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Progress Report

DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF THE LIGHT HYDROCARBONS AT HIGH PRESSURE AND LOW TEMPERATURE

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INTRODUCTION

The construction of equipment suitable for measurements of the specific heat at constant pressure and of Joule-Thomson coefficients of light hydrocarbon mixtures at temperatures from 32° to -280°F and at pressures to 2500 lb/sq in. has been completed. Measurements of the specific heat of nitrogen at -50° and -100°F, with pressures to 900 lb/sq in. have been made and found to be in agreement with the literature values. After more preliminary measurements with nitrogen, the equipment will be ready for taking data on hydrocarbon gases.

GENERAL DESCRIPTION OF EQUIPMENT

The entire apparatus, except for the source of liquid nitrogen coolant, is located in a 30-by-17 ft test cell in the Automotive Laboratory on the North Campus of The University of Michigan. Figure 1 is a flow diagram of the low-temperature calorimetric system. Figure 2 is a photograph of the entire apparatus for measuring thermodynamic properties of gases at low temperature as assembled in the test cell.

The apparatus consists of four primary components: (1) the compressor for circulation of gases and a purification system through which the gases are recirculated; (2) cooling baths for bringing the gas to the desired temperature under pressure; (3) the low-temperature bath containing the specific heat calorimeter and the Joule-Thomson expansion device; and (4) the measurement device for metering the circulation rate.

In the cell adjacent to the low-temperature thermodynamic apparatus is a liquid nitrogen machine capable of producing 25 liters of liquid nitrogen per hour (Fig. 3). A machine shop and other services required for the operation of the equipment are available in the Automotive Laboratory.

Preliminary testing of the equipment has been accomplished to eliminate leaks in the system. Operational testing and calibration of the major components have been completed to the point that measurements can be made of specific heat at constant pressure. Preliminary measurements made on the specific heat of nitrogen are shown in the table. To prove that the equipment performs satisfactorily before starting with hydrocarbons, work will continue to obtain other measurements of the specific heat of nitrogen. Values of this specific heat under pressure are available as a result of Joule-Thomson and PVT measurements.

DETAILS OF CONSTRUCTION AND OPERATION OF FLOW SYSTEM

The flow diagram can be best explained by following the path of a typical volume of fluid being studied as it flows through the equipment. Beginning at the compressor buffer tank shown in the upper left-hand corner of Fig. 1, the path of the gas in the flow system will be followed. The buffer tank serves to supply the high-pressure compressor and to insure stable operation. Gas from the buffer tank on the way to the compressor goes through charcoal and desiccant to remove water, traces of heavy hydrocarbons, and other foreign material. After the gas is purified, it is compressed and circulated by means of a Höfer three-stage compressor having a capacity of 1.6 cu m/hr at a suction pressure of 6.5 atmospheres and a maximum discharge pressure of 170 atmospheres. The oil necessary for the compressor operation, together with water condensing in the compressor, are removed in two separators. The first is integral to the compressor and is simply a gravity separator; the second incorporates a combination of gravity separation and filtering through activated charcoal and glass wool. The heat of compression is partially removed by the inter-stage cooler in the compressor; after-cooling is carried out in an ice bath.

The gas leaving the compressor may be throttled through a gas re-cycle line to the buffer tank or it may be permitted to continue through the calorimetric system. High-pressure cylinders, which are integral to the system, are used for gas storage. As one of the degrees of freedom in specifying the operating variables in a given run, gas from these cylinders may be added to or removed from either the high- or low-pressure side of the compressor. In addition, the cylinders may be used to buffer either the low- or high-pressure portion of the system.

The fluid flowing to the calorimeters passes through a counter-current heat exchanger, a cooler employing dry ice and a cooler employing liquid nitrogen. The order in which gas passes through the exchanger and dry ice depends on the temperature at which measurements are to be made. Before the gas enters the low-temperature bath, it passes through a heater in which, by manual adjustment, heat may be added to the system to bring the temperature to the desired level. Final conditioning of the gas to the temperature of the low-temperature bath is accomplished by a conditioning coil.

A low-temperature bath contains a liquid such as isopentane, the temperature of which is precisely controlled by means of a liquid nitrogen cooling coil, a manual heater, and an automatically operated heater. The specific heat calorimeter and the Joule-Thomson calorimeter are submerged in the bath medium which is vigorously agitated to minimize temperature gradients in the bath and to decrease bath response time. The quantity of coolant passing through the coil in the low-temperature bath is controlled approximately by means of gas pressure applied to liquid nitrogen stored in a metal dewar. The excess cooling is partially balanced by a manually operated heater; the precise addition of heat necessary to control the bath temperature at a given level is supplied automatically. The automatic heater is controlled by a Wheatstone bridge circuit, one leg of which is located in the bath in the form of a nickel resistance.

For both specific-heat and Joule-Thomson measurements, the initial fluid temperature is that of the bath medium. This temperature is measured by means of a platinum resistance thermometer located in the bath. The temperature changes of the fluids in both specific-heat and Joule-Thomson work are measured by means of multiple junction thermocouples located in the measuring instruments. Absolute and differential pressure measurements are made using a dead-weight pressure balance obtained from the University of Wisconsin through the courtesy of Professor J. R. Roebuck.

Figure 4 is an assembly drawing of the specific-heat calorimeter. A measured addition of heat is made to the fluid passing through the calorimeter by means of an electrical heater. An electronically regulated d-c power supply is employed. The temperature change is measured by a difference thermocouple between the inlet and exit thermocouple wells. To minimize heat losses, the upper portion of the calorimeter in which the heater and exit thermocouple well are located is surrounded by an isothermal shield held at the exit gas temperature. The calorimeter is also subjected to a high vacuum.

Figure 5 is a drawing of the Joule-Thomson throttle. The pressure drop through the instrument is obtained by means of a set of interchangeable porous plugs. The inlet-gas-temperature thermocouple junction is located on a small shield surrounding the plugs. The exit gas junction is located inside a flow guide in the interior of the plug. Pressure taps on each side of the plug are used to measure the pressure differential on a dead-weight pressure balance.

The gas, after passing through the measuring instruments, is throttled to the compressor suction pressure and flows through a meter so that the rate of flow can be determined. The gas is brought near the metering temperature by means of counter-current heat exchange and electrical heating and then flows through a conditioning coil in a constant-temperature bath to assure that it is at a uniform constant temperature as it enters the meter. The mass flow rate of gas is found by measuring the pressure drop across a flow restriction with a cathetometer and a U-tube containing water. The pressure and temperature at the metering point are measured carefully. After being metered, the gas returns to the point of origin, the compressor buffer tank.

The measurements of thermocouple voltage are made using a Leeds and Northrop K3 potentiometer. The platinum thermometer resistance and the power input to the calorimeter are determined by the K3 via an elaborate electrical circuit including a number of highly precise standard resistors.

Approximate temperatures at various points around the flow system are read on a multi-point indicating potentiometer. The entire operation of the equipment is conducted from a panel board shown in Fig. 6. Practically all the valves are located on a valve switchboard which facilitates operation and maintenance. Figure 7 is a view of the metering bath and dead-weight pressure balance. The high-pressure compressor is illustrated in Fig. 8. In the background, the tops of several of the high-pressure cylinders, which serve for gas storage, can be seen. The low-temperature bath containing the calorimeters is located in the first insulated box in the foreground in Fig. 9. The cooling device containing dry ice is in the second box in Fig. 9 and the cooling coil employing liquid nitrogen is in the third box. The heat exchanger is contained in the largest box in the background. Styrofoam insulation is used around the equipment in the boxes.

It will be seen that much of the equipment is located inside a steel barricade. This barricade is constructed of 1/4-in. boiler plate; it is 15 ft long by 12 ft wide by 8 ft high, and serves to protect the operating personnel from the hazard of fire or rupture of the equipment. One end of the barricade has a door, open in Fig. 2, for access to the equipment for maintenance and construction. A battery of six carbon dioxide nozzles is distributed around the room, both inside and outside the barricade. Six cylinders of carbon dioxide are at a position to give easy access to the operator if he desires to flood the room with carbon dioxide.

Most of the individual pieces of equipment have performed in a highly satisfactory manner since the initial operation. The flow rate and pressure throughout the system are extremely stable during steady-state operation. Flow-rate variation at the meter can scarcely be detected on the cathetometer which reads pressure differential to 0.001 in. of water. Short-term pressure fluctuations, due largely to the compressor, are not more than 0.02 in. of mercury at the meter. The low-temperature bath in which specific-heat and Joule-Thomson measurements are made is normally constant over a range of from 32° to -250°F to better than 0.05°F. The calibration of individual items of equipment, including the flowmeter which was calibrated at the National Instruments Laboratories, has been completed. The remainder of the calibrations were performed with the equipment in place. Considerable use has been made of the IBM 650 computer for curve-fitting of polynomial functions, for solving certain implicit forms, and for tabulating certain functions required in converting readings of equipment to finished measurements.

CONTINUED WORK

Work is continuing on the specific heat of nitrogen to provide experience with the operation of the equipment and to eliminate minor difficulties. Once the work on nitrogen has been completed, experimental work with methane will begin. Pure methane has been procured and is available for this purpose. Following the measurements on methane, it is expected that gaseous mixtures of methane and other light hydro-carbon gases, such as ethane, propane, and butane, will be investigated.

A P P E N D I X

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TABLE I

TRIAL RUNS WITH NITROGEN

Experimental Conditions		Our Measured Value of Cp Btu/lbm °F	Millar and Sullivan Calculated Cp (1)	IGT Calculated Cp (2)	$\frac{\text{Our Results} - (1)}{(1)} \times 100$	$\frac{\text{Our Results} - (2)}{(2)} \times 100$
Temp. (°F)	Pres. (psi)					
-50.64	308.6	.260	.262	.264	-0.8	-1.5
-100.90	308.6	.268	.267	.272	+0.4	-1.5
-98.50	308.6	.303	.300	.299	+1.0	+1.3
-100.42	896.5	.323	.321	.331	+0.6	-2.4

[1]Millar, Russell N., and Sullivan, John D. Thermodynamic Properties of Oxygen and Nitrogen, U. S. Bureau of Mines Technical Paper 424, 1928.

[2]Bloomer, O. T., and Rao, K. N., Thermodynamic Properties of Nitrogen, Institute of Gas Technology Research Bulletin 18, Chicago October, 1952.

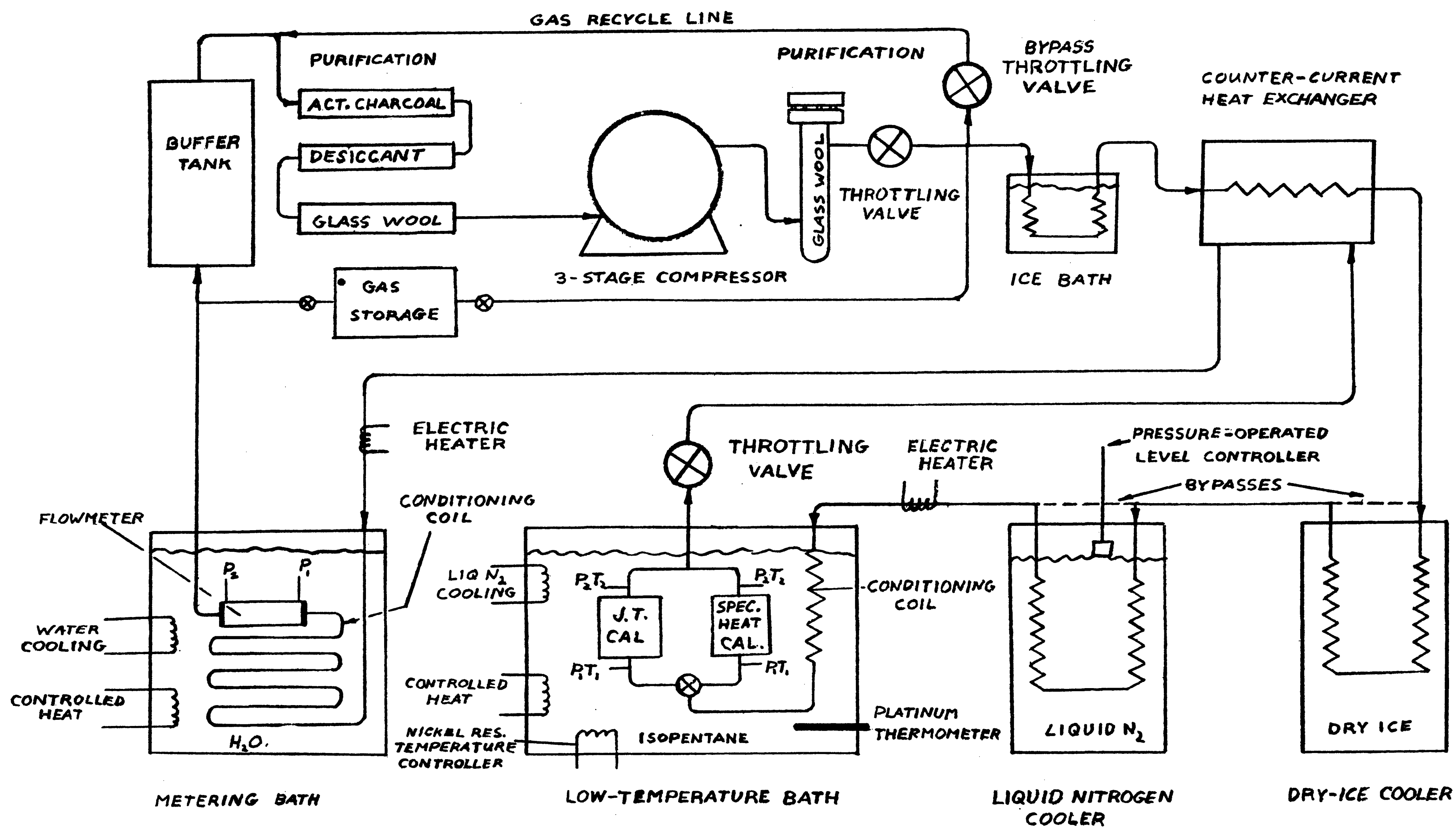

Fig. 1. Flow diagram, low-temperature calorimetric system.

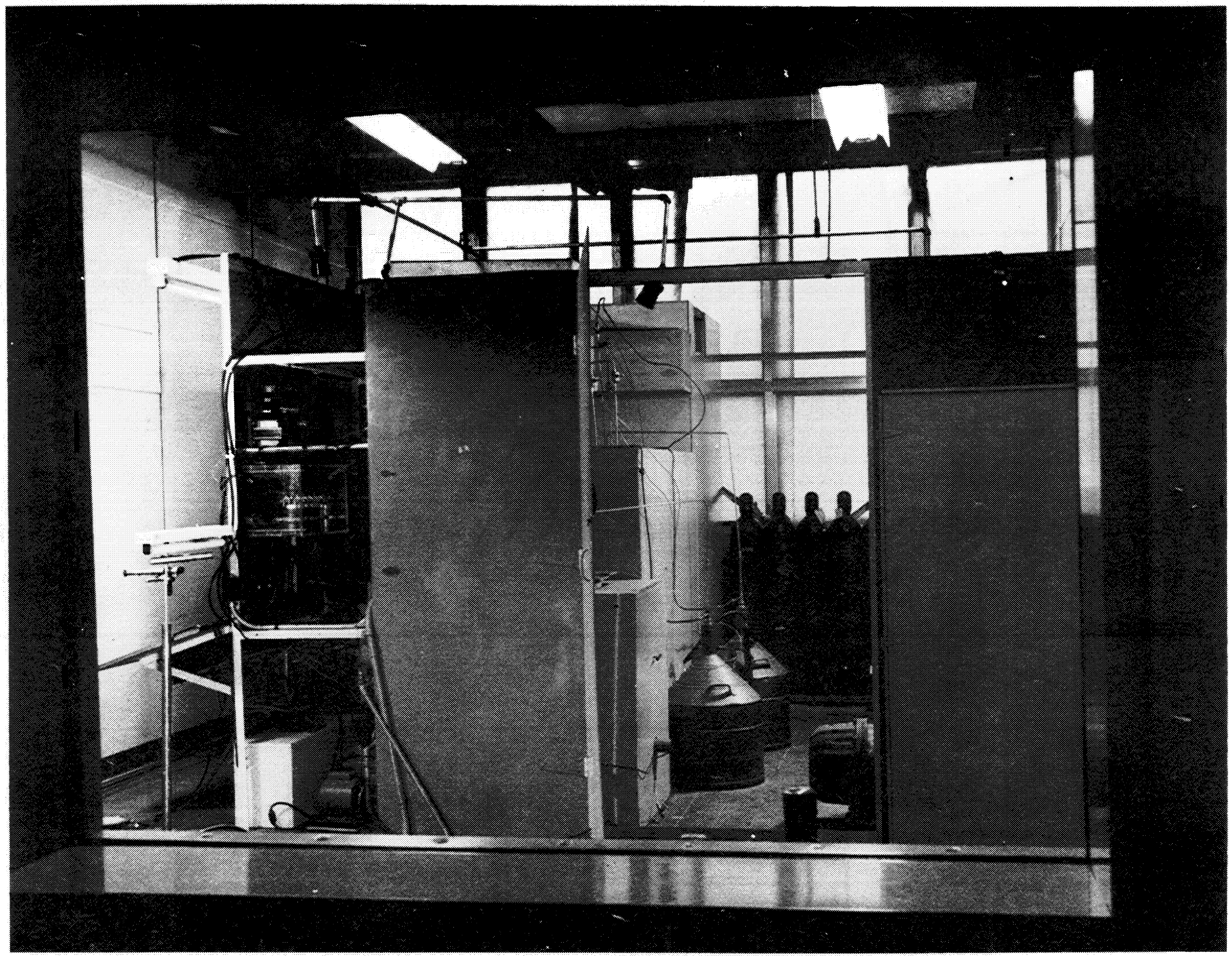

Fig. 2. Automotive Laboratory test cell 247.

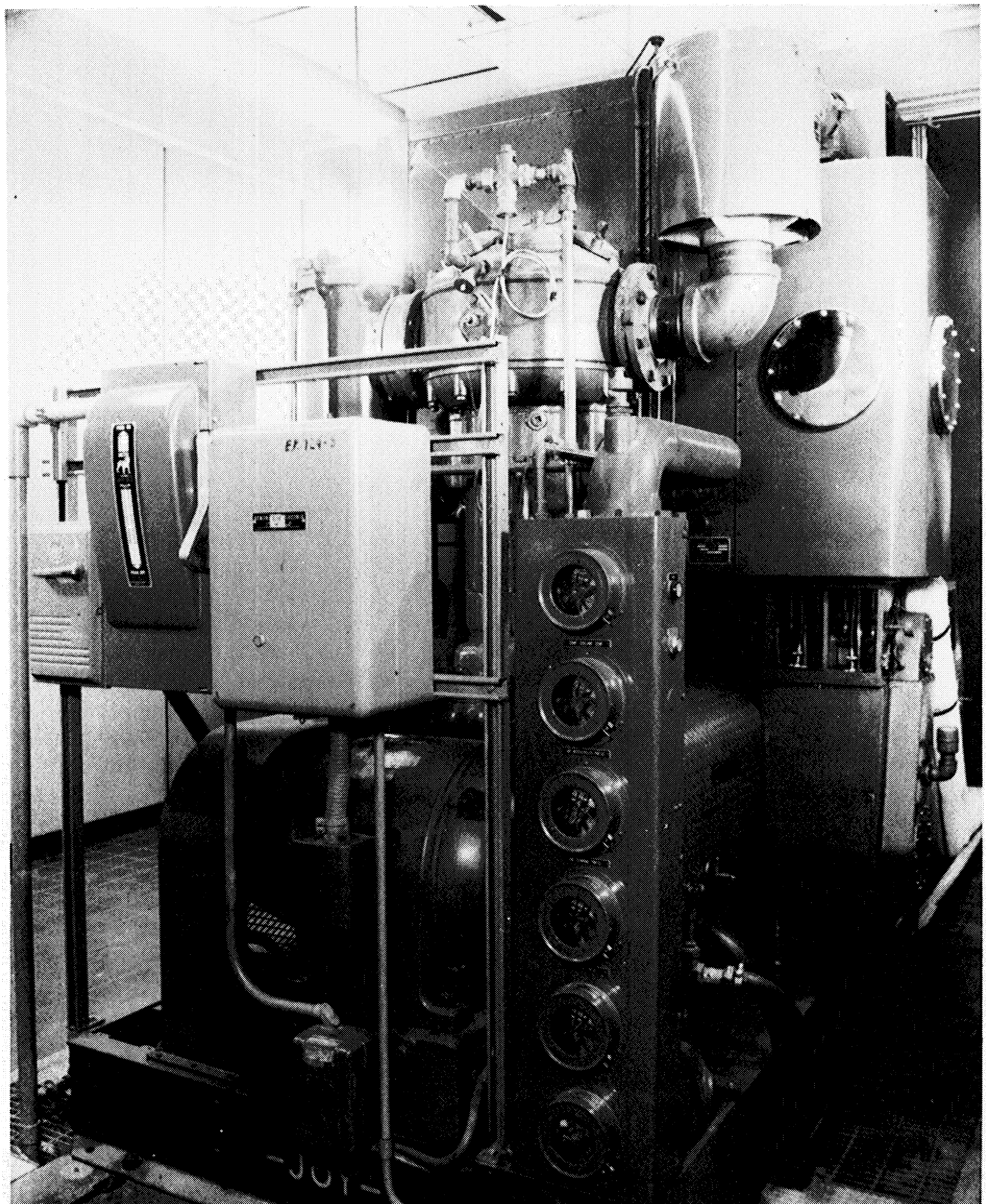

Fig. 3. Liquid nitrogen machine.

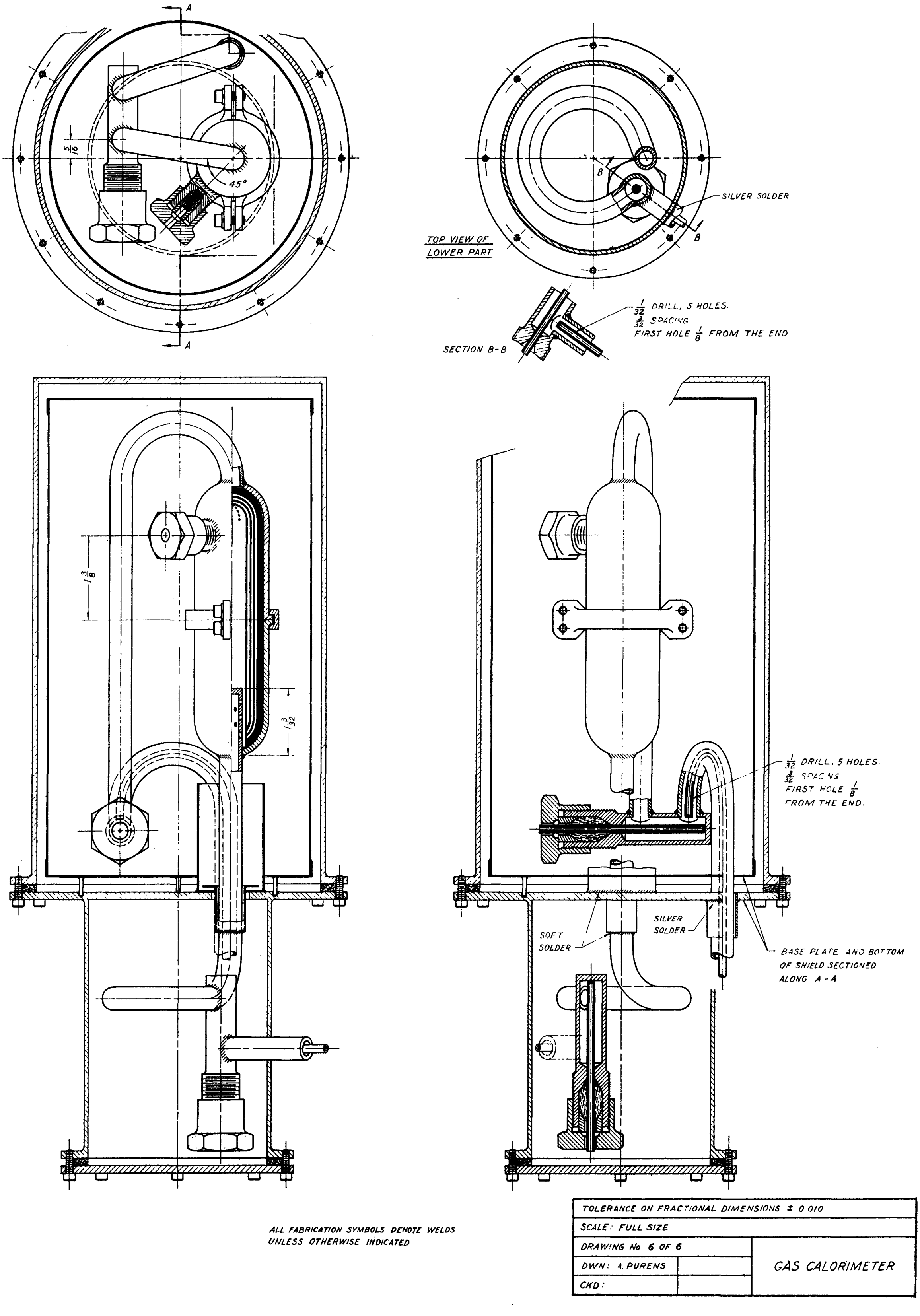

Fig. 4. Specific-heat calorimeter.

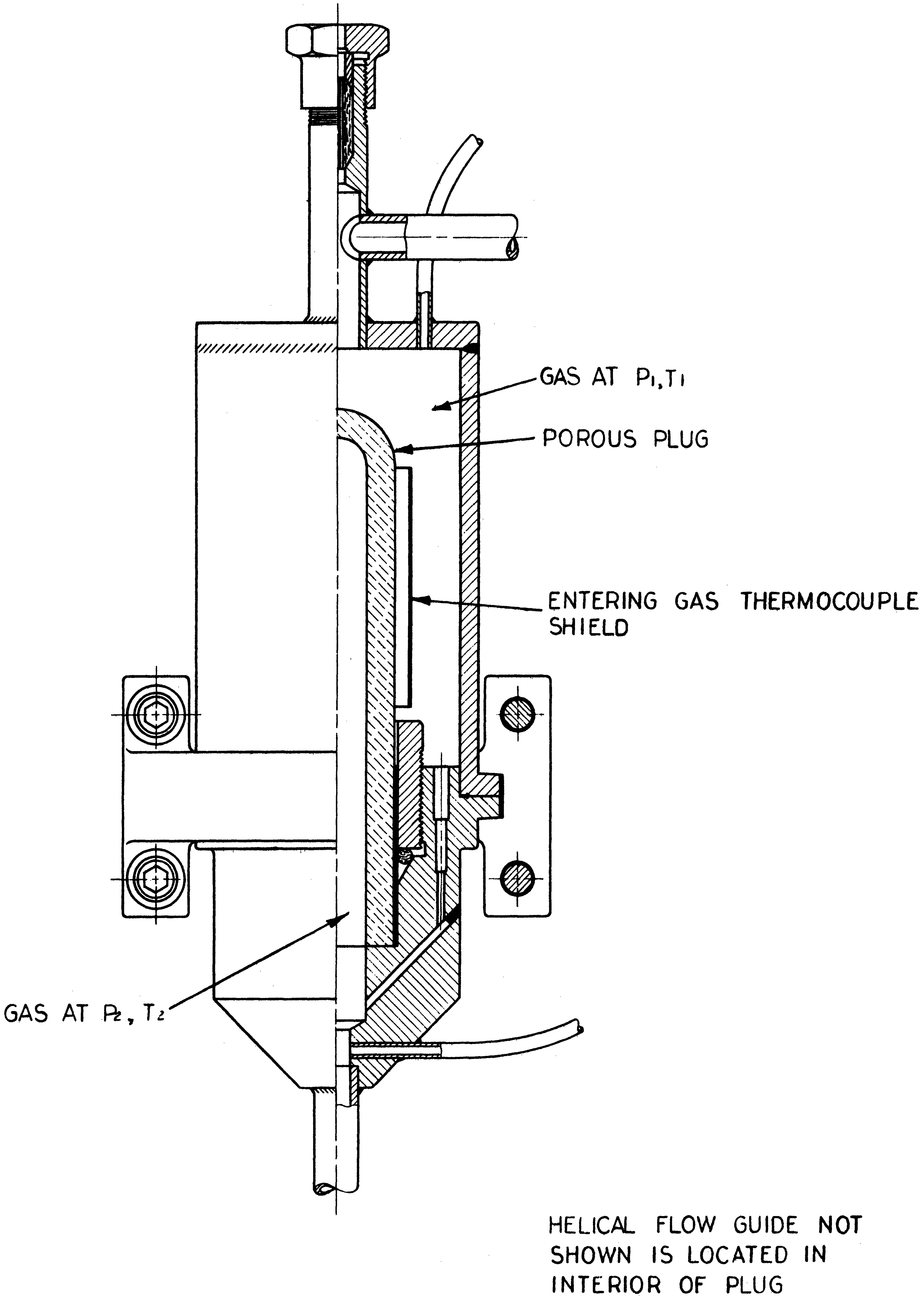

Fig. 5. Joule-Thompson throttle.

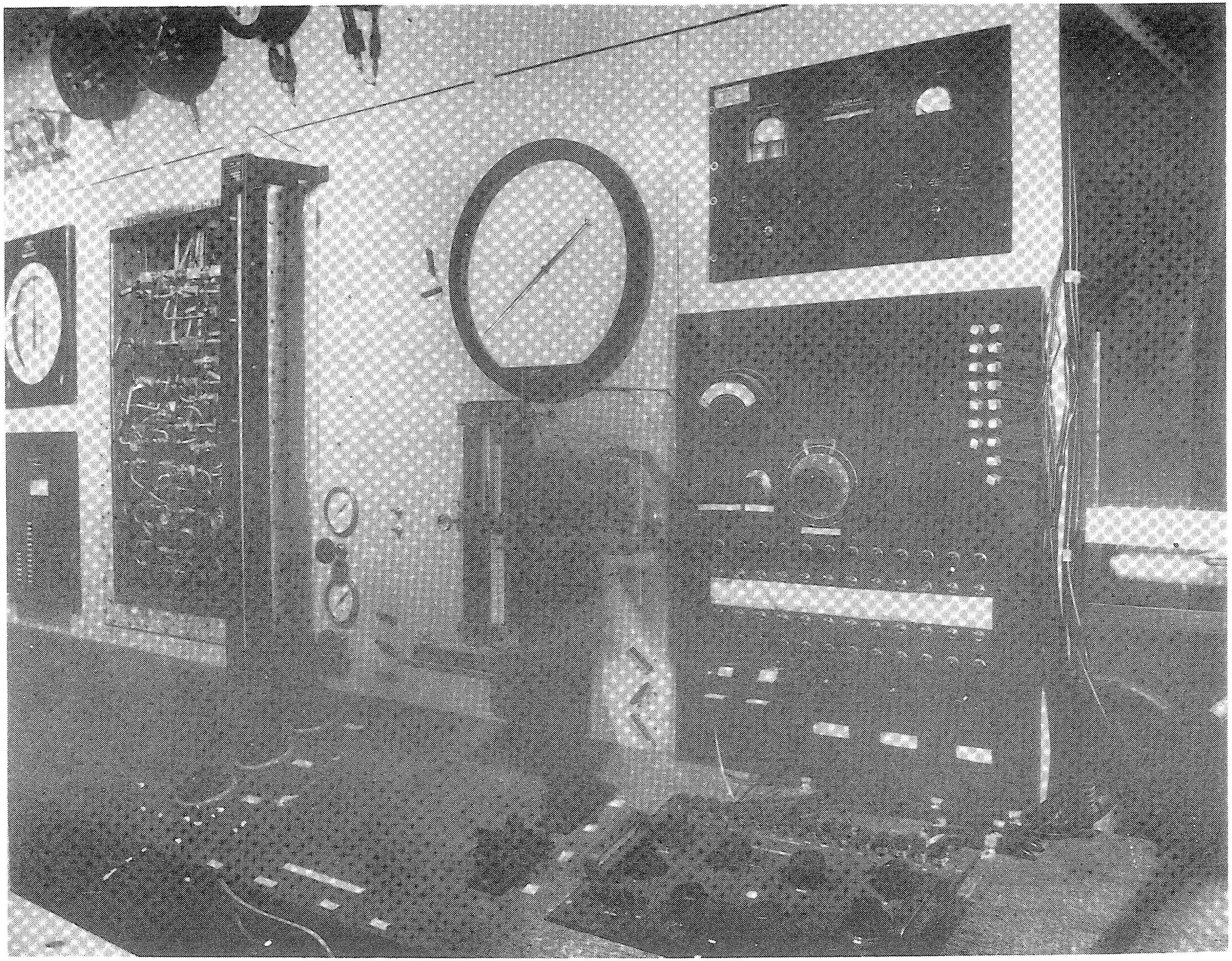

Fig. 6. Panel board.

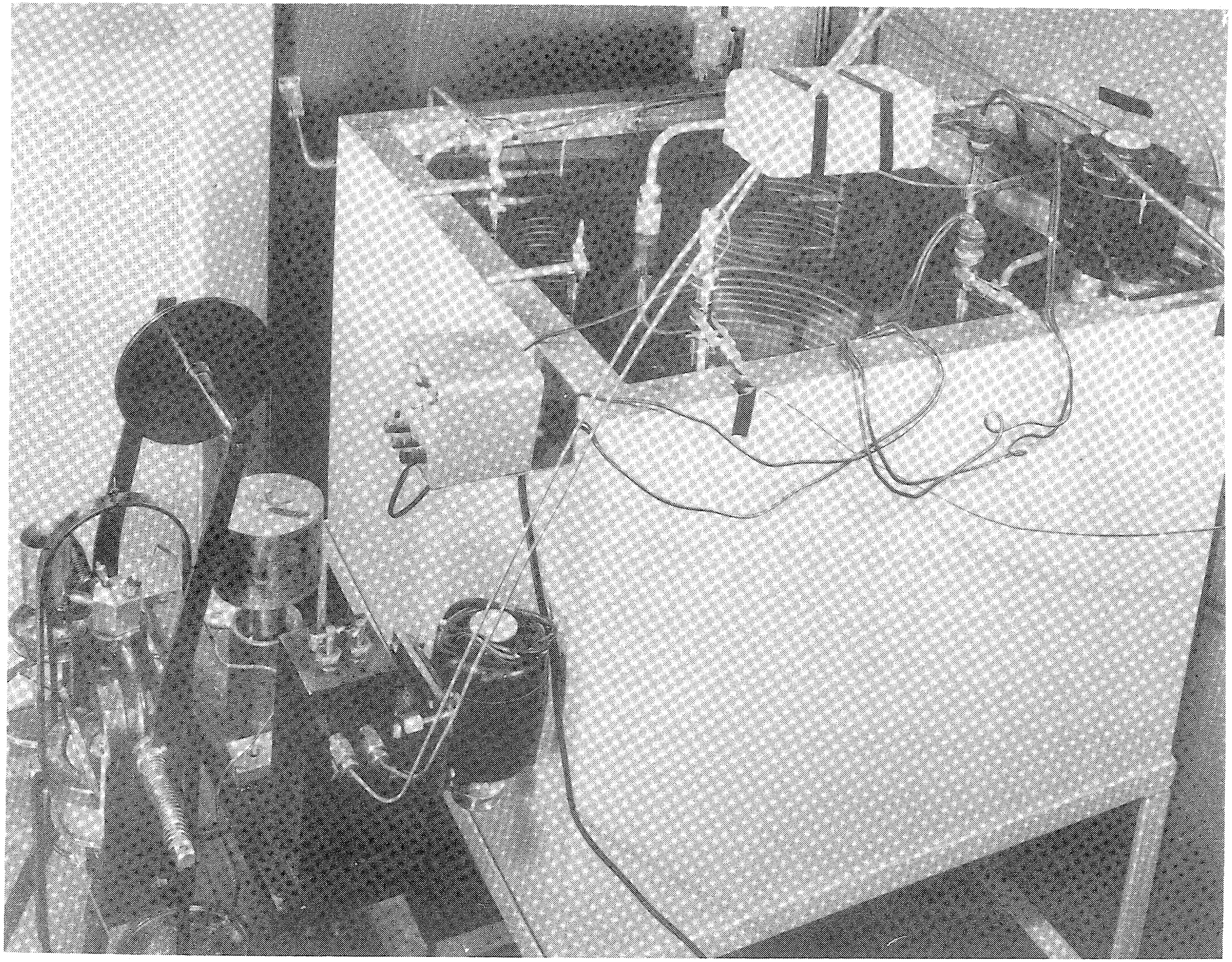

Fig. 7. Metering bath and pressure balance.

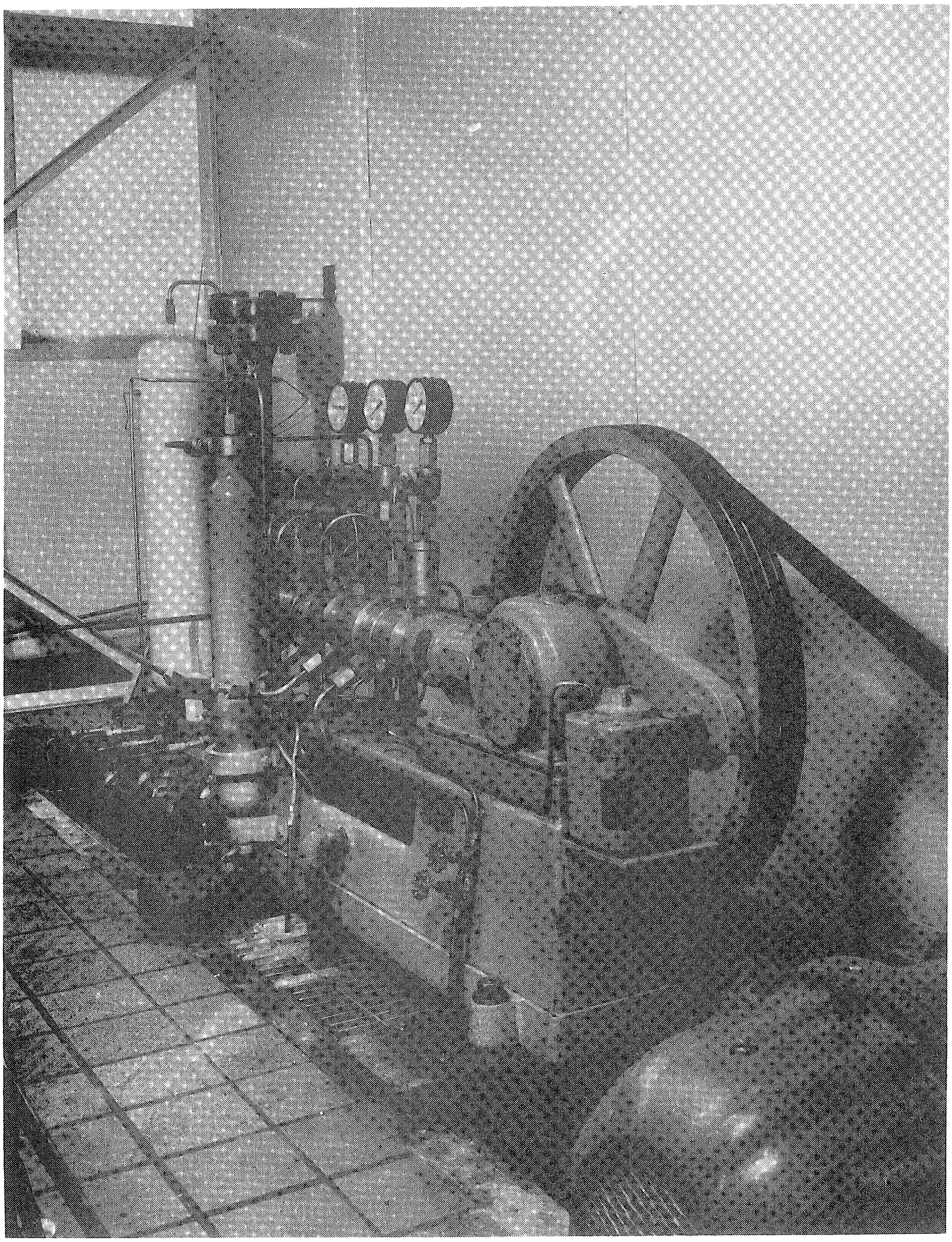

Fig. 8. High-pressure compressor.

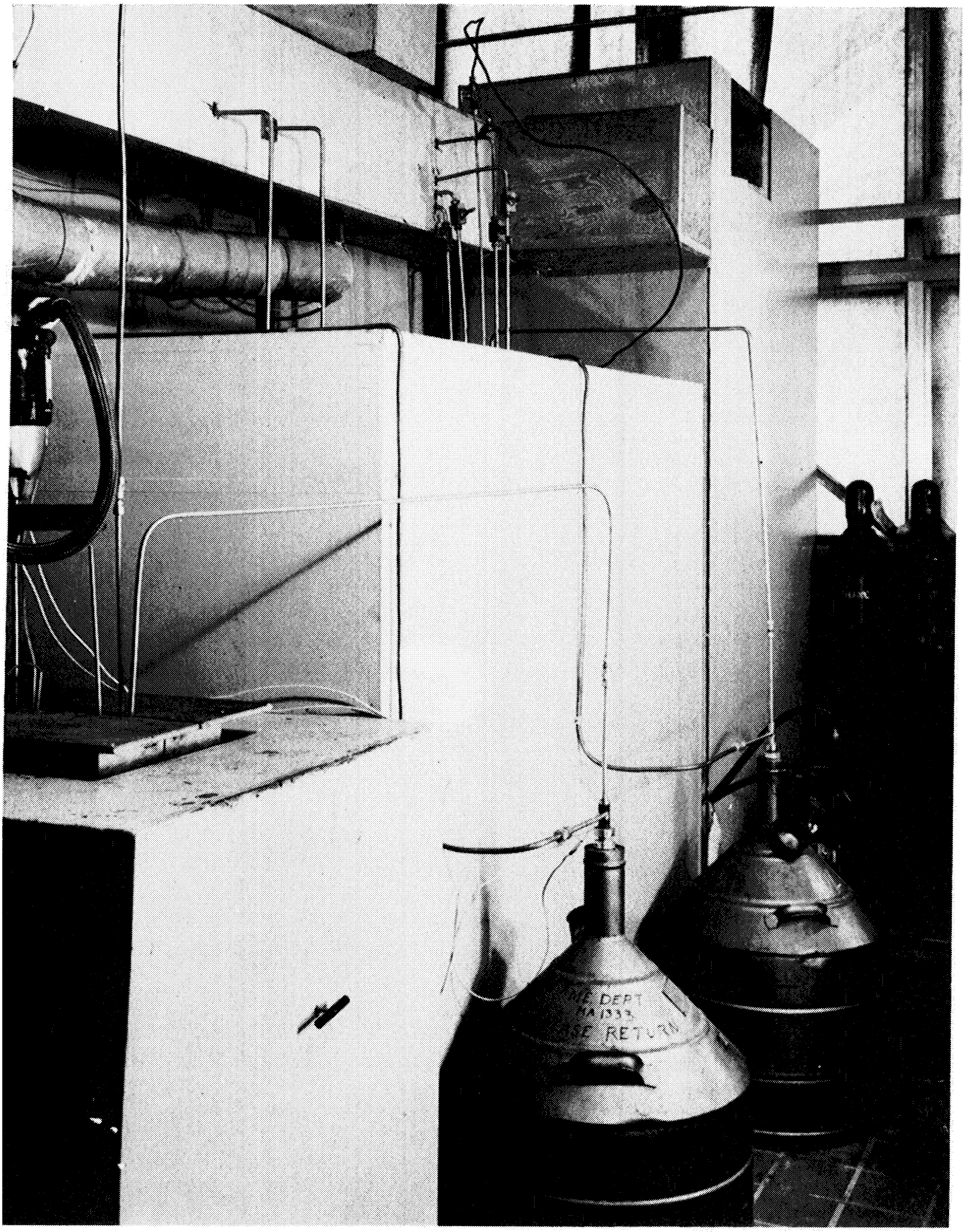

Fig. 9. Refrigeration equipment and low-temperature bath.