500 atm of pressure have low molecular weights, while the products at 1000 atm of pressure are high molecular weight solids. A catalytic amount of oxygen is necessary.

This may be as low as 0.01%, but 0.03 to 0.10% is preferable. The preferred temperature of the reaction is 150 to 250°C.

A typical experiment described, in which the ethylene:oxygen ratio was 1:0.05 at a pressure of 1500 atm and a temperature of 210°C, gave after 5 hr an 80% yield of polymer having a molecular weight above 6000 and a melting point of 100 to 110°C. The product was soluble in xylene.

The oxygen catalyst may be added either as elemental oxygen or in the form of peroxides. The best catalyst found by actual experiment was benzoyl peroxide dissolved in benzene. Hydrogen peroxide as a catalyst gave a discolored product because of oxidation of the bomb. Benzoyl peroxide without solvent gave low yields.

Experimental Procedure

Catalytic reduction of acetylene to ethylene

The equipment used for the experiments involving the catalytic reduction of acetylene to ethylene is shown in Fig. 1. A 12-liter gas reservoir A was filled with a 1:1 mixture of hydrogen gas and acetylene. The two gases were mixed by heating one side of the gas reservoir with an infrared lamp while cooling the opposite side with a jet of cold air. This gas container and all other similar containers were wrapped in a spiral fashion with electricians' black tape as a safety precaution in the event of collapse of the walls. The filled reservoir was attached to the all-glass system which consisted of catalyst chamber B, the reversible Topler pump C, a mercury manometer D, and an evacuated 12-liter gas reservoir E. The system was evacuated through stopcock F. With stopcock G closed, the acetylene-hydrogen mixture was allowed to flow over the catalyst and into reservoir E, by the proper manipulation of stopcock H, until the pressure in the two reservoirs was equal. Stopcock G was then opened and the remaining gas in reservoir A was Toplered into E by the proper manipulation of stopcocks G and H until the manometer D indicated no change in pressure. The gas mixture in E was then recycled over the catalyst B and into A by the appropriate manipulation of the pump stopcocks G and H. The recycling process was repeated until no change in volume of the gas was shown by the manometer.

In the theoretical reaction

$$CH{\equiv}CH + H_2 \longrightarrow CH_2{=}CH_2$$

two volumes of gas should react to form one volume. At the end of the reaction the manometer should read one half the starting pressure. In none of the experiments tried was this found to be true.

The first experiments showed a gradual decrease in catalyst activity, and the catalyst appeared moist. A polymerization of acetylene on the surface of the catalyst was suspected. Several experiments were tried in which the temperature of the catalyst was varied, and some experiments were performed with the catalyst suspended in water. The catalyst reaction chambers tried are illustrated in Fig. 2.

The attempts at catalytic reduction, the catalyst and the conditions tried, and the results are summarized in Table 1.

All attempts along this path of investigation were abandoned.

Preparation of deutero-polythene

1. Preparation of deutero-acetylene

Calcium carbide prepared by the usual commercial process from lime and coke contains as impurities compounds of phosphorous, nitrogen, sulfur, arsenic, silicon, and iron.[2] The hydrolysis of the carbide with water yields acetylene contaminated with hydrogen and carbon derivatives of these elements. These impurities are usually the simple hydrides such as phosphine, ammonia, hydrogen sulfide, arsine, and silane. At the high local temperatures present at the surface of calcium carbide during the reaction with water, the acetylene generated reacts with these hydrides to give organic compounds somewhat difficult to remove. Kennedy and Holm identified divinyl sulfide as an impurity in acetylene.[5] Since too extensive a purification procedure leads to H-D exchange, the acetylene was used directly for reduction to ethylene without purification. The ethylene was then submitted to a purification step before polymerization.

Calcium carbide (200 g), which had been previously either freshly heated to 600°C or which had been brushed with a stiff brush and broken up into small grains, was introduced into reaction chamber A of the acetylene generator shown in Figs. 3 and 4. Tubes B and C were likewise filled with calcium carbide granules. The two latter fillings served the purpose of reacting with any water vapor entrained in the acetylene issuing from the reaction flask A. Two 12-liter gas reservoirs previously evacuated to 3 microns were connected to the generator at stopcocks D and E in the manner shown in Fig. 5. With stopcocks F and G closed, the system was evacuated to 10 to 12 microns using a mechanical pump connected at H. Deuterium oxide was placed in dropping funnel J (F and G closed). Flask A was then immersed in a basin containing ice and water. The dropwise addition of the deuterium oxide generated the acetylene smoothly and it was collected in the reservoirs. When one reservoir was filled, as indicated by the mercury manometer L, the acetylene was then collected in the other reservoir. Any excess acetylene was condensed in M while the filled gas reservoirs were replaced with empty ones.

2. Preparation of deutero-ethylene

The reaction involved in the reduction of acetylene to ethylene is the following:

1. $2CrCl_2 + 2HCl + C_2H_2 \longrightarrow 2CrCl_3 + C_2H_4$

The chromous chloride and deuterium chloride required for the reaction were prepared and involved the following reactions:

2. $SO_2Cl_2 + 2D_2O \longrightarrow D_2SO_4 + 2DCl$
3. $D_2SO_4 + 2NaCl \longrightarrow Na_2SO_4 + 2DCl$
4. $6DCl + 2Cr \longrightarrow 2CrCl_3 + 3D_2$
5. $2CrCl_3 + Zn \longrightarrow 2CrCl_2 + ZnCl_2$

Preliminary experiments indicated that reaction "1" became exceedingly slow when the concentration of chromous chloride was too low. A strong concentration of acid is necessary for the reduction of chromic chloride with zinc according to reaction "5."

Deuterium chloride was made by the dropwise addition, from a dropping funnel, of 240 ml (405 g, 3 moles) of sulfuryl chloride into 800 ml of deuterium oxide in a 2-liter flask equipped with a reflux condenser and containing a magnetic stirrer. The flask was cooled with ice water. The addition of the acid chloride should be at such a rate that the mixture is maintained just under the refluxing temperature. The top of the reflux condenser was closed with a guard tube filled with calcium chloride.

When the sulfuryl chloride was completely hydrolyzed, the mixture of sulfuric and hydrochloric acids was added to a flask containing 400 g of dry sodium chloride. A distilling head and condenser were then attached to the flask, and all the acid was distilled and recovered as deuterium chloride solution. The last traces of deuterium chloride were removed from the heated distilling flask with a stream of dried nitrogen.

The chromous chloride was prepared by dissolving 208 g (4 moles) of chromium metal in the deuterium chloride-deuterium oxide mixture contained in a 200 ml flask attached to a reflux condenser. The deuterium gas generated was reoxidized to deuterium oxide by passing a stream of dry nitrogen through the flask and through a heated tube containing cupric oxide. An appreciable quantity (42.5 g) of deuterium oxide was recovered in this manner. Two such preparations of chromous chloride were made, combined, diluted with a liter of deuterium oxide, and divided equally in three portions into specially constructed 1-liter flasks similar to the illustration B shown in Fig. 6. The chromous-chromic chloride was completely reduced to the chromous state in a large Jones Reductor containing a 1:1 mixture of glass beads and amalgamated mossy zinc (in an atmosphere of nitrogen). After reduction was complete (1 to 2 hr), the solution was returned to the special flasks which had been filled with nitrogen. The three flasks were then attached to the reservoirs containing the acetylene to be reduced (shown as C, Fig. 6) and secured to a shaking machine as is shown in Fig. 7. The acetylene was completely reduced, as was indicated by a negative cuprous chloride-ammonia test, in 30 to 40 hr of agitation.

The deutero-ethylene was simultaneously pumped out of the large reservoirs, purified, and condensed in tube F, Figs. 8 and 9. The reservoir containing ethylene was attached to the apparatus through tube B and the deutero-ethylene was removed with the Topler pump C adjusted for automatic cycling. The gas was conducted through U-tube B which was cooled with a dry ice-trichloroethylene mixture. The gas was then scrubbed in a basic solution of mercuric oxide-potassium iodide complex in gas wash tube D, dried in drying train E with calcium chloride, and condensed in tube F which was filled with pellets of nickel and cooled with liquid nitrogen. The guard tube G was also filled with calcium chloride.

During preliminary studies of the polymerization of ethylene the apparatus shown in Figs. 10 and 11 for the purification of ethylene was constructed.

Dried commercial ethylene was passed into the system through inlet J and condensed in A. The liquid was fractionally distilled into tubes

B and C. The lines D, E, F, and G are safety outlets dipping in mercury reservoirs. Tube C was calibrated in milliliters from which the volume of liquid ethylene to be condensed into the high pressure reaction chamber connected at I, could be determined. Deutero-ethylene, in excess to that required to fill the reaction chamber, was stored in gas reservoir K, which replaced tube F.

Tube F, Fig. 8 , containing the condensed deutero-ethylene, was attached to H and the gas distilled into C. After the volume was recorded, the gas was distilled into the reaction chamber connected through outlet I. Sufficient deutero-ethylene was distilled into the bomb to give a pressure of 2500 to 3000 psi at room temperature and usually required about 35 ml of liquid ethylene. After the bomb was filled and while still cooled with liquid nitrogen, the inlet tube fitting attached to the lid was unscrewed (see Fig. 12), and a solution of 0.1 g of benzoyl peroxide in 1 ml of benzene was introduced into the chamber with a hypodermic needle. The bomb was again closed, and the liquid nitrogen bath was removed. A wax bath* heated with an element wrapped around the container, the temperature of which was controlled by a variable auto transformer, was placed around the bomb, and the temperature was gradually raised to 200 to 240°C.

Temperature-pressure curves were plotted for each experiment. When normal ethylene was used, the slope of the curve showed a pressure drop between 150 to 160°C as shown in curves 1 and 2, Fig. 13. The slope of

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* Fisher Bath Wax. Flash point, 325°C.

the curve is clearly a function of rate of heating, but the break in the curve became more apparent with a slow rise in temperature. When the deutero-ethylene was polymerized, the break in the curve occurred at a much lower temperature, 110 to 120°C, and was much more pronounced. A typical curve is shown in Fig. 15 and indicates that the deutero-ethylene is easier to polymerize than normal ethylene. This is also borne out by the yields which were 30 to 40% greater when deutero-ethylene was polymerized.

When polymerization began, indicated by a drop in pressure while the temperature remained constant, a time-pressure curve was plotted. Curve 1, Fig. 14, shows the decrease in pressure vs time at 260 to 265°C; curve 2, in the same figure, shows the decrease in pressure of deutero-polythene at the same maximum polymerization (temperature, 260 to 265°C). It may be noted that whereas curve 1 had begun to level off after 4 hr, curve 2, although beginning at a higher and ending at a lower gas pressure, was still decreasing in pressure after 6 hr, again indicating the greater reactivity of the deutero-ethylene.

The high pressure equipment is shown in Figs. 12, 16, and 17. The high pressure bomb, Fig. 16, was constructed from stainless steel bar to the following dimensions: length, 25 cm; diameter, 4.8 cm. Flange: diameter, 7.3 cm; thickness, 1.6 cm. Chamber: diameter, 1.6 cm; length, 22.7 cm. The chamber was sealed with a round, annealed copper ring which was compressed into a square-sided annular groove cut into the chamber and cover. The system was connected with high pressure steel tubing and consisted of Bourdon gauge (reading to 15,000 psi), close-off valve, safety disk, reaction chamber, thermocouple, wax bath, and Dewar flask for cooling with liquid nitrogen. The entire assembly, shown in Fig. 16, was enclosed within a safety shield of 1/4 in. iron plate (Fig. 17).

The complete system, excluding the safety device, was tested with oil to a pressure of 15,000 psi. The safety device contained a blow-out disk of stainless steel which ruptured at 13,500 psi.

Discussion

The polymerized product obtained upon opening the bomb consisted of two fractions: (1) a higher melting, slightly discolored solid lump from the bottom of the reaction chamber, and (2) stringy material which adhered to the walls of the bomb. Part (1) always was yellowish and contained a slight gray impurity apparent as a "marbled" effect throughout the polymer. The exact nature and source of this impurity are unknown. It was noticed that whenever the chamber was cleaned first with steel wool and then with alcohol and dried, appreciably greater quantities of the grayness were apparent. This practice was therefore discontinued. The fact that the gray impurity dissolves in the molten polymer would indicate that it is organic in nature.

In the experiment dealing with the last polymerization, the bomb was not opened when reaction ceased but was cooled, additional deutero-ethylene was added, more catalyst was introduced, and the bomb was reheated. A yield of over 20 g was obtained.

During one experiment the safety disk ruptured at 9400 psi. The reason is unknown since the same disk had been tested previously at 13,500 psi without breaking.

Yields obtained in the polymerization of ethylene and deutero-ethylene, and other data, are shown in Tables 2 and 3.

In preliminary experiments higher concentrations of oxygen than those discussed here lowered the temperature at which polymerization began and also increased the yield. The polymer, however, was soft and had a lower molecular weight.

Densities were determined on three samples (see Table 4).

The fate of the benzene used as solvent for the benzoyl peroxide is unknown.

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2. J. A. Niewland and Richard R. Vogt, "The Chemistry of Acetylene," Reinhold Pub. Corp., New York, 1945, p. 11.
3. M. Berthelot, Bull. soc. chim. France (2) 5, 182 (1866).
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5. D. J. Kennedy and A. C. Holm, Can. Chem. Process Inds. 23, 490 (1939).

Table 1

REDUCTION OF ACETYLENE WITH HYDROGEN AND CATALYSTS

Catalyst	Conditions of Reaction	Results
Nickel, reduced at 500°C	Cooled to 20°C	Slight amount of polymerization
"	Heated to 100°C	Ethane and liquid polymers
"	Heated to 280°C	Polymers only
Nickel, poisoned with H_2S	Cooled to 20°C	No reaction
"	Heated to 120°C	No reaction
"	Heated to 280°C	Some polymerization only
Pd on carbon poisoned	Cooled to 20°C	Polymers and ethane
"	Heated to 120°C	Butane and vinyl acetylene
"	Heated to 280°C	Butane and vinyl acetylene
Nickel, reduced at 300°C	Cooled to 20°C	No polymers; ethane only
"	Repeated with same catalyst	Vinyl acetylene only
"	Suspended in H_2O, 25°C	No reaction
"	Heated to 100°C	No reaction
"	Heated in basic solution, 100°C	No reaction

Table 2

POLYMERIZATION OF ETHYLENE

No.	Gas Used	Initial Pressure (psi)	Initial Temperature (°C)	Final Pressure (psi)	Final Temperature (°C)	Catalyst	Yield (g)	Remarks
1	Ethylene	3,100	25	5,600	260	1.5 ml H_2O_2	4.67	Bled off gas at 9,000 lb
2	Ethylene	2,500	24	6,200	250	0.1 g Bz_2O_2	4.92	
3	Ethylene	2,100	24	4,000	290	0.1 g Bz_2O_2 in benzene	8.91	
4	Ethylene	2,500	25	4,100	240	0.1 g Bz_2O_2 in benzene	1.65	Apparatus leaked gas
5	Ethylene	2,700	20	800	22	0.1 g Bz_2O_2	6.68	Polymerization very slow
6	Ethylene	2,400	24					Safety disk ruptured
7	Ethylene:Ethane 1:2	3,000	16					No reaction
8	Ethylene	2,200	20	10,000	220	No catalyst		No reaction
9	Ethylene	2,200	20	5,900	260	0.1 g Bz_2O_2, 2 ml benzene	8.20	

Table 3

POLYMERIZATION OF DEUTERO-ETHYLENE

No.	Gas Used	Initial Pressure (psi)	Initial Temperature (°C)	Final Pressure (psi)	Final Temperature (°C)	Catalyst	Yield (g)	Remarks
1	d_4-ethylene	2,500	26	5,300	280	0.1 g Bz_2O_2 in benzene	10.37	
2	d_4-ethylene	3,300	26	5,600	270	0.13 g Bz_2O_2 in benzene	11.53	
3	d_4-ethylene	2,600	25	4,000	270	0.13 g Bz_2O_2 in benzene	10.83	
4	d_4-ethylene	5,400	25	9,400	120			Safety disk ruptured
5	d_4-ethylene	3,100	25	4,800	250			
6	Cooled bomb repeated	2,200	25	4,000	260	0.2 g Bz_2O_2 in benzene	22.46	

Table 4

DENSITIES OF DEUTERO-POLYTHENE

No.	Polythene	Weight (g)	Calculated Volume (cc)	Density Found
1	Run No. 5	18.67923	17.7261	1.0533
2	Run No. 1, upper	5.50066	5.2083	1.0204
3	Run No. 1, lower	3.14213	2.9729	1.0569
4	Normal polythene	32.0059	34.7503	0.9210

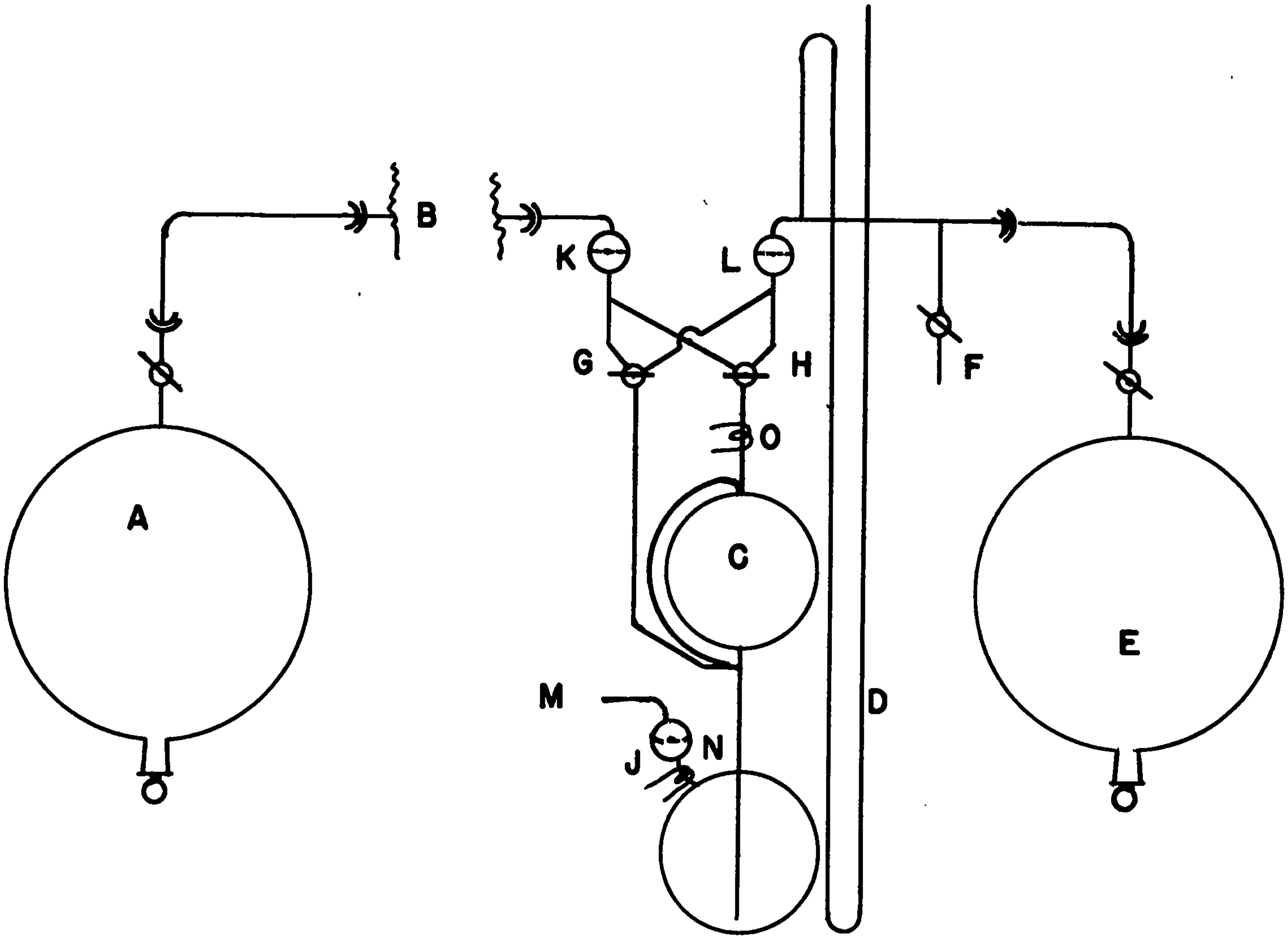

Fig. 1. Equipment for catalytic reduction of acetylene to ethylene.

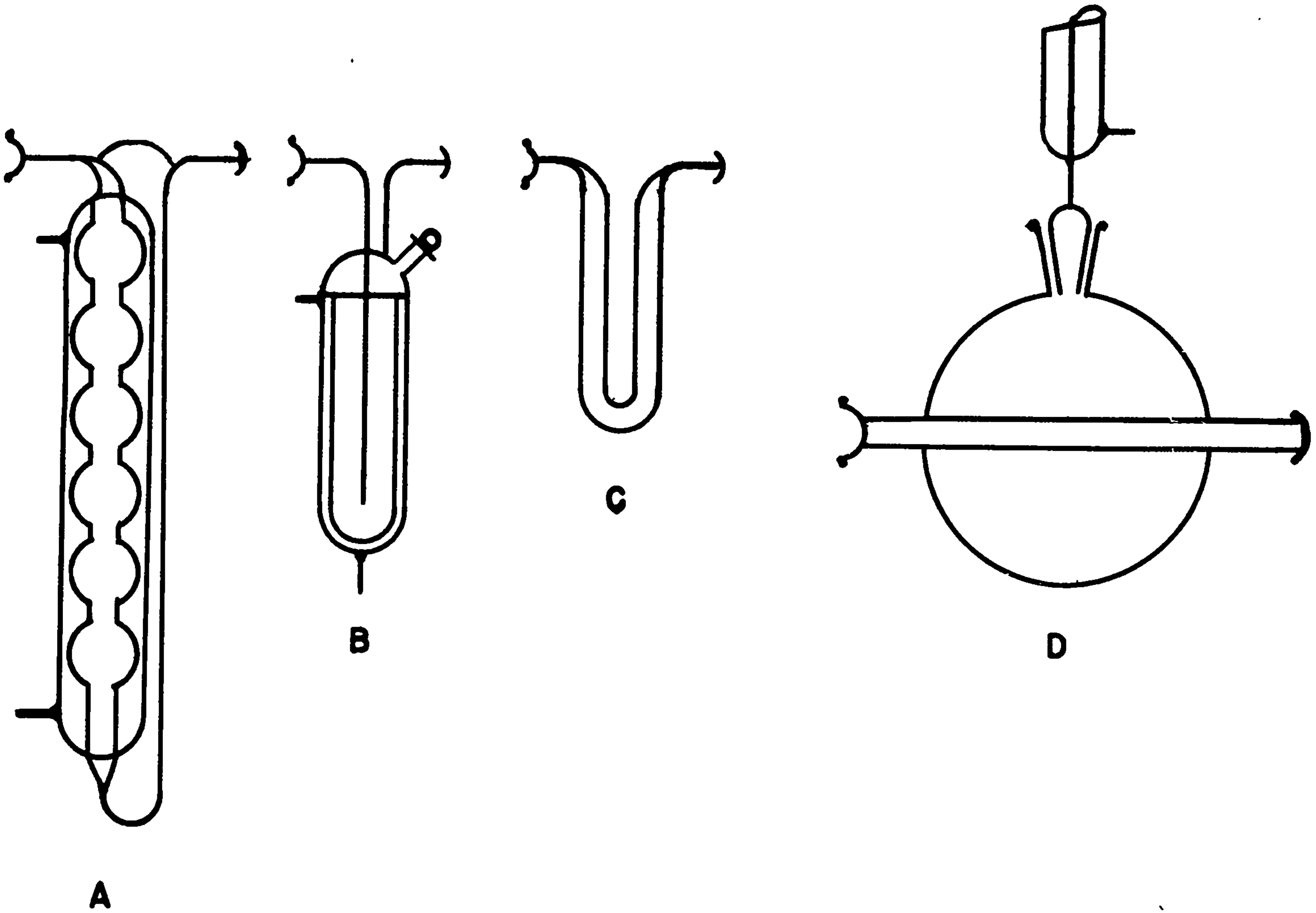

Fig. 2. Catalyst reaction chambers.

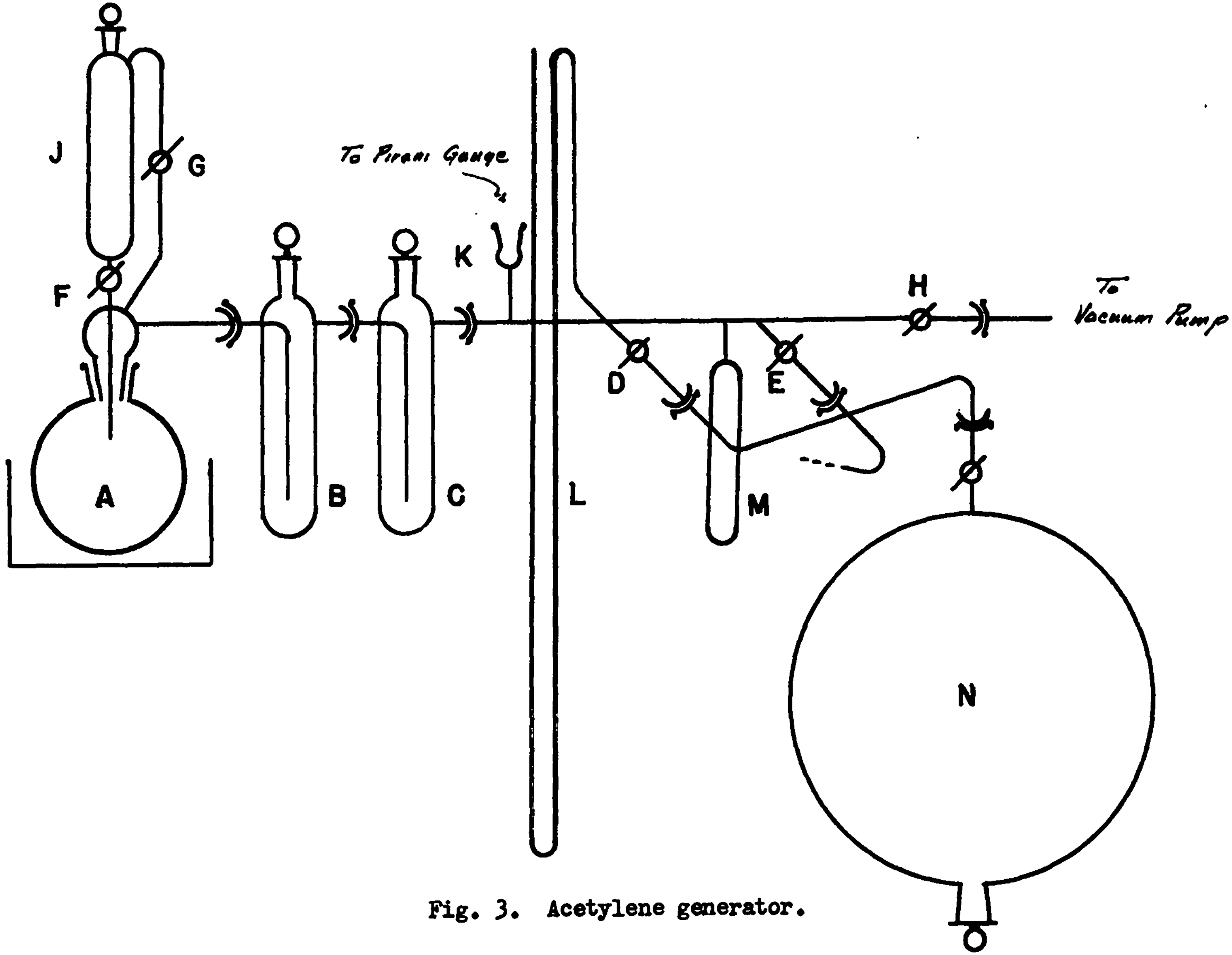

Fig. 3. Acetylene generator.

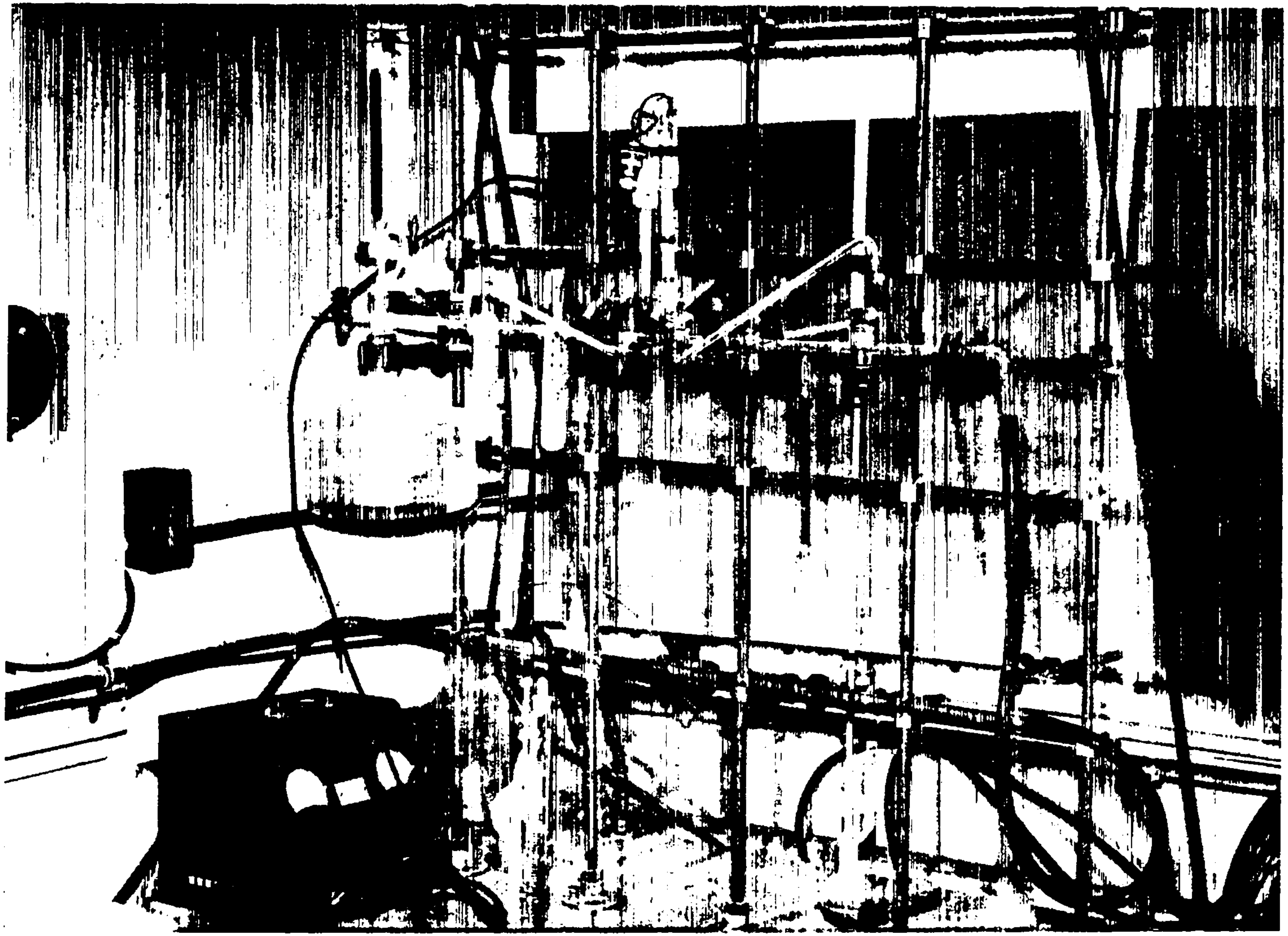

Fig. 4. Acetylene generator.

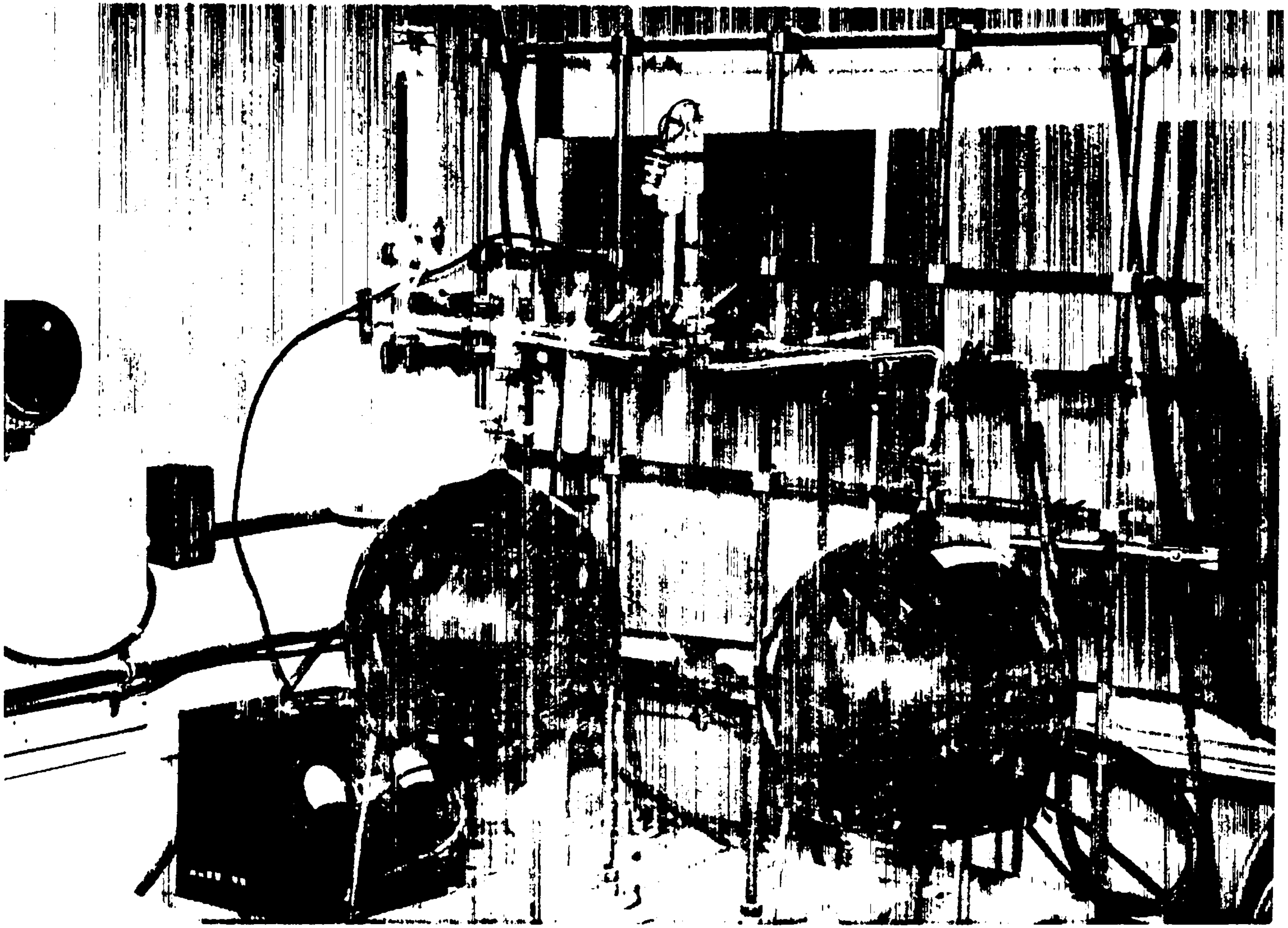

Fig. 5. Acetylene generator and gas reservoir.

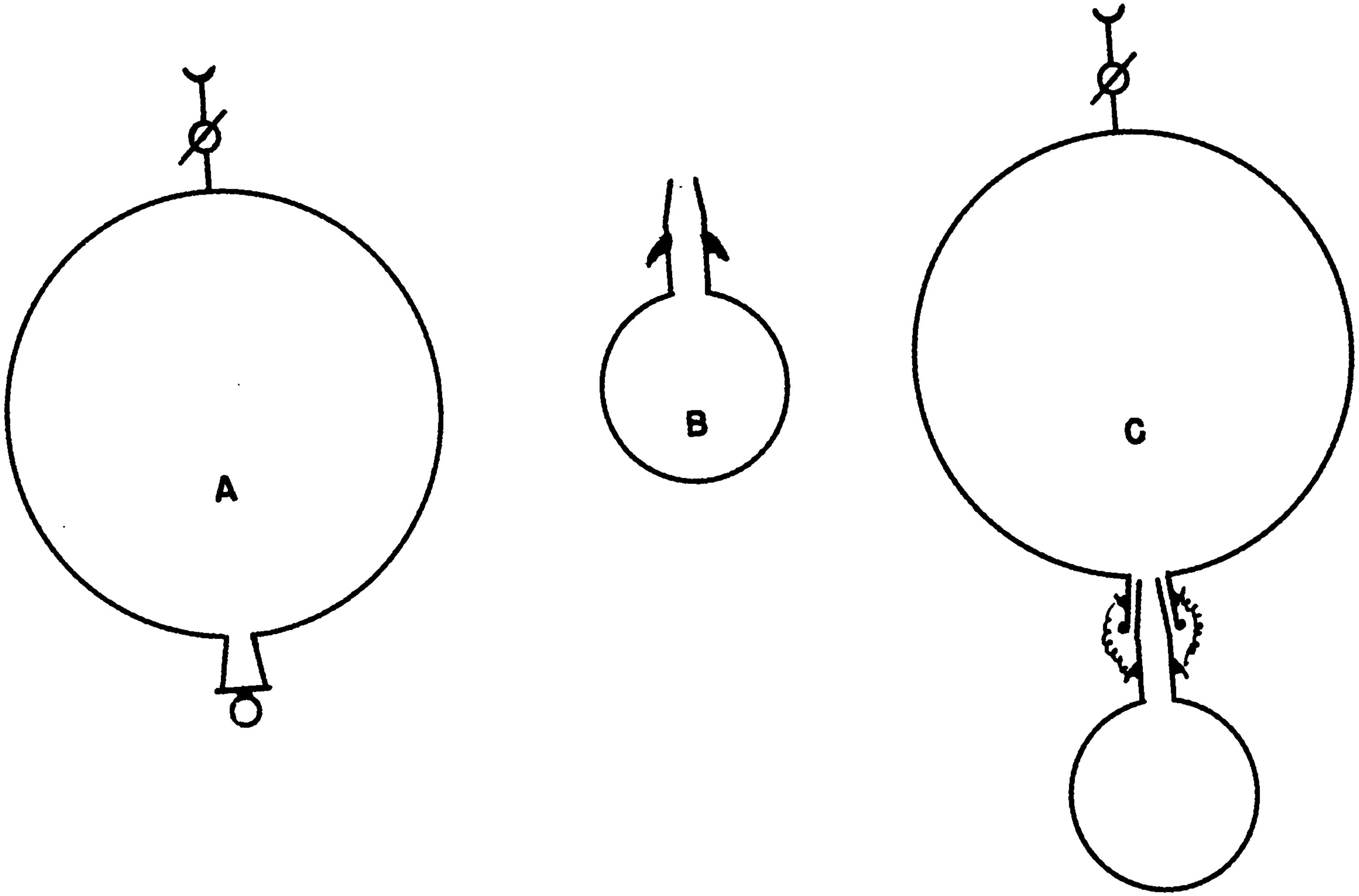

Fig. 6. Flasks for reduction of acetylene to ethylene.

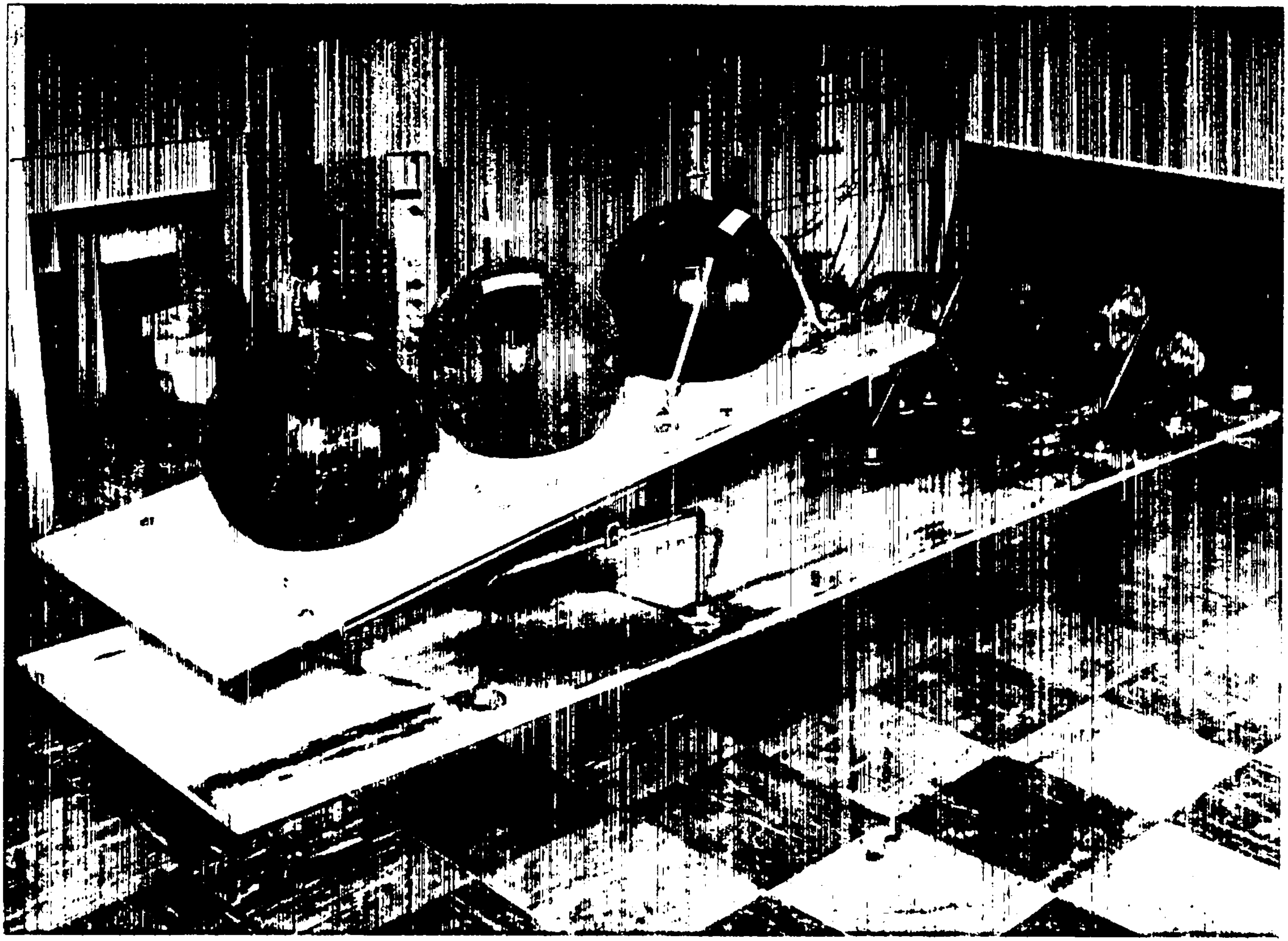

Fig. 7. Shaker machine.

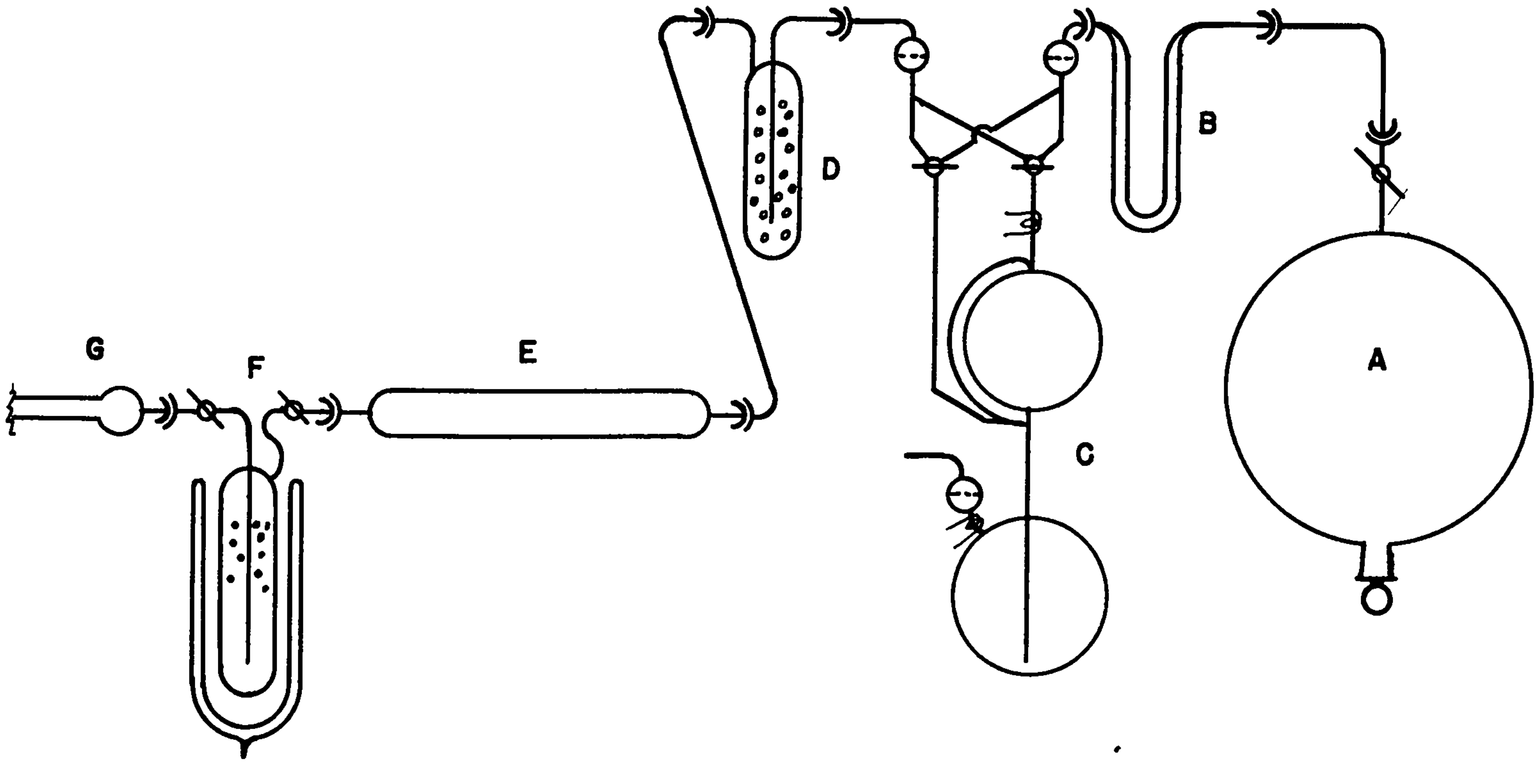

Fig. 8. Apparatus for purifying and isolating ethylene-d_4.

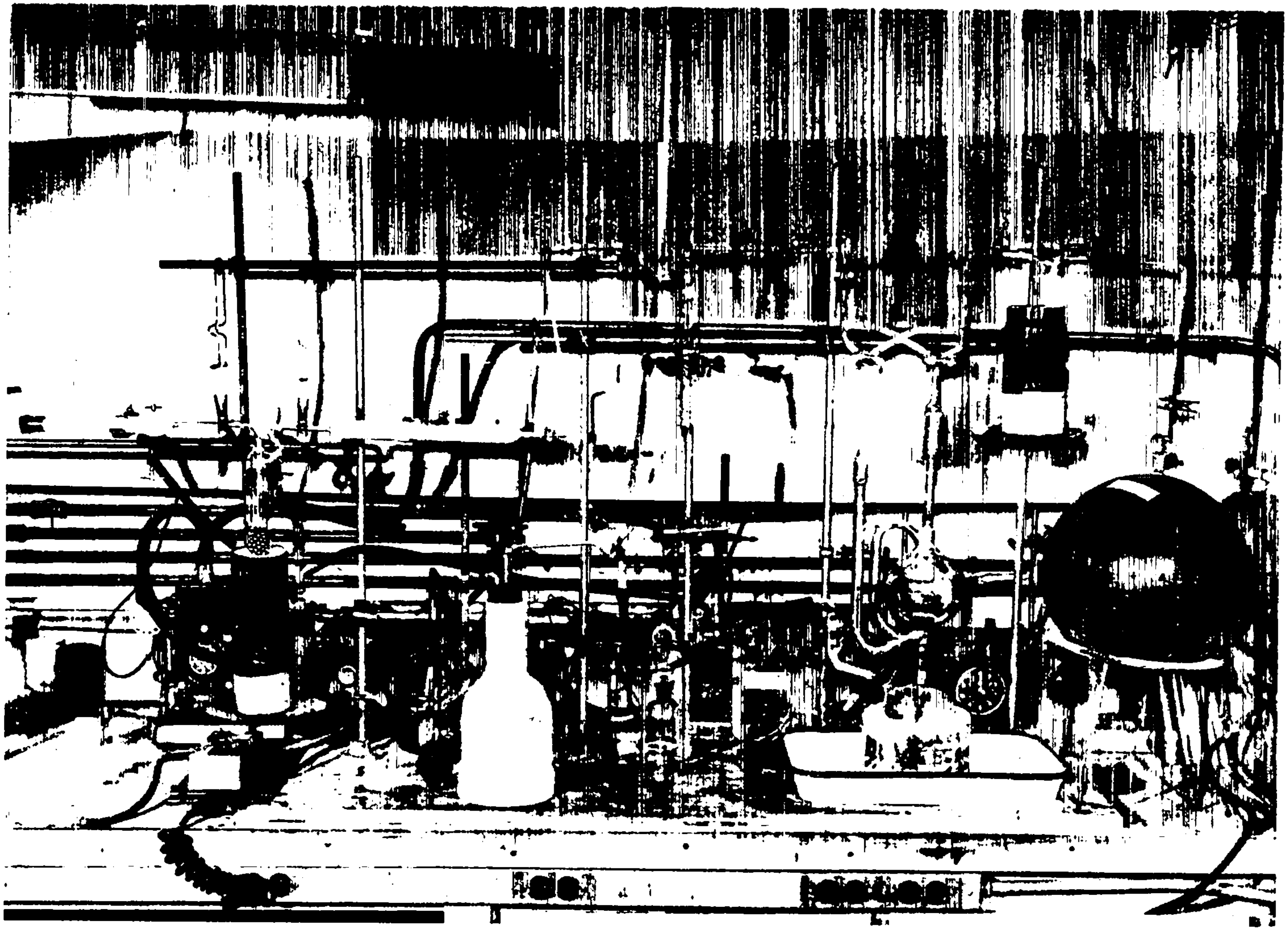

Fig. 9. Apparatus for purifying and isolating ethylene-d_4.

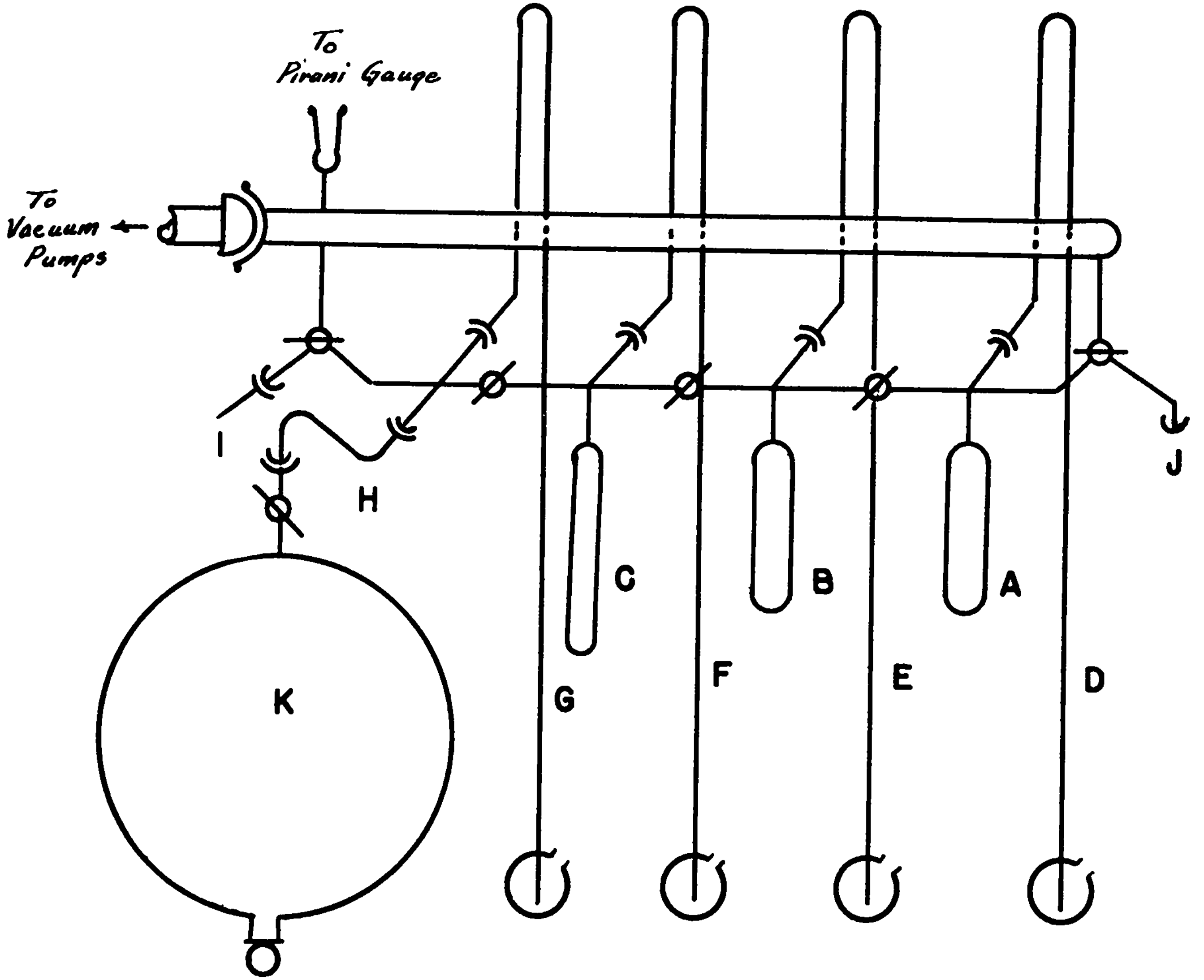

Fig. 10. Still for purifying ethylene.

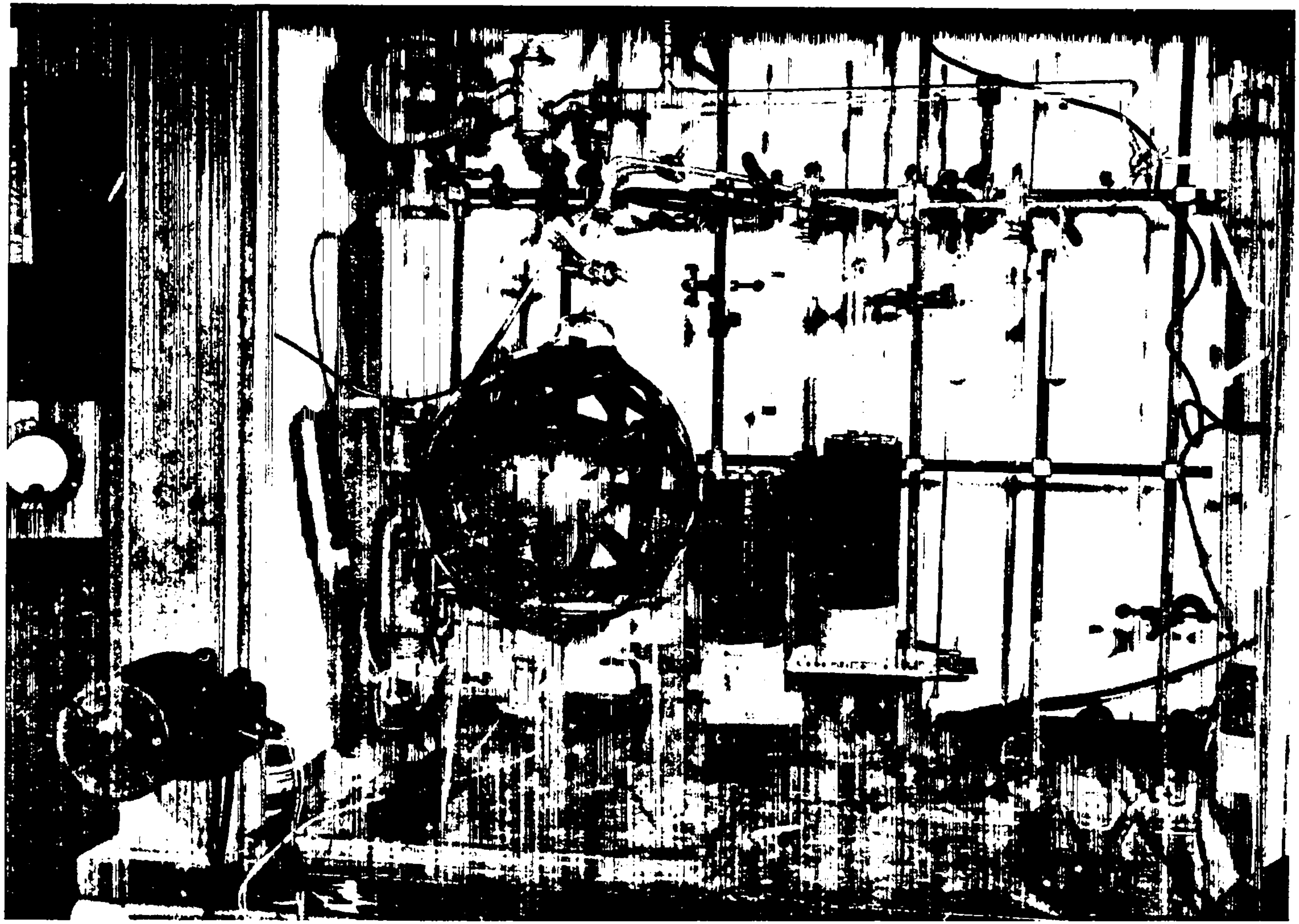

Fig. 11. Still for purifying ethylene.

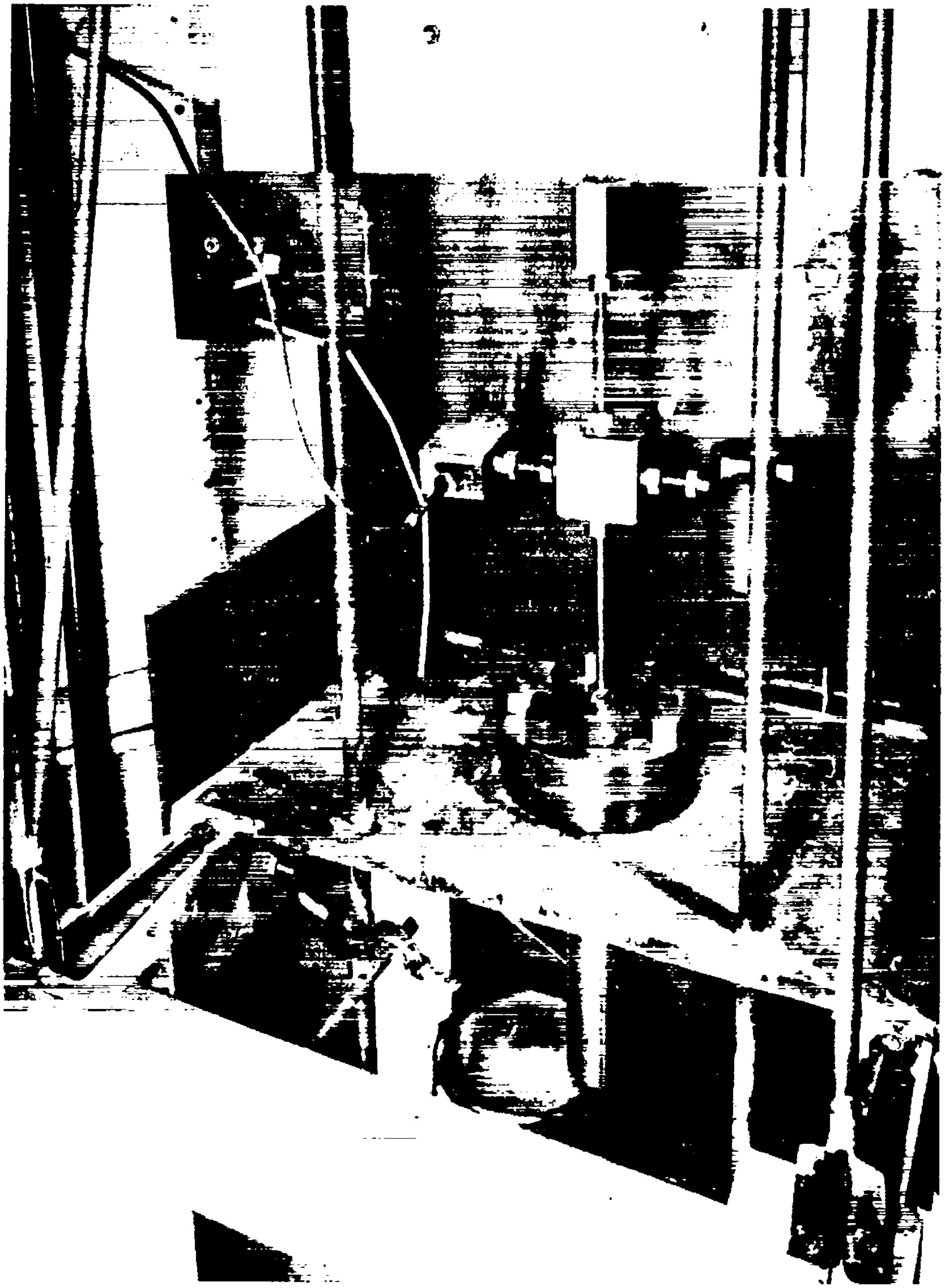

Fig. 12. High pressure reaction chamber assembly.

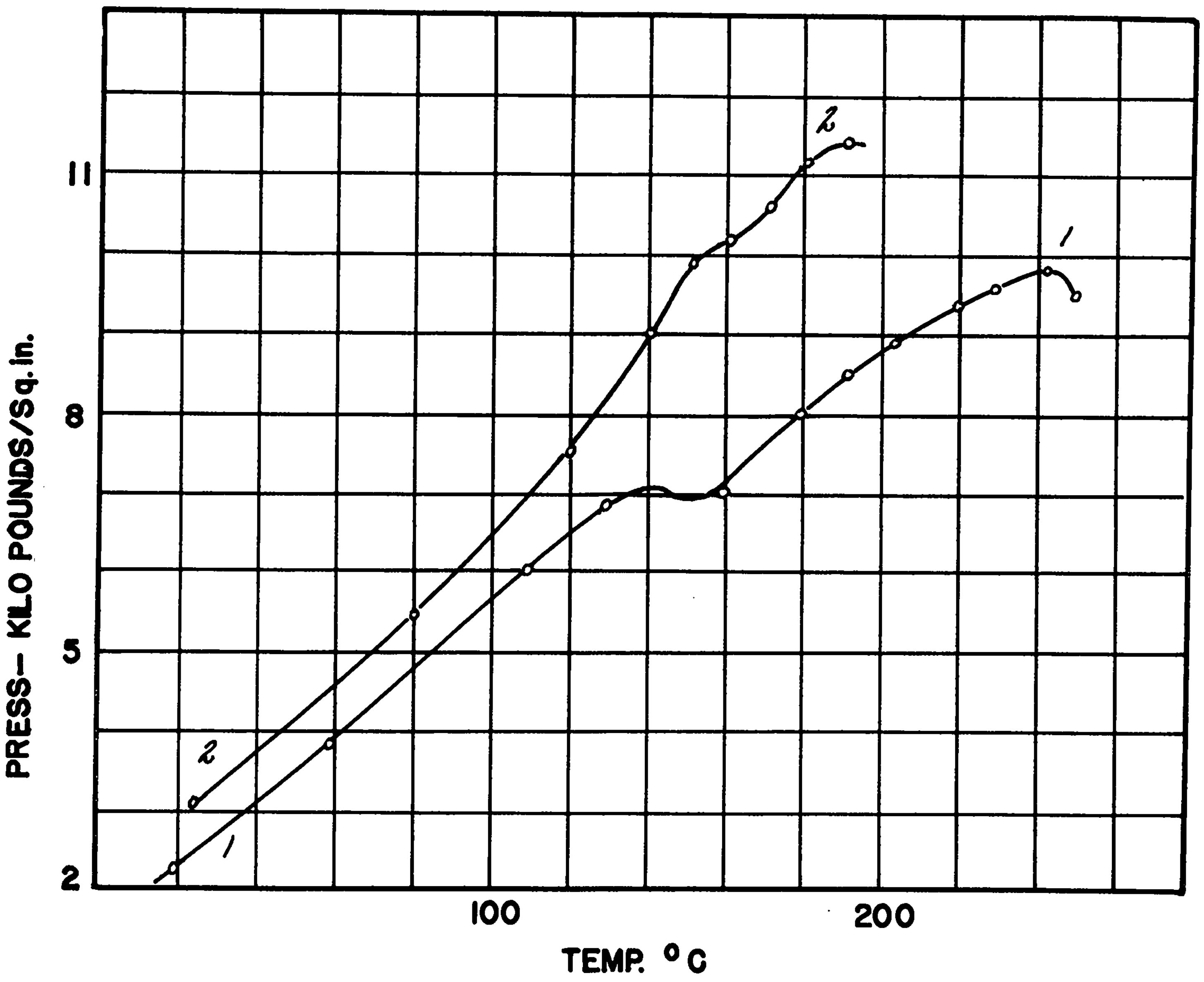

Fig. 13. Temperature-pressure curve for polymerization of ethylene.

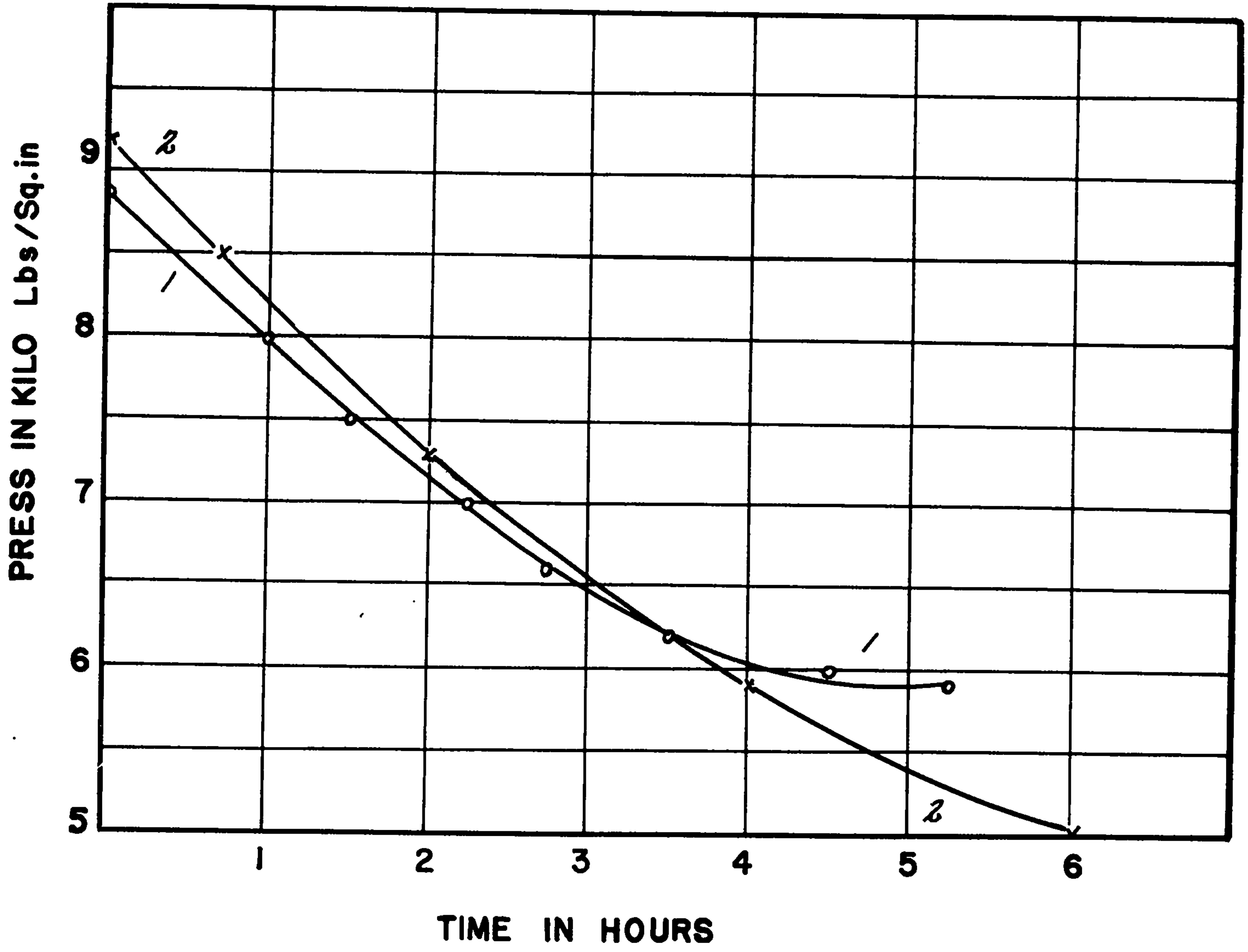

Fig. 14. Time-pressure curve for polymerization of ethylene.

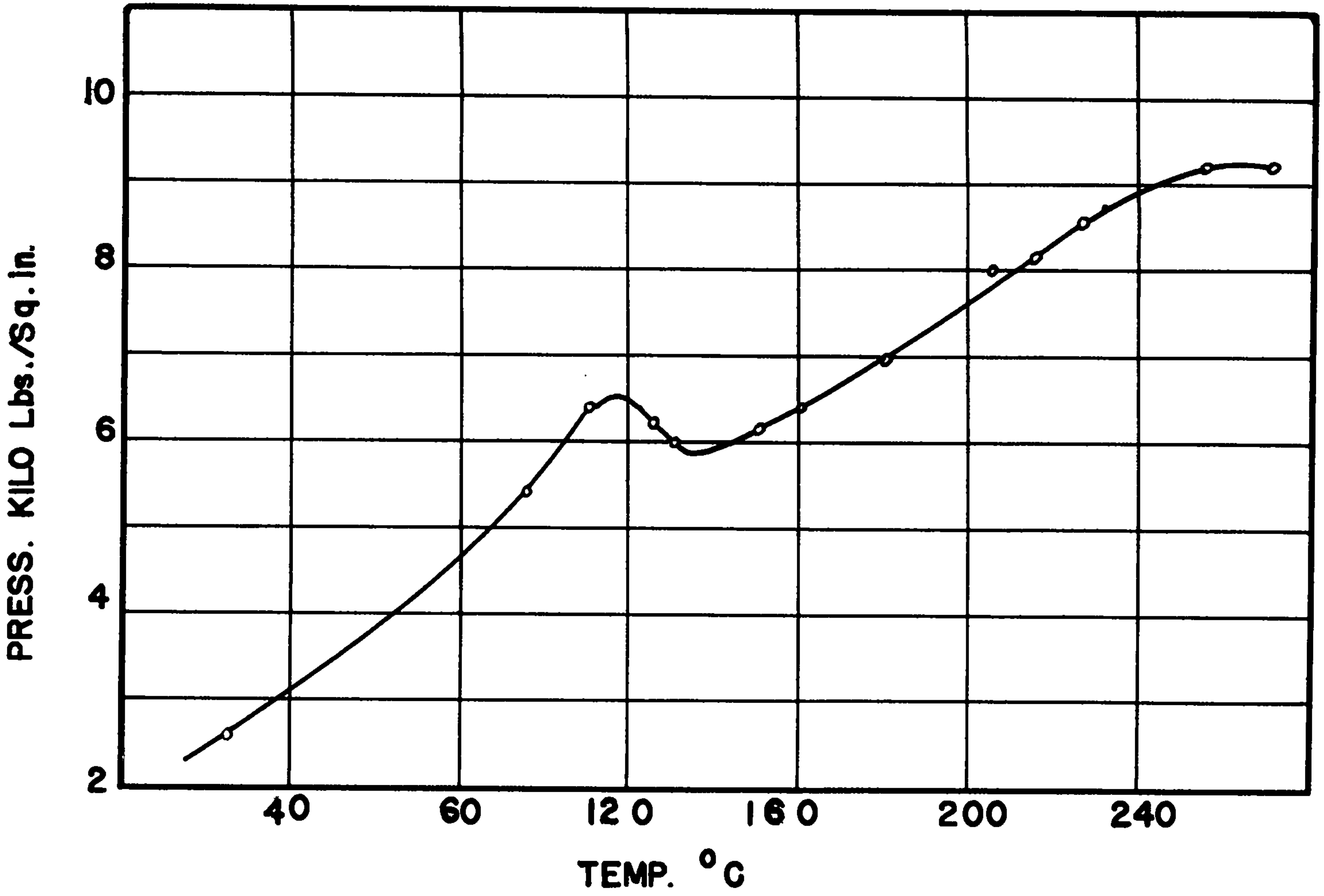

Fig. 15. Temperature-pressure curve for polymerization of deutero-ethylene.

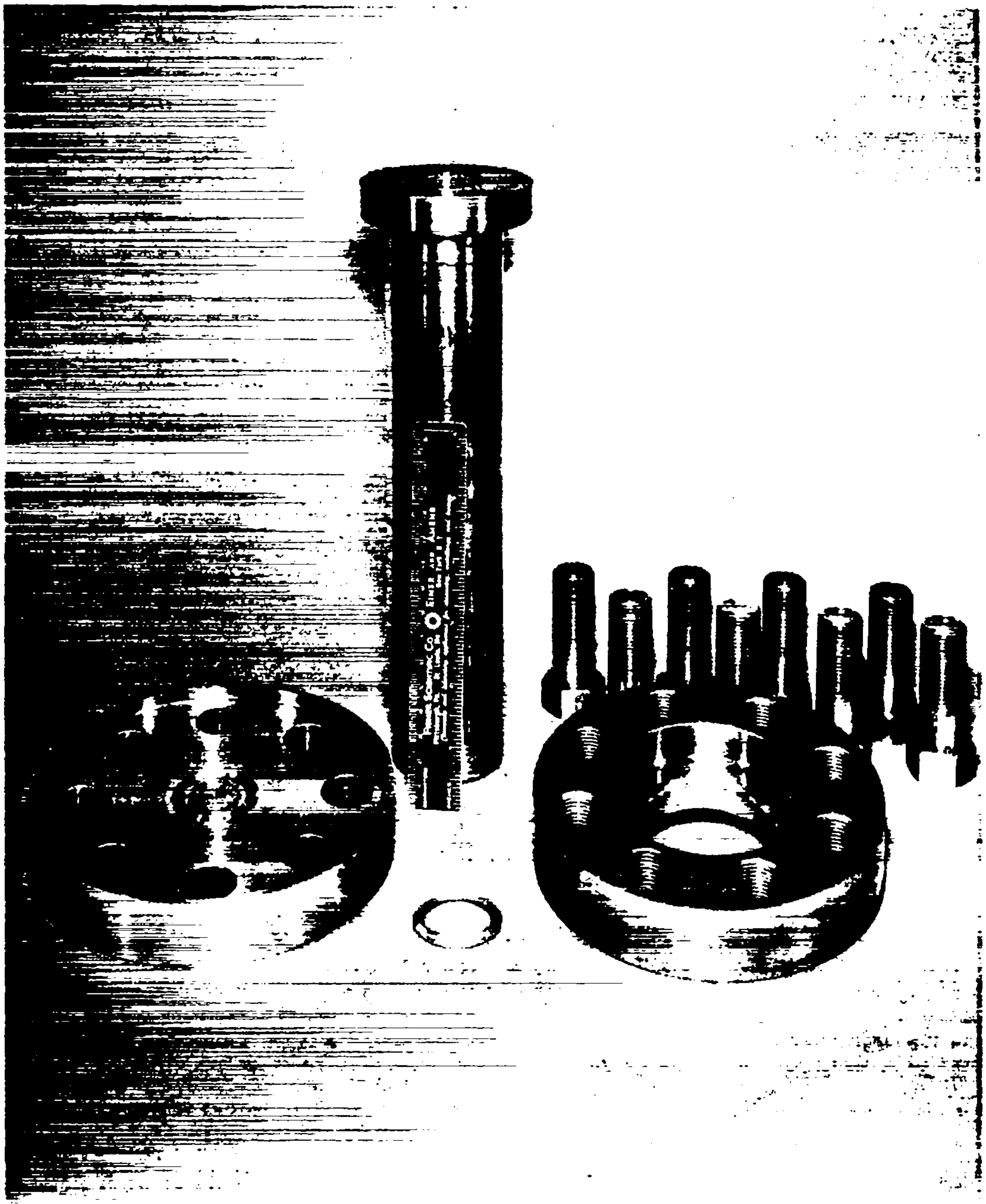

Fig. 16. Reaction chamber.

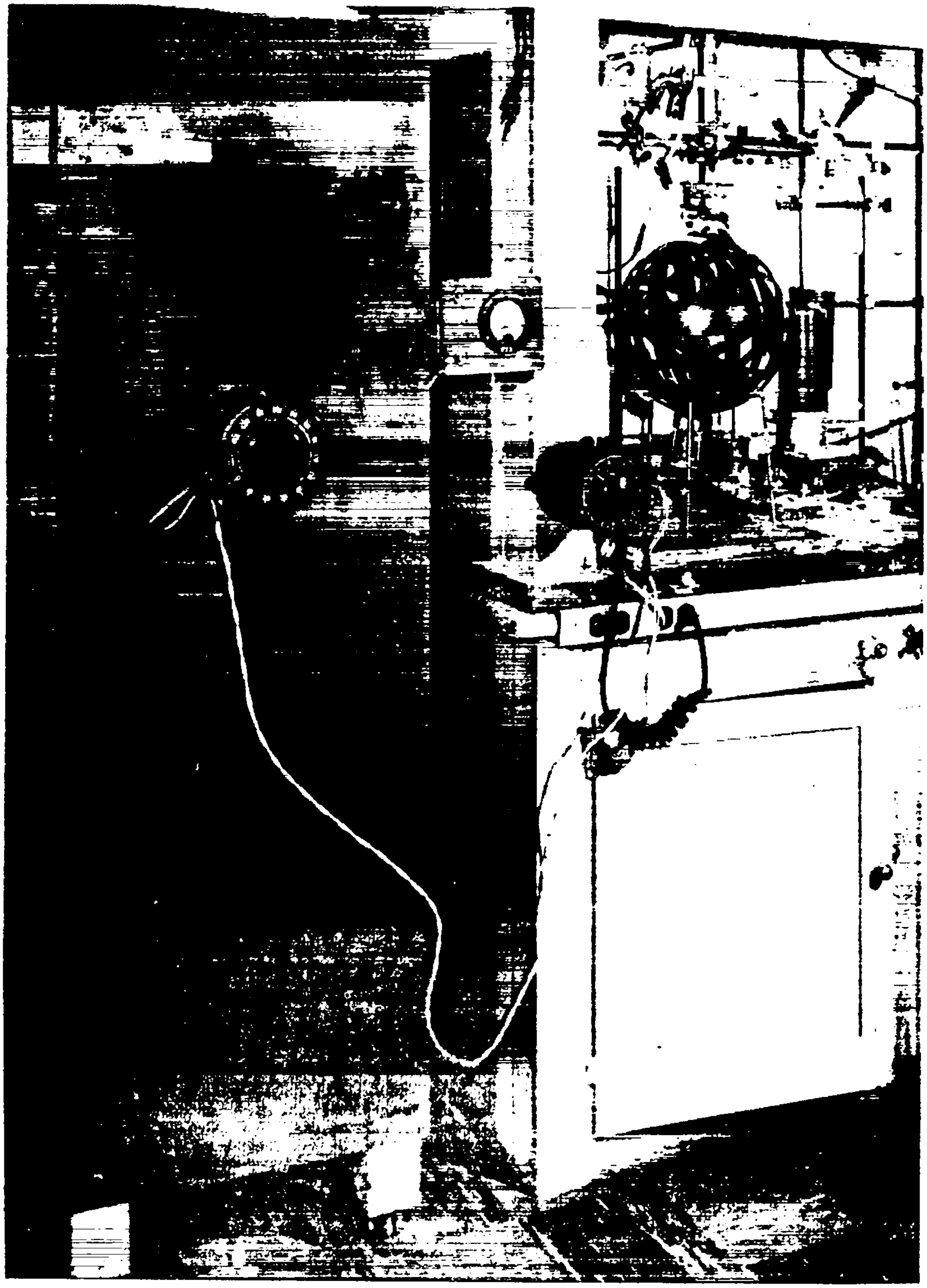

Fig. 17. Safety shield for the high pressure chamber.