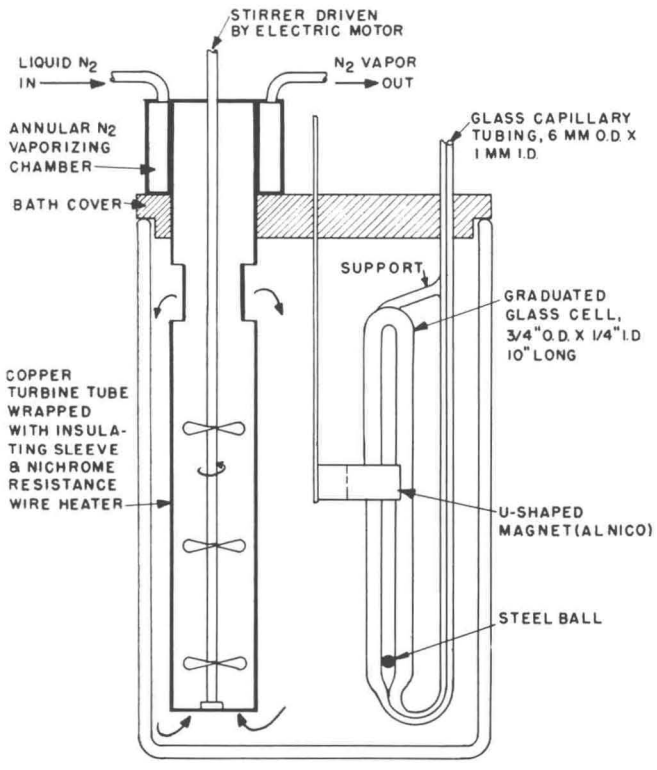

Fig. 8.— Equilibrium Cell, Low-Temperature Bath Assembly

A. Description of Apparatus

1. Gas Measurement and Storage. All gas measurements required for preparing the mixtures and measuring the gas into the equilibrium cell were made with two high-pressure (2,000 psi) Jerguson sight gages (D_1 and D_2 in Fig. 7), each 28 in. long and of approximately 225 cc volume. They were calibrated by attaching arbitrary scales and adding mercury; fifty approximately equal increments of mercury were then withdrawn from each gage successively and weighed after the corresponding liquid levels were noted. Calibration curves were prepared from these data. The calibrations were checked at 600 psia, to observe the effect of pressure on gage volume, by applying cylinder nitrogen gas to the gages when nearly full of mercury, then withdrawing and weighing the mercury in the gage, maintaining the gage pressure constant. The volume obtained by this method agreed with the original calibration to within 0.1 cc.

The Jerguson gages were connected at the top by a manifold system, as shown in Fig. 7. All valves and fittings were of the "Aminco" high-pressure type. A 1200 psi Bourdon-type gage was used to measure the manifold pressure. This gage was read to ± 1.0 psi and was calibrated frequently with the deadweight gage. For high pressure measurements this gage was isolated from the system and a 3000 psi pressure gage attached on the cylinder side of valve 9 in Fig. 7. The pressure in the gas measuring system was determined with the deadweight gage. The entire Jerguson gage and manifold system was mounted in a thermostatically-controlled air bath held constant within $\pm 0.2°$F. A blower continuously circulated air over a strip heater and through the cabinet around the manifold and gages. Mercury was added to or withdrawn from the Jerguson gages by controlled changes in the pressure of the nitrogen in the mercury reservoir C.

2. Equilibrium Cell. The Pyrex glass equilibrium cell, shown in detail in Fig. 8, was constructed of heavy-wall tubing with a bore of 0.25 in. and an OD of 0.75 in. It was connected to a glass-to-metal tubing connector by a section of capillary tubing with a 1 mm bore and 6 mm OD. The cell contained a close-fitting steel ball which when raised and lowered by movement of a magnet provided excellent agitation of the fluid in the cell.

3. Glass-to-Metal Connector. A modification of the closure developed by Davis *et al.*[11] proved satisfactory at the high pressures encountered. The advantages of the seal (shown in Fig. 9) over other types are ease of construction and assembly, and ability to absorb vibrations. The seal is effected by compression of a rubber O-ring, confined in a groove in the brass male fitting, against the flat end of the glass capillary. The glass tubing is connected to the brass adapter by a metal female coupling threaded over a brass ring mounted on the capillary tube. The end of the glass tubing is upset, and forms a thrust point for the brass ring. A teflon insert insulates the brass ring from direct contact with the glass and provides even stress distribution. This seal was tested at 2000 psi for a 24-hour period without bursting or leaking.

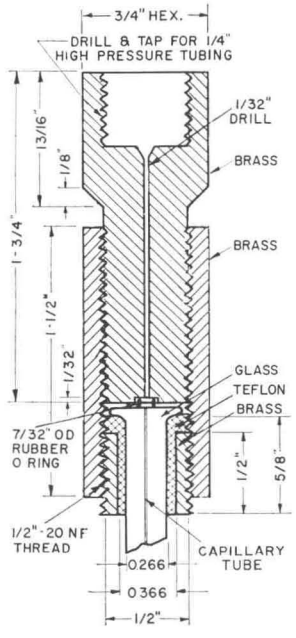

Fig. 9.—High-Pressure Metal-to-Glass Connector

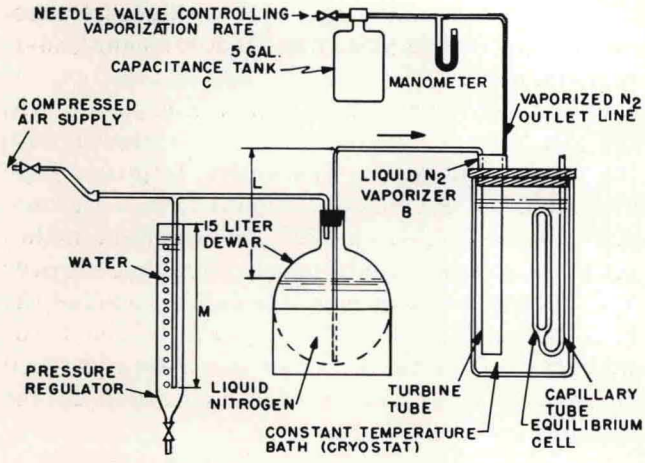

Fig. 10.—Low-Temperature Bath Cooling System

4. Low-Temperature Bath. The low-temperature bath was modified from that described by Walters and Loomis,[24] and is diagrammed in Fig. 10. The liquids used in this bath were either propane or pentane. Liquid nitrogen, which served as the refrigerant, was forced by air pressure from the Dewar flask into the vaporization chamber B on top of the bath. Heat was conducted by the copper turbine tube from the bath to the vaporization chamber, where the liquid nitrogen gave up its latent heat; the turbine tube served as a "cold finger" in the bath.

The refrigeration rate was maintained constant within very narrow limits by the water column which regulated the air pressure in the liquid nitrogen Dewar, and by the needle valve and the 5-gallon capacitance tank C. (The capacitance tank and needle valve are analogous to a capacitance and resistance, respectively, used in a DC electric circuit to stabilize current.) Normally, the pressure in the vaporizer B was equal to the depth of the water column M minus the hydrostatic head of the liquid nitrogen column. The pressure in C was lower by an amount equal to the resistance to flow of the vaporized nitrogen from B to C. If the liquid nitrogen vaporization rate decreased, the pressure in C tended to fall off. This lowered the pressure in B and thus created a differential pressure which forced more liquid nitrogen into B and, thereby, increased the vaporization rate. If the vaporization rate increased, the system functioned in the opposite manner. The refrigeration rate was regulated by opening and closing of the needle valve. The water column height was about 4 feet, and the water column equivalent of the liquid nitrogen column varied from about 1 to 1.5 feet, depending on the depth of the liquid nitrogen in the Dewar. Thus the pressure in C varied from about 3 to 2.5 feet of water. Since the gas flow rate through the needle valve was proportional to the square root of the pressure in C, the vaporization rate fell off only 7% as the Dewar vessel went from full to empty; this was a gradual and continuous decrease during the course of an experiment.

The temperature of the bath was maintained constant by partially offsetting the refrigeration effect with a small manually-controlled current to the nichrome heating coil wound on the outside of the turbine tube. The temperature was controllable to $\pm 0.01°F$ by adjustment of the variac.

5. Temperature and Pressure Measurement. The temperature of the bath, which was assumed to be the temperature inside the cell at equilibrium, was measured by a triple-junction copper-constantan thermocouple connected to an L & N type K-2 potentiometer and an L & N type E self-contained galvanometer. With this equipment, temperature changes of the order of 0.002°F were detected, and fluctuations of the bath temperature were held to less than 0.01°F.

The thermocouple was calibrated by use of a platinum resistance thermometer with a Meuller Bridge as primary standard. The resistance thermometer had been previously calibrated by the National Bureau of Standards. Readings were taken at the ice point, the normal boiling point of liquid propane (—43.7°F), the sublimation point of carbon dioxide (—109.3°F), the normal boiling point of liquid nitrogen (—320.4°F), and at temperatures between —109.3° and —320.4°F obtained by controlling the bath temperature as described above. The calibration was believed to be accurate within $\pm 0.05°F$ down to —240°F.

The pressure inside the equilibrium cell was measured with either a 1000 or 4000 psi capacity Refinery Supply Company deadweight gage. Pressure balance between the equilibrium cell and the deadweight gage was determined from the position of the mercury-gas interface in a lucite sight gage which served as one leg of a mercury manometer. Oil filled the space above the mercury in the other leg of the manometer, which connected to the deadweight gage. The volume of the gas space in the pressure-measuring system was held to a minimum by use of capillary tubing and by using a 1/16 in. ID bore in the lucite sight gage. The total volume of the piping system between valve 6 (Fig. 7) and the capillary glass tube of the equilibrium