

LOW-TEMPERATURE CALORIMETRY AT THE BARTLESVILLE STATION OF THE BUREAU OF MINES^{1, 2}

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In the present review an attempt has been made to survey briefly the utility of thermodynamic data and to illustrate the methods in use at the Bartlesville Laboratory of the Bureau of Mines to obtain entropy data.

INTRODUCTION

Thermodynamic data are useful and important both for the solution of practical problems in chemistry and as an adjunct for theoretical studies of molecules. The general utility of thermodynamic data may be illustrated by the following relations of thermodynamic functions. The free energy, ΔF , is related to the equilibrium constant of a chemical reaction by the expression

$$\Delta F = -RT \ln K \quad (1)$$

In the general reaction



the equilibrium constant is given by the following expression

$$K = \frac{C^c \times D^d}{A^a \times B^b} \quad (3)$$

where A, B, C, and D represent the thermodynamic concentrations of the reactants at equilibrium and the products, and a , b , c , and d are the number of moles of reactants and products taking part in the reaction. By combining equations 1 and 3 the following equation is obtained:

$$\Delta F = -RT \ln \frac{C^c \times D^d}{A^a \times B^b}$$

If it is assumed as a first approximation that the thermodynamic concentration is equivalent to the actual concentration (or pressure), it is readily seen that this equation serves as a useful tool for calculating the yield of a given reaction. If the free energy ΔF is known as a function of temperature, the relative concentrations at any given temperature and pressure may be calculated. This fact is of considerable importance to the chemist, as it allows him to determine, with-

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out resort to experiment, whether a postulated reaction is practical and also the optimum conditions of temperature and pressure for maximum yields.

The free energy is also related to certain other thermodynamic quantities by the expression:

$$\Delta F = \Delta H - T\Delta S \quad (4)$$

The interesting thing about this expression is that it permits determination of ΔF from purely thermal quantities. If studies of certain properties are made over a wide temperature range, ΔF may be evaluated at any desired temperature in this range.

The Bureau of Mines has long been interested in obtaining data that would be generally useful to the petroleum and other industries. For this reason a laboratory was established in 1943 at the Petroleum Experiment Station of the Bureau of Mines in Bartlesville, Oklahoma, for the purpose of determining the thermal data required for the solution of equation 4 over a wide temperature range.

This report is concerned with only a single phase of the general program: namely, the evaluation of ΔS , the change in entropy from low-temperature calorimetric data in conjunction with the Third Law of Thermodynamics. The Third Law may be stated simply as "The entropy of all perfect crystals at absolute zero is zero." It can be shown that the entropy of a substance which is a perfect crystal at absolute zero is given by the expression

$$S = \int_0^{T'} \frac{C_p}{T} dT + \frac{\Delta H'}{T'} + \int_{T'}^{T''} \frac{C_p}{T} dT + \frac{\Delta H''}{T''} + \int_{T''}^{T'''} \frac{C_p}{T} dT \dots$$

where C_p is the heat capacity at constant pressure and ΔH is the change in enthalpy accompanying an isothermal change in state, i.e., transition, fusion, vaporization. If this expression is evaluated from 0°K., an absolute value of the entropy is obtained.

In practice, heat-capacity measurements are made from sufficiently low temperatures and an extrapolation method is employed to cover the gap between 0°K. and the temperature at which measurements are started. In the Bureau, measurements in low-temperature work are started at a temperature of about 12°K., which is attained by converting liquid hydrogen to the solid by reducing the pressure by means of large vacuum pumps.

HYDROGEN LIQUEFIER

Liquid hydrogen is not commercially available, so it was necessary for the Bureau to set up a plant for its production. Several types of hydrogen liquefiers are in use in this country, all of which involve precooling of the high-pressure gas with liquid air or nitrogen, followed by regenerative cooling to the temperature at which a portion of the hydrogen is liquefied by Joule-Thomson expansion. After consideration of various types, it was decided to adopt in principle the modified Kapitza liquefier described in detail by Blanchard and Bittner (1).

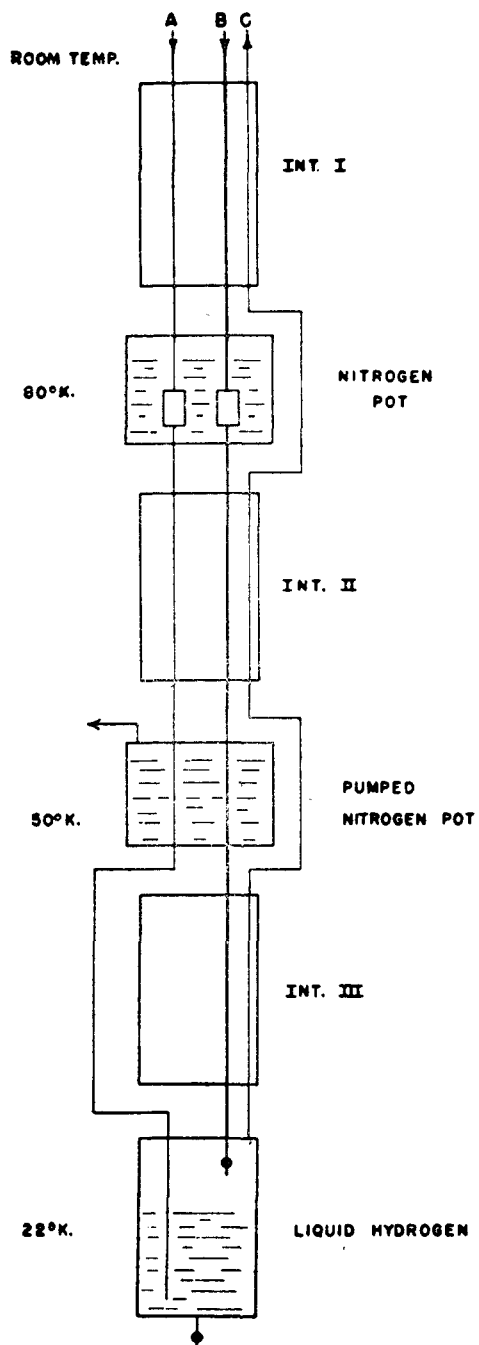


FIG. 1. Schematic flow diagram of the Kapitza scheme for hydrogen liquefaction. A, feed hydrogen; B, compressed hydrogen; C, exhaust hydrogen.

The principal advantage of this system is that relatively impure commercial hydrogen may be used for liquefaction.

The Kapitza principle involves two cycles: (1) a high-pressure cycle in which pure hydrogen is liquefied by Joule-Thomson expansion and (2) a low-pressure cycle in which commercial feed hydrogen is liquefied by condensation at the expense of the liquid produced in the high-pressure system. Essentially, the system is simply a method for purifying the feed hydrogen so that it may pass through the high-pressure system without plugging.

Since the system has been described in detail by Blanchard and Bittner (1), only a brief description will be given here. Figure 1 shows schematically the flow system of the liquefier. High-pressure hydrogen from the compressor enters the system at B, passes through interchanger I to coils in the liquid-air pot, where it is cooled to the temperature of liquid air boiling at atmospheric pressure,

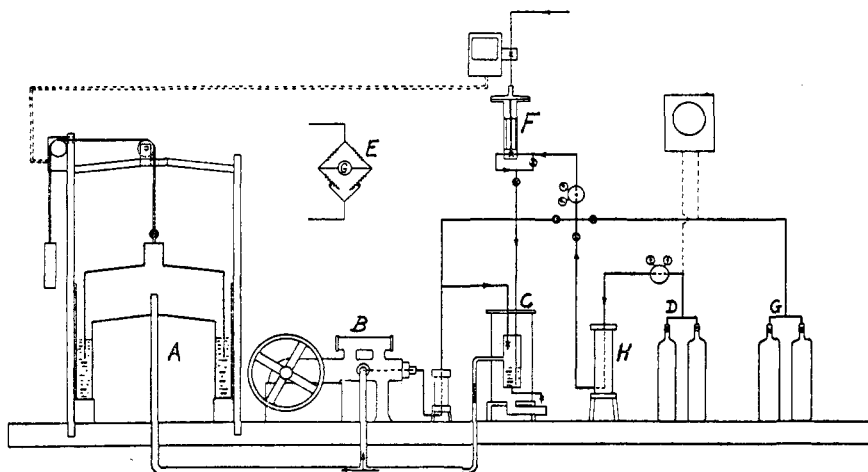


FIG. 2. Simplified flow chart of hydrogen-liquefying system

and then over activated charcoal for the removal of nitrogen. This hydrogen then passes through interchanger II to coils in the pumped air pot, where it is cooled to approximately 55°K ., and then through the regenerative interchanger to the expansion valve.

The commercial feed gas is passed over a heated copper catalyst to remove oxygen and over activated alumina to remove water; it then enters the interchanger system at A (figure 1) and passes in parallel over the same path as the high-pressure gas, except that it goes directly from the pumped pot to the liquid-hydrogen receiver. Here it is passed through the accumulated liquid and the impurities are frozen out. The purified exhaust gas from the receiver is interchanged with the incoming gas up to room temperature and then enters the gasometer on its way to the high-pressure system.

In figure 2 is shown a simplified flow chart of the liquefying system, in which

only the principal units are indicated. The compressor (B) draws pure hydrogen from the gasometer (A) and delivers it to the liquefier (C). When a sufficient quantity has been liquefied, the flow of feed hydrogen stored in the cylinders (D) is started. As more hydrogen is liquefied the level of the gasometer will tend to drop. The gasometer bell is connected to the counterbalance by a chain. The chain passes over a gear, which drives a slide wire mounted in one arm of a wheatstone bridge, shown at E. The change in resistance is picked up by a micromax controller, which operates a pneumatic valve (F) in the feed line. By this arrangement the feed gas is automatically supplied at the same rate as it is liquefied. The purified hydrogen is stored in cylinders (G) when the system is not in operation. The furnace containing the copper catalyst for removing oxygen from the feed gas is shown at H.

It would be very gratifying if it were possible to say that this system was trouble free. Actually, there has been trouble from time to time with the formation of plugs in both the high-pressure system and the low-pressure system. It is believed that one of the sources of the trouble is the location of the charcoal tubes. They are so mounted in the interchanger system that it is impossible to reactivate them properly without dismounting the liquefier.

Figure 3 is a detailed cross-section drawing of the liquefier and interchanger system. This is shown only to give an idea of the complexity of the system and indicate the care that must be given to details of construction. For example, there are many silver-soldered joints, all of which must be vacuum-tight since the system is thermally isolated from the environment by evacuating the entire space within the two brass cans which contain the system.

Figure 4 is a photograph showing a general view of the liquefier and accessories. In the foreground is shown the three-stage Norwalk compressor. The control panel and the assembled liquefier are in the background. Figure 5 is a close-up view of the assembled liquefier and shows clearly the Dewar tube through which liquid hydrogen is transferred to the glass Dewars in which it is carried to the cryostats.

The main control panel is shown in figure 6. At the left of the panel is shown the micromax recording controller, which automatically controls the supply of feed hydrogen to the liquefier. The next instrument is a recording pressure gauge with two pens. One pen records the pressure in the cylinders containing the feed hydrogen. As liquefaction proceeds the pressure drops, and a record is made which is related to the amount of hydrogen liquefied. The second pen gives a record of the supply of purified hydrogen. The third instrument is a recording rotamatic flowmeter and gives a record of the flow of the gas returning from the liquefier to the gasometer or compressor. The instrument on the right is a controller which maintains the catalyst furnace, for removing oxygen from the feed hydrogen, at a constant temperature.

Below the instruments are shown the various valves and gauges which are required to control the flow and to enable the operator to know what is going on in the liquefying system. For example, there are three gauges in the high-pres-

sure system, located at strategic points, that allow the operator to locate plugs when they are formed. The complete flow system is quite complicated and has many connections so that the gas may be directed in any chosen way. An example of the necessity for this is that gas from the compressor may be sent either to the liquefier or to high-pressure storage.

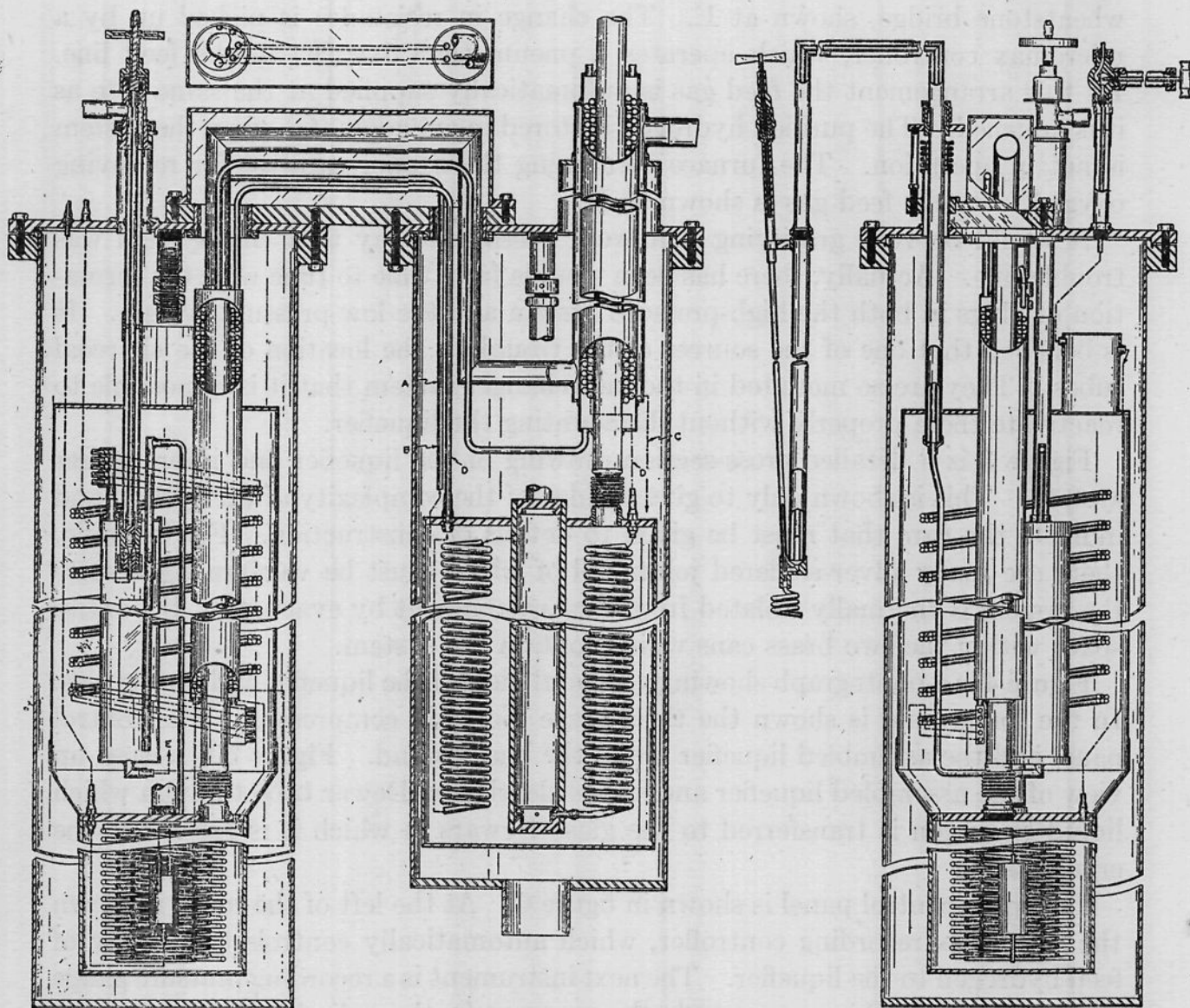


FIG. 3. Detailed cross section of liquefier and interchanger assembly. A, feed hydrogen; B, low-pressure feed hydrogen from cooling coils in nitrogen pot (these coils not shown); C, low-pressure feed hydrogen to cooling coils in nitrogen pot (these coils not shown); D, 2500 lb. per square inch; E, to liquid-hydrogen transfer tube.

The vacuum cans in which the liquefier and interchangers are mounted are equipped with blow-out plugs for safety in case the high-pressure system should open up in this closed space. There is also a safety valve in the low-pressure return line to take care of any surges that may occur across the throttling valve.

In addition to the hydrogen liquefier discussed above, the station also has its own plant for liquefying air. This is a commercial installation having a capacity of approximately 15 liters per hour.

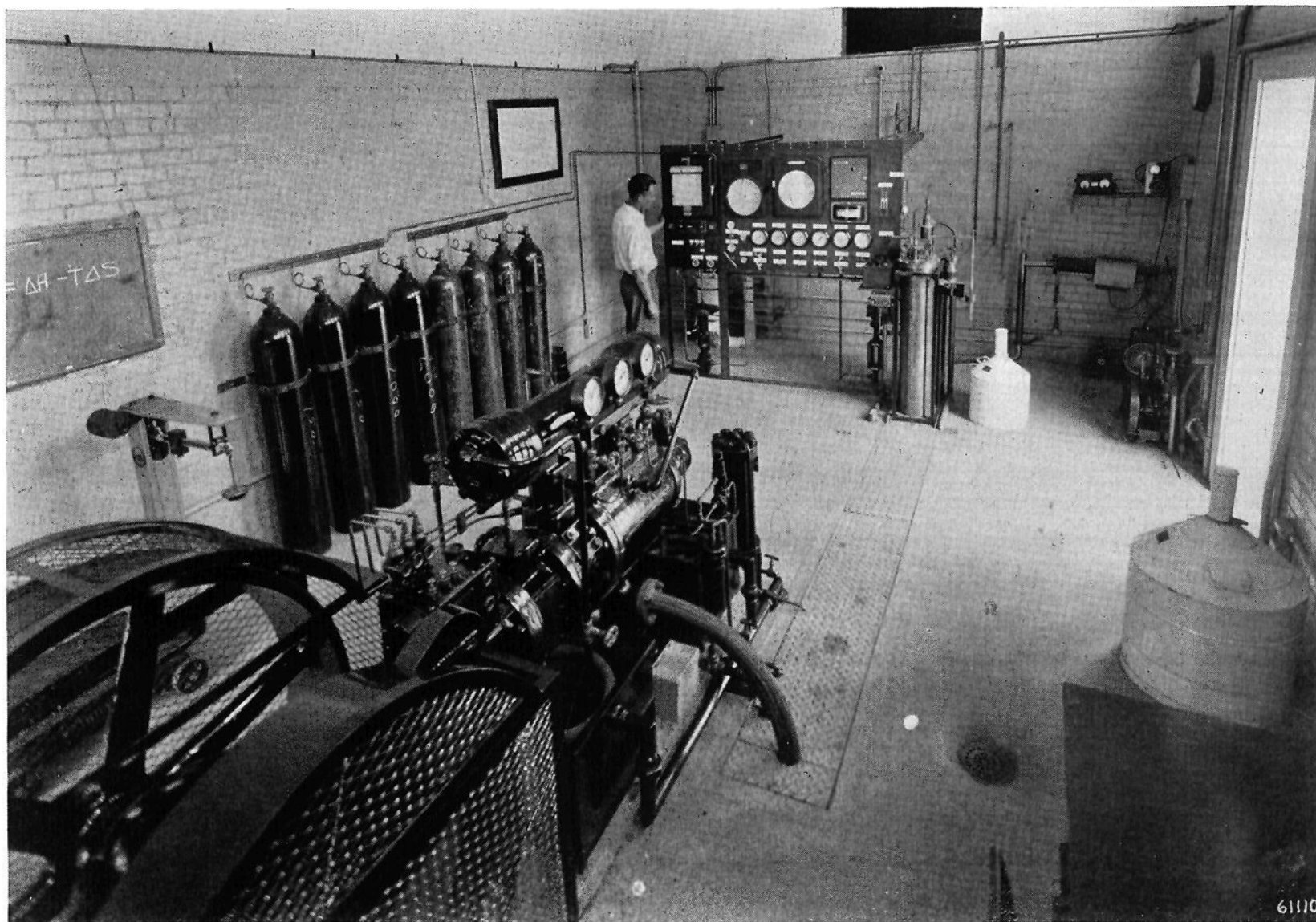


FIG. 4. General view of room in which hydrogen is liquefied

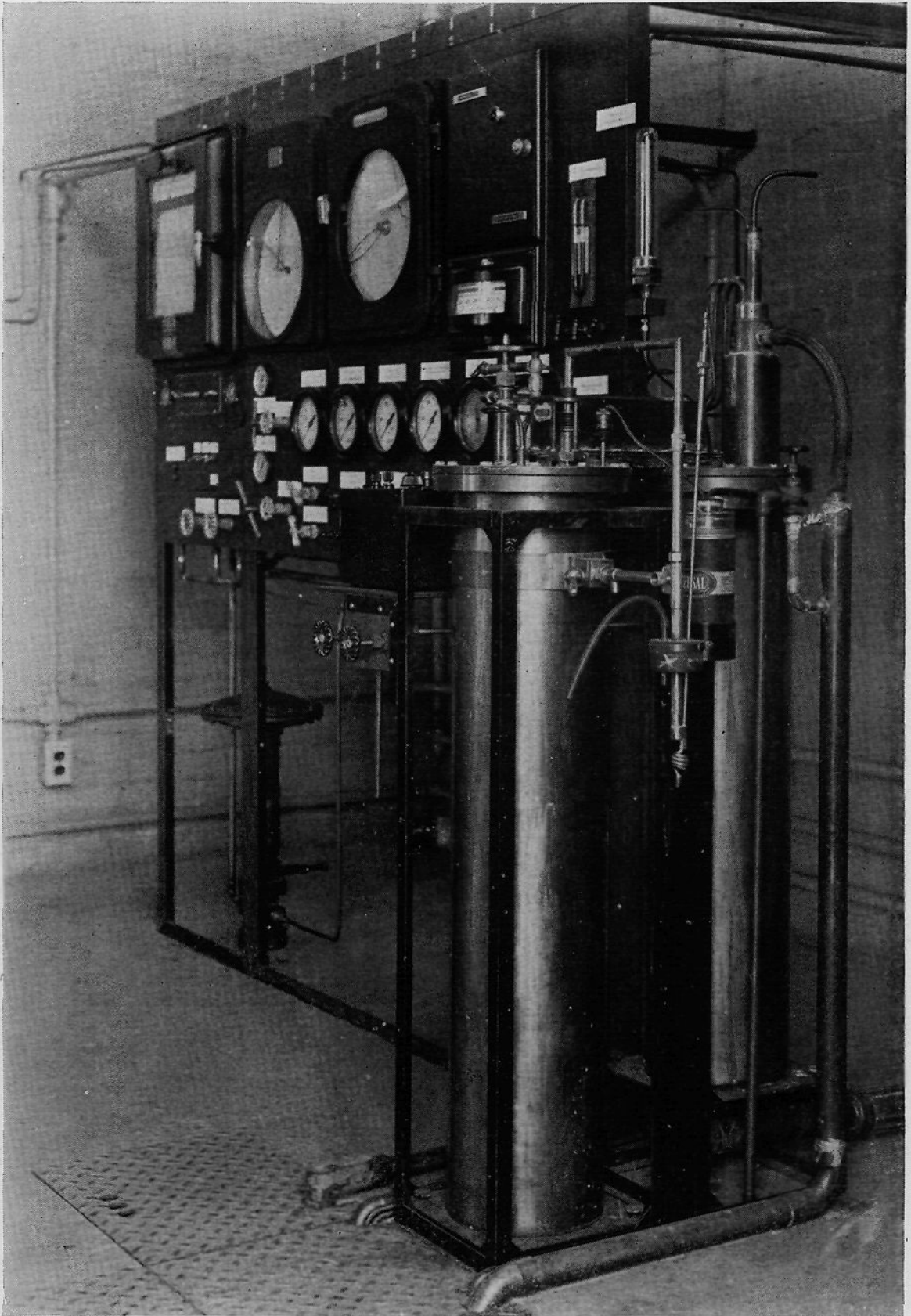


FIG. 5. Close-up view of liquefier-interchanger assembly

THE CRYOSTAT AND CALORIMETER

The cryostat is similar to that described by Blue and Hicks (2), except that a simpler device is employed to transfer heat from the calorimeter during the

cooling operation. Figure 7 is a schematic drawing of the apparatus, and figure 8 is a photograph of the unassembled cryostat, showing the various tanks, radiation shields, etc. In this figure *j* and *i* are chromium-plated copper reservoirs for liquid air and liquid hydrogen, respectively, and *d*, *e*, and *f* are chromium-plated, thin-walled, copper radiation shields. The reservoirs are provided with thin-walled Monel-metal tubes (*l*, *m*, and *n*), which serve for filling, emptying, and pumping as well as for supports. The whole assembly fits into a removable

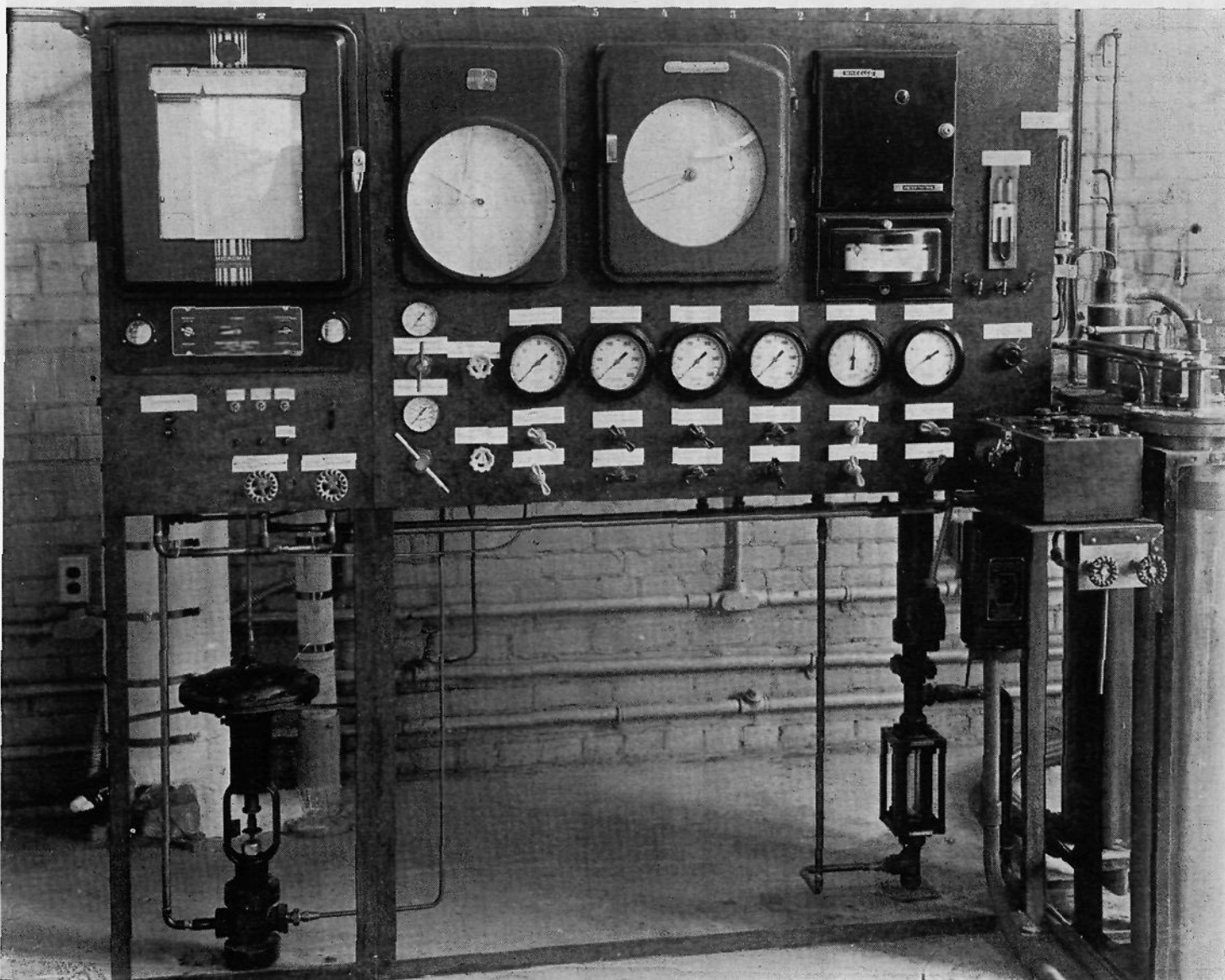


FIG. 6. Main control panel showing controls

brass can (*g*) which is connected to the top at *k* by a joint which can be made vacuum-tight by means of a rubber gasket and screws. This joint is always at room temperature and, consequently, is easy to make and maintain tight. The space enclosed by the can is evacuated by means of an oil diffusion pump backed by a Cenco Hyvac pump.

The calorimeter is surrounded by a lightweight, chromium-plated, copper adiabatic radiation shield consisting of three parts,—top, tube, and bottom. Each part of the adiabatic shield is provided with a closely wound, non-inductive,

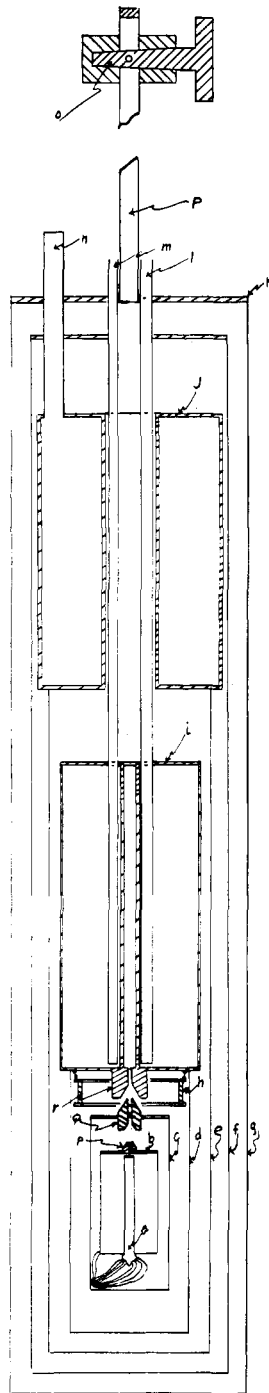


FIG. 7. Schematic cross section of assembled cryostat for low-temperature heat-capacity measurements.

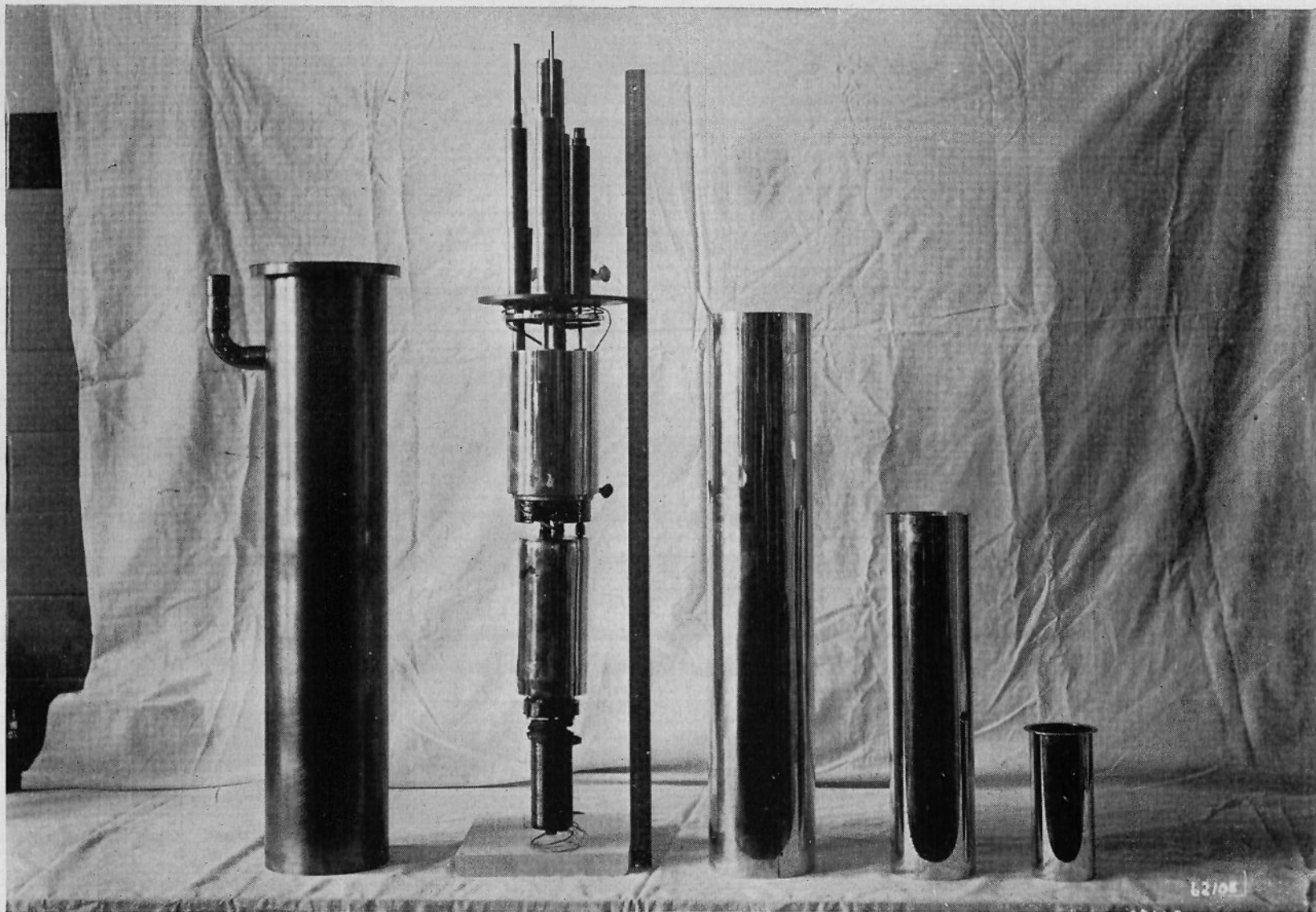


FIG. 8. Photograph showing parts of unassembled cryostat

constantan heater which covers nearly all of the external surface. The No. 32 enamel- and silk-covered copper lead wires are laid in a shallow helical groove, about 50 cm. in length, under the tube heater windings; good thermal contact and insulation for the heaters were assured by the application of electrician's enamel and baking. All of the leads are continuous to the outside and are thermally anchored successively to the floating ring (h), the hydrogen reservoir, and the liquid-air reservoir. The floating ring and the three parts of the adiabatic shield can be heated independently, and their relative temperatures may be observed by means of interconnected copper-constantan difference thermocouples in conjunction with a high-sensitivity Leeds & Northrup galvanometer. By this arrangement of heaters and thermocouples it is possible by suitable manual control to keep the ring, the shield, and the calorimeter at the same

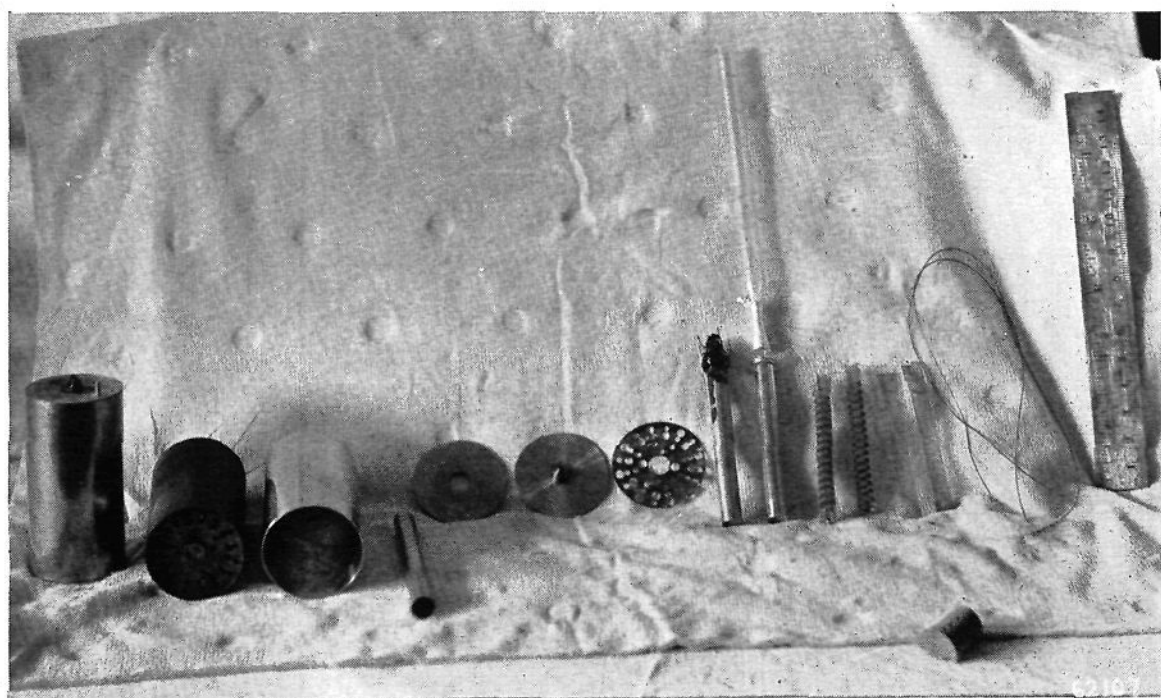


FIG. 9. Assembled calorimeter and parts shown at the left; assembled thermometer-heater and parts shown at the right.

temperature, within close limits, and at any desired temperature above that of the hydrogen reservoir.³

The calorimeters are of copper and have the following approximate dimensions: length, 67 mm.; diameter, 35 mm.; internal volume, 55–60 ml.; mass, 45–50 g. Thin copper discs spaced along the reëntrant thermometer well and making contact with the wall aid in the rapid attainment of thermal equilibrium. A small screw and nut serve to secure one junction of the difference thermocouples to the bottom of the calorimeter. Liquids are admitted through a small tube in the top of the calorimeter, the tube being soldered shut after the remaining free space is filled with helium. The calorimeter parts and various stages of the assembly are shown in figure 9.

³ This method of maintaining adiabatic conditions in low-temperature calorimetry was first described by Southard and Brickwedde (*J. Am. Chem. Soc.* **55**, 4378 (1933)).

THE METHOD OF HEAT TRANSFER

Heat transfer from the calorimeter and its radiation shield to the reservoirs of liquid air and liquid hydrogen is effected by a mechanical device or thermal switch, rather than by the more cumbersome method employing conduction through helium gas and the subsequent evacuation of the helium. In the present cryostat the calorimeter is attached to a stout cord (not shown) passing through a hole in the shield and terminating at a vacuum windlass (o), the windlass being on the outside of the brass can and hence always at room temperature. In operating the thermal switch the calorimeter and shield are drawn tightly into contact between accurately turned 60° conical fittings, shown at p, q, and r. When the temperature has dropped to that of the reservoir, the shield and calorimeter are lowered to their normal, isolated positions, a knot in the cord just above the shield serving to hold the calorimeter isolated in about the center of the adiabatic shield.

The cooling operation is normally carried out in two steps. In the first the calorimeter and shield are cooled to $51\text{--}52^\circ\text{K}$., both reservoirs in this operation containing liquid air under partial vacuum. In the second operation the liquid air in the lower reservoir is emptied and replaced by liquid hydrogen, which is subsequently frozen by pumping on it. The calorimeter and shield are again brought into contact with the hydrogen reservoir and held there until they have reached its temperature, this operation requiring 2–4 hr.

In general the cooling operations require a longer time than is the case when helium gas is used, but the advantages of the present method are obviously many. For example, a number of cooling and heating curves may be obtained in succession in the neighborhood of a transition region without having to break the vacuum in the apparatus.

TEMPERATURE SCALE AND RESISTANCE THERMOMETERS

The resistance thermometers

A set of five strain-free platinum resistance thermometers were constructed according to the design published by Myers (5). With one exception, each thermometer contained a coil of annealed platinum wire and a coil of No. 40 constantan wire mounted on a mica cross, the former serving for temperature measurements and the latter as a heater. The thermometer-heater assemblies were enclosed in 65×7.6 mm. platinum tubes, and the six platinum leads were brought out through glass heads sealed to the tubes. After repeated evacuation and annealing the thermometers were filled to $\frac{1}{3}$ atm. with purified helium and then sealed. The thermometer well in the bottom of the calorimeter is such that a thermometer fits snugly into it, thermal contact being made by the use of Apiezon grease M.

The thermometers were compared at frequent temperature intervals from $12\text{--}320^\circ\text{K}$. with one, H25, calibrated at the Bureau of Standards over the international temperature scale range, -183° to 444.6°C ., and over the range $14\text{--}90^\circ\text{K}$. Carefully smoothed tables (4) of R/R_0 against temperature were constructed for both the standard thermometer and the working thermometer-heaters; as a

result of the method used in calibrating the thermometers and in constructing the smoothed tables, the temperatures defined by all of the thermometers are internally self consistent over the entire range from 12–320°K. According to Brickwedde (3) the scale of the standard thermometer used by the Bureau may be expected to deviate as much as 0.02° from the thermodynamic scale in the range 14–90°K. In view of the accuracy with which R/R_0 may be measured, it is believed that both H25 and the working thermometer-heaters define the thermodynamic scale within 0.02 to 0.03° in the range 14–90°K. Above 90°K. the deviations may be larger than this, since it is known that the international scale does not coincide with the thermodynamic scale within the accuracy of measurements with resistance or gas thermometer. It will be evident from this discussion that the temperature scale consists of two parts: namely, the thermodynamic scale up to 90°K. and the international scale above 90°K.

Resistance measurements were made by comparing the drop in potential across the thermometer with that across a 100-ohm or 25-ohm Leeds & Northrup certified standard resistor in series with the thermometer. Below 36°K. a current of 4 ma. and the 25-ohm resistor were used; above 36°K. the current was 1 ma. and the 100-ohm standard was employed. A decade box in series with the thermometer permits adjustment of the current so that it is always the same no matter what the changes in the thermometer resistance or in the source of the current. By this arrangement the potentiometer reading with 1-ma. current gives a very close approximation of the resistance of the thermometer. The true values of the standards when used in resistance thermometry are not important, but a comparison with thermometer H25 at the ice point showed the standards to be within 0.01 per cent of the values certified by the manufacturer.

All potential measurements were made with a White autocalibrated double potentiometer and a sensitive galvanometer. A bank of six saturated cadmium cells certified by the Bureau of Standards serves as the laboratory standard of potential.

The first low-temperature calorimetric measurements were made at the Bureau in January 1945. Up to the time of this report (April 1946) measurements have been completed on sixteen compounds. One phase of this work is the study of complete series of isomers in order to determine the effect of branching on the entropy. With this point in view, studies have been made of the five hexanes and the six pentenes, and a study of the C_8H_{12} alkylcyclohexanes is in progress.

In addition to the above complete series, studies have been made on several other cycloparaffins.

Because of the importance of petroleum as a source material for many chemical compounds, the laboratory has started and will expand the work on sulfur and halogenated compounds.

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