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COLLEGE OF ENGINEERING
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Technical Report

LIQUID-VAPOR EQUILIBRIUM IN THE SYSTEM NORMAL HYDROGEN-HELIUM

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PREFACE

This report consists essentially of the doctoral thesis of Mr. William Streett. Since it represents a complete report of all work done to date on Contract No. 8-5256, National Aeronautical and Space Administration, George C. Marshall Space Flight Center, Huntsville, Alabama, it is also being submitted as a progress report of all work completed to date.

This work was carried out under the immediate supervision of Professor Richard E. Sonntag.

The advice and assistance of Professors J. J. Martin, H. Merte, Jr., E. F. Westrum, and G. E. Smith, is acknowledged with gratitude.

Sincere thanks are extended to Mr. Frank B. Drogosz and Mr. David Williams of the Department of Chemical and Metallurgical Engineering Instrumental Analysis Laboratory for their work in the mass spectrometer analysis of the gas samples. The assistance of Mr. Jack Brigham and the members of the staff of the Instrument Shop of the Automotive Engineering Laboratory is also appreciated.

The relative ease with which the experimental work was carried out was due in large measure to the efforts of Mr. Sudhir Savkar who assisted in taking the final experimental data.

Special thanks are extended to the Linde Company for their many contributions which included the construction of the cryostat, supply of the liquid hydrogen, and advice on safety precautions in handling liquid hydrogen. The contribution of a cylinder of high purity analyzed helium by the U. S. Bureau of Mines Helium Research Center, Amarillo, Texas is also gratefully acknowledged.

G. J. Van Wylen
October, 1963

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NOMENCLATURE

Symbols

f_A	Partial molal fugacity of component A
G_A	Partial molal free energy of component A
P	Pressure
S	Entropy
T	Temperature
V	Specific volume
x_A	Mole fraction of component A
γ_A	Activity coefficient of component A

ABSTRACT

Experimental vapor and liquid phase compositions are presented for the binary system normal hydrogen-helium, covering the temperature range 15.50-32.50°K and pressures up to 500 psia. The critical curve is located in the temperature range 30.6-32.5°K. The behavior of the system, as described by P-x, T-x, and P-T plots, is typical of binary systems in which the critical points are far apart.

The experimental equipment consists of a vapor recirculating equilibrium system with a vapor pressure controlled liquid hydrogen bath. Temperatures have been controlled to within ±0.02°K, or better, and measured with a platinum resistance thermometer. Pressures have been measured to within ±0.5 psi with a 0-500 psig calibrated 16 inch Heise Gage. A detailed description of the construction and operation of the equipment is included.

A comparison of the experimental results with previous work is given, and conflicts in existing data are resolved. The problems of rigorous thermodynamic analysis of the data are briefly discussed.

I. INTRODUCTION

A. GENERAL

Hydrogen and helium are the lightest known elements, having molecular weights of 2.02 and 4.00 respectively. They have the lowest normal boiling temperatures of all known substances.

Pure hydrogen liquefies at atmospheric pressure at a temperature of 20.4°K (-423.2°F), and under varying vapor pressures it exists as a liquid from its triple point at 13.8°K to its critical temperature of 32.9°K. Liquid hydrogen is colorless and odorless. At 20.4° the liquid has a density of 0.07 g/cc and a viscosity about 1/70 that of water.

In the diatomic hydrogen molecule the two nuclear spins may be oriented in the same direction or in opposite directions, giving rise to two molecular modifications designated as orthohydrogen and parahydrogen respectively. The equilibrium ortho-para composition is temperature dependent. Hydrogen gas at room temperature has an equilibrium composition of 75% orthohydrogen and 25% parahydrogen (commonly called normal hydrogen), while at 20.4°K, the equilibrium composition is 0.21% orthohydrogen and 99.97% parahydrogen (commonly called equilibrium hydrogen). If normal hydrogen gas at room temperature is cooled and condensed, the conversion to equilibrium ortho-para composition will proceed slowly unless catalyzed. In the present work, the composition of the hydrogen in the vapor-liquid mixture was essentially that of normal hydrogen (see Chapter IV, Section B-2).

Only helium liquefies at a lower temperature than hydrogen; at atmospheric pressure it liquefies at 4.2°K. It has a critical temperature of 5.2°K; therefore in the range of liquid hydrogen temperatures pure helium cannot exist in the liquid state.

On the high temperature side the substances with normal boiling temperatures nearest that of hydrogen (excluding the isotopes of hydrogen) are neon (27.4°K) and nitrogen (77.3°K).

With the rapid growth of cryogenic technology in recent years liquid hydrogen has assumed an increasingly important role as a commercial chemical. The development of liquid hydrogen fueled rockets in the aerospace industry has created a demand for liquid hydrogen on a tonnage basis in contrast to the liter quantities produced for laboratory use only a few years ago.

The practical problems associated with the use of liquid hydrogen as a rocket fuel are enormous. Its low boiling temperature and relatively small heat of vaporization require the use of highly efficient insulation in storage and transfer facilities, and its wide explosive limits in air (4 to 74% by volume) and low ignition energy create a significant explosion hazard wherever it is used. However, because of its low molecular weight, hydrogen is theoretically capable of developing a higher specific impulse than any other chemical fuel, and the potential gain in weight reduction and rocket performance over conventional fuels has been considered sufficient to justify its use.

For many years liquid hydrogen has been used in low temperature research. Among its more important research applications is the hydrogen bubble chamber used by physicists to study the interaction of high energy particles with hydrogen nuclei.

In the transfer of liquid hydrogen it is often necessary to pressurize the hydrogen reservoir with helium gas to effect a rapid transfer and to prevent flashing if mechanical pumps are used. In such cases it is desirable to know the maximum extent to which helium may dissolve in the liquid phase. In many applications the presence of helium in the liquid is undesirable—such as in its use as a rocket fuel—however if it is found to be soluble to a significant extent it may be possible to use a hydrogen-helium mixture in a bubble chamber to study the interaction of high-energy particles with helium nuclei.

Beyond the practical uses of the results of a study of this system, it is interesting in itself simply because its vapor-liquid mixture exists at a lower temperature than that of any other binary system (with the exception of mixtures of the two isotopes of helium He^3 and He^4).

The present investigation was undertaken to determine the equilibrium liquid and vapor phase compositions in the hydrogen-helium system in the temperature range 15.0-33.0°K and pressures from hydrogen saturation pressure up to 500 psia. This temperature span covers almost the entire range over which pure hydrogen normally exists in the liquid state.

B. PREVIOUS WORK

Data on low temperature vapor-liquid equilibrium in binary and multi-component systems is abundant in the literature. A considerable amount of work on such systems was done prior to 1950. In 1927 Dodge and Dunbar[1] made a thorough study of the system nitrogen-oxygen. A large amount of work was done by the Russians Fastovski and Gonikberg[2,3,6-9] and their associates in the late thirties and early forties on such systems as hydrogen-methane, argon-nitrogen, nitrogen-methane, helium-methane, helium-nitrogen, and hydrogen-nitrogen. Other important work was done by Ruhemann[10,13] and by Verschoyle.[14,15]

With the rapid growth of cryogenics in the last 10 or 15 years, a large number of papers have been published dealing with low temperature phase equilibria. In Russia the work of Fastovski[4,5] has continued, and in the United States work in this area has been influenced considerably by Katz[17-21,58] of The University of Michigan, several of whose former students are now prominent researchers in this field. Other important contributions in this country have been made by Bloomer[22-24,30] and his associates at the Institute of Gas Technology in Chicago, and by Brandt, Stroud, Dalton, DeVaney, _et al._,[25-29] at the U. S. Bureau of Mines Helium Research Center in Amarillo, Texas.

Several useful surveys and bibliographies of low temperature vapor-liquid equilibrium data have been published. Ruhenmann[16] summarized the low temperature phase equilibrium data taken up to 1945 and discussed the relative merits of the experimental equipment used by different investigators. Ruhemann's work is quite comprehensive and provides an excellent general introduction to the experimental techniques of low temperature vapor-liquid equilibrium work. Bloomer and Parent[30] made a survey of the literature on experimental methods for low temperature vapor-liquid equilibrium measurements which includes many references to systems studied up to 1950. Hala, *et al.*,[47] published a list of references covering all systems for which vapor-liquid equilibrium data had been published in the literature up to February 1957 inclusive. In 1960 the U. S. National Bureau of Standards[31] published a bibliography of approximately 700 references on the physical equilibria and related properties of some cryogenic systems. Included in this compilation are references to papers dealing with binary and multi-component mixtures containing these substances: hydrogen, helium, nitrogen, carbon dioxide, carbon monoxide, methane, ethane, and propane. While the document does not contain any explanatory information, it does include a convenient summary, in table form, of the references dealing with each component.

No attempt will be made here to summarize the work which has been done in low temperature vapor-liquid equilibrium. The excellent surveys described above may be consulted for further information.

Up to the present time only two reports have been published containing experimental vapor-liquid equilibrium data at liquid hydrogen temperatures; both deal with the system hydrogen-helium and cover a limited range of temperatures and pressures.

The first of these is a Ph.D. thesis done by S. R. Smith[32] at Ohio State University in 1952. Smith reported experimental values of vapor and liquid phase compositions at three temperature 17.40, 20.39, and 21.80°K, and at pressures up to 850 psia. The experimental apparatus and procedures used by Smith and the results of his work are discussed elsewhere in this paper.

More recently Roellig and Giese[33,34] reported nine isolated pressure-temperature points in the hydrogen-helium system covering a temperature range of 16.3-26.8°K and pressures up to 12.7 atmospheres.

Comparison of the data from these two sources is difficult due to the small number of points reported by Roellig and Giese; however a cursory comparison seems to indicate poor agreement, especially in the liquid phase compositions where the reported helium concentrations differ by as much as a factor of ten.

Roellig and Giese did not measure temperatures directly, but estimated them by finding the partial pressure of hydrogen in the vapor phase (from the mass spectrometer analysis of the vapor samples), and then taking the temperature from a vapor pressure curve for pure hydrogen, after first calculating the depression of the vapor pressure due to helium in the liquid, using Raoult's law. The assumption of ideal behavior in the liquid solution and in the vapor phase hardly seems justified; moreover the temperature arrived at in this manner is dependent upon the helium content of the liquid, which is perhaps the least reliable portion of the experimental data. Eckert and

Prausnitz[35] criticized the temperature calculations of Roellig and Giese and concluded that even at the relatively low pressures involved, the temperatures reported were in error by as much as 2.7°K.

In addition to the two reports of experimental work on hydrogen-helium vapor-liquid equilibrium, two additional reports[36,37] have been published which deal specifically with this system, although they contain no original experimental data. The first of these is a bibliography of references on hydrogen and helium and their mixtures with other substances. The second is a theoretical development of a thermodynamic consistency test applied to the data of Smith, and is discussed elsewhere in this work.

II. REVIEW OF EXPERIMENTAL METHODS

A. GENERAL

For a two component system with co-existing liquid and vapor phases the phase rule gives

$$V = C + 2 - P = 2 + 2 - 2 = 2 .$$

At fixed pressure and temperature the system is invariant, and it is completely determined if the compositions of the two phases are known.

A discussion of some commonly used methods of experimental study of vapor-liquid equilibria has been presented by Sage and Reamer;[44] however it does not include a consideration of the problems of work at low temperatures. The book by Hala, *et al.*,[47] includes an extensive discussion of experimental methods used in vapor-liquid equilibrium studies; however it gives little attention to the problems of work at low temperatures.

The surveys of Ruhemann[16] and of Bloomer and Parent[30] have been mentioned above.

The determinations to be made in phase equilibria studies are those of pressure, temperature, and composition. Methods of measuring pressure have been well established and can generally be applied to cryogenic systems without difficulty. The practical problems associated with accurate temperature and composition determinations may be summarized as follows:

1. A means of maintaining a low temperature within narrow limits and of accurately measuring the temperature.
2. A method of achieving equilibrium between the liquid and vapor.
3. A means of withdrawing samples of the liquid and vapor phases without altering the equilibrium compositions.
4. A means of analyzing the samples for composition.

Each of these problems is discussed separately below.

B. TEMPERATURE MEASUREMENT AND CONTROL

For measuring temperatures in cryogenic systems the methods of gas thermometers, vapor pressure thermometers, thermocouples, and resistance thermometers have been successfully used. Detailed discussions of the techniques of low temperature thermometry have been given by Scott,[45] White,[38] and Hudson,[46] and will not be repeated here.

In the present work the primary temperature measuring element is a platinum resistance thermometer. Secondary temperatures are measured by differential thermocouples referenced to the resistance thermometer. A complete description of this system will be found in a later section.

The means available to achieve and maintain steady low temperatures over a given range depend on the characteristics of the substances which exist as a liquid at those temperatures and below. Some of the more commonly used cryogenic fluids are methane, argon, oxygen, nitrogen, hydrogen, and helium.

In low temperature vapor-liquid equilibrium studies the most commonly used method of temperature control[30,48-50] is one in which liquid nitrogen is used in a "cold finger" to cool a bath of freon or some other low-boiling liquid. Such systems usually include an electrical heating system and an automatic temperature controller which senses any temperature change and provides the necessary heating or cooling to restore the temperature to its preset value.

A cryogenic liquid at atmospheric pressure may be used[25,33] as a primary bath fluid to obtain temperatures above its normal boiling temperature by partially insulating the equilibrium vessel from the liquid and supplying sufficient heat to maintain it at a temperature above that of the bath. Still other methods employ a loop of circulating gas which flows through the cryogenic liquid and then into a secondary liquid bath or through a coil around the equilibrium vessel.

When the temperature range of interest falls within the normal range of liquid temperatures of a cryogenic fluid, the method of vapor pressure control may be used[1,32] to maintain steady temperatures. In this case the equilibrium vessel is immersed in the boiling liquid whose temperature remains steady as long as the vapor pressure is held constant. Such a system may require a cryostat capable of withstanding considerable internal pressure; this rules out the use of conventional glass dewars.

In the present work the temperature range of interest is precisely that over which hydrogen normally exists as a liquid (13.8-32.9°K).

This limits the choice of refrigerating fluids to helium, hydrogen (and its isotopes), and neon. Of these, normal hydrogen and helium are the most practical. Although neon has a normal boiling temperature of 27.0°K and a relatively large heat of vaporization, it is not readily available in the liquid state and could not provide cooling over the entire range of interest. The isotopes of hydrogen (deuterium, hydrogen derteride, and tritium) offer no advantage over normal hydrogen and would be prohibitively expensive.

Since helium has a critical temperature of 5.2°K it could only be used with some method of back-heating or with a secondary loop of circulating helium gas. The equilibrium cell used by Roellig and Giese[33,34] in their studies of the hydrogen-helium system is cooled by a series of fins attached to the rod at the base of the cell and immersed in a bath of liquid helium.

Helium offers the convenience of being non-explosive; however its high cost and low heat of vaporization made its use in the present work impractical.

For temperatures above 20.4°K liquid hydrogen at atmospheric pressure may be used with some method of back-heating or with a secondary loop of circulating helium gas. For temperatures below the normal boiling temperature liquid hydrogen can only be used by pumping a vacuum over the bath.

By maintaining steady pressures over a bath of pure boiling liquid hydrogen, from the triple point pressure (0.07 atmospheres) to the critical pressure (12.7 atmospheres), very close temperature control can be maintained over the entire range of interest.

A vapor pressure controlled liquid hydrogen bath was selected for use in the present work after considering numerous other possibilities.

Several methods of vapor pressure control have been described by White[38] and have been used with liquid hydrogen to control temperatures to within 0.01°K. The method used in the present work is a modification of that used by Dodge and Dunbar[1] in their study of the oxygen-nitrogen system. This method was also used by Smith[32] in his study of the hydrogen-helium system. He reported temperature control to within 0.01°K.

C. METHODS OF ACHIEVING EQUILIBRIUM BETWEEN LIQUID AND VAPOR

1. Classification of Methods

Experimental methods for obtaining an equilibrium mixture of liquid and vapor at low temperatures have been classified by Ruhemann,[16] Bloomer and Parent,[30] and Hala, _et_ _al_.[47] Their classifications are similar and are as follows:

(a) Static Method

(b) Flow Method

(c) Vapor Recirculating Method; and

(d) Dew and Bubble Point Method

(a) Static Method

In the static method a vapor-liquid mixture is confined in a closed equilibrium cell and maintained at constant temperature. The mixture is agitated until equilibrium is achieved, after which samples of the equilibrium phases are withdrawn and analyzed for composition. The static method is simple and straightforward. It has been used successfully in the early work of Verschoyle[14,15] and Fedoritenko and Ruhemann,[10] and is commonly used for studies at higher temperatures.

This method was used by Roellig and Giese[33,34] in their recent study of the hydrogen-helium system. Their apparatus consisted of a glass-walled equilibrium vessel which permitted visual observation of the equilibrium mixture at all times. Agitation was provided by a vertical-action stirring mechanism consisting of several discs attached to a long shaft and operated manually from a point above the cryostat.

Ruhemann[16] states that the chief disadvantage of the static system is that equilibrium is apt to be destroyed when the samples are withdrawn, so that the resulting compositions are not those of a true equilibrium mixture.

(b) Flow Method

In the flow method a mixture of gases of fixed composition is cooled as it flows through a series of coils and into the equilibrium cell, all of which are maintained at the equilibrium temperature. The coils are so arranged that all condensate flows into the equilibrium cell where it accumulates and is periodically sampled. The vapor flows out in a continuous stream.

Sampling is convenient when using the flow system, as there is no upsetting of the equilibrium pressure as the samples are withdrawn. If suitable analysis equipment is available, either the vapor or the liquid, or both, may be continuously analyzed.

The disadvantages of this system are that one is never sure whether equilibrium is achieved, and unless a windowed cell is used it is difficult to determine the quantity of liquid present and to prevent swamping of the cell.

This method was used in some early work by Ruhemann[10-12,51] and others, and more recently by Brandt, *et al.*[39,25] It is also used frequently in solid-vapor equilibrium studies.

(c) Vapor Recirculating Method

In the vapor recirculating method the equilibrium vessel is connected to a closed loop of tubing, some of which may be at room temperature, through which the vapor is continuously withdrawn from the top of the equilibrium vessel and bubbled through the liquid at the bottom. The continuous flow of small bubbles through the liquid serves to bring the two phases into intimate contact and to agitate the liquid.

This method was prefected by Dodge and Dunbar[1] and has been frequently used[43,48,50] in recent years. Ruhemann[16] describes it as the most accurate and reliable of all existing methods, but points out that it requires rather elaborate equipment.

Its chief advantages are that equilibrium is certain to be achieved through continuous recirculation, and, if properly designed, it brings the mixture to equilibrium rapidly.

A portion of the equilibrium vapor may be isolated in the external portion of the loop and sampled at room temperature, without lowering the pressure over the liquid in the equilibrium cell. The liquid sample must be withdrawn from the equilibrium cell.

This method was used by Smith[32] in his study of the hydrogen-helium system. He reported that approximately 1-1/2 to 2 hr were required to reach equilibrium under fixed conditions; however he did not indicate the volume of the external circulating loop or the flow rate of the vapor.

A vapor recirculating system similar to that used by Smith, but with several modifications, was selected for use in the present work.

(d) Dew and Bubble Point Method

In the dew and bubble point method a gas of accurately known composition is charged slowly into an equilibrium vessel maintained at constant temperature. The pressure at which this mixture first begins to condense is observed and provides a point on the dew point curve for mixtures of that composition. In practice the dew point pressure is obtained by visual observation of the first formation of liquid droplets, or by charging in metered increments of gas and plotting a graph of total amount of gas vs. total pressure. A sharp break in the curve will occur at the dew point. If additional gas is added, the equilibrium cell will eventually become filled with liquid and upon further addition the pressure will rise sharply, causing a second break to appear in the graph described above. The pressure in the system as the last bubble of vapor disappears defines a point on the bubble point curve (saturated liquid curve) for mixtures of that composition. This method has been used by Bloomer and Parent[30] and by Gore, _et_ _al_.[49]

The chief advantage of this method is that it eliminates the need for the withdrawal and analysis of samples of the equilibrium phases, since all necessary data can be obtained from cross-plots of the dew and bubble point data for mixtures of known composition. This is a very significant advantage since it is often difficult to obtain representative samples of two co-existing phases without upsetting the equilibrium.

In order to obtain accurate results it is necessary to observe the contents of the equilibrium vessel so that the dew and bubble points may be exactly determined. Even then it must be done with great care.

For work at low temperatures and high pressures the use of glass in the system presents some difficult practical problems, especially where the substances used are highly flammable.

D. SAMPLING

1. General

Unless the dew and bubble point method is used, samples of the two co-existing phases must be withdrawn and analyzed for composition. The sampling of the vapor phase presents no particular problems since the composition of the gas is not likely to change as the sample is withdrawn.

The liquid phase will generally consist of two or more components of differing volatilities, all of which exist as gases at room temperature. The problem is one of insuring that the composition is not altered as the sample is withdrawn and vaporized to a gas at room temperature.

2. Batch Method

Two different methods of liquid sampling have been used successfully in low temperature vapor-liquid equilibrium studies. In the frist method a small closed volume, with a valve at each end, is attached to the equilibrium cell in the cold portion of the equipment (see Fig. 1). Valve A is first opened, the volume is evacuated, and valve A is closed; valve B is then opened and the small volume fills with liquid from the equilibrium cell. Valve B is then closed and valve A opened, allowing the trapped liquid sample to vaporize into a large expansion volume, from which samples are later withdrawn. Since the small volume is at the equilibrium temperature, it may be necessary to warm it slightly to insure that all of the liquid evaporates.

This method of sampling was used in both of the previous investigations of the hydrogen-helium system. Both Smith,[32] and Roellig and

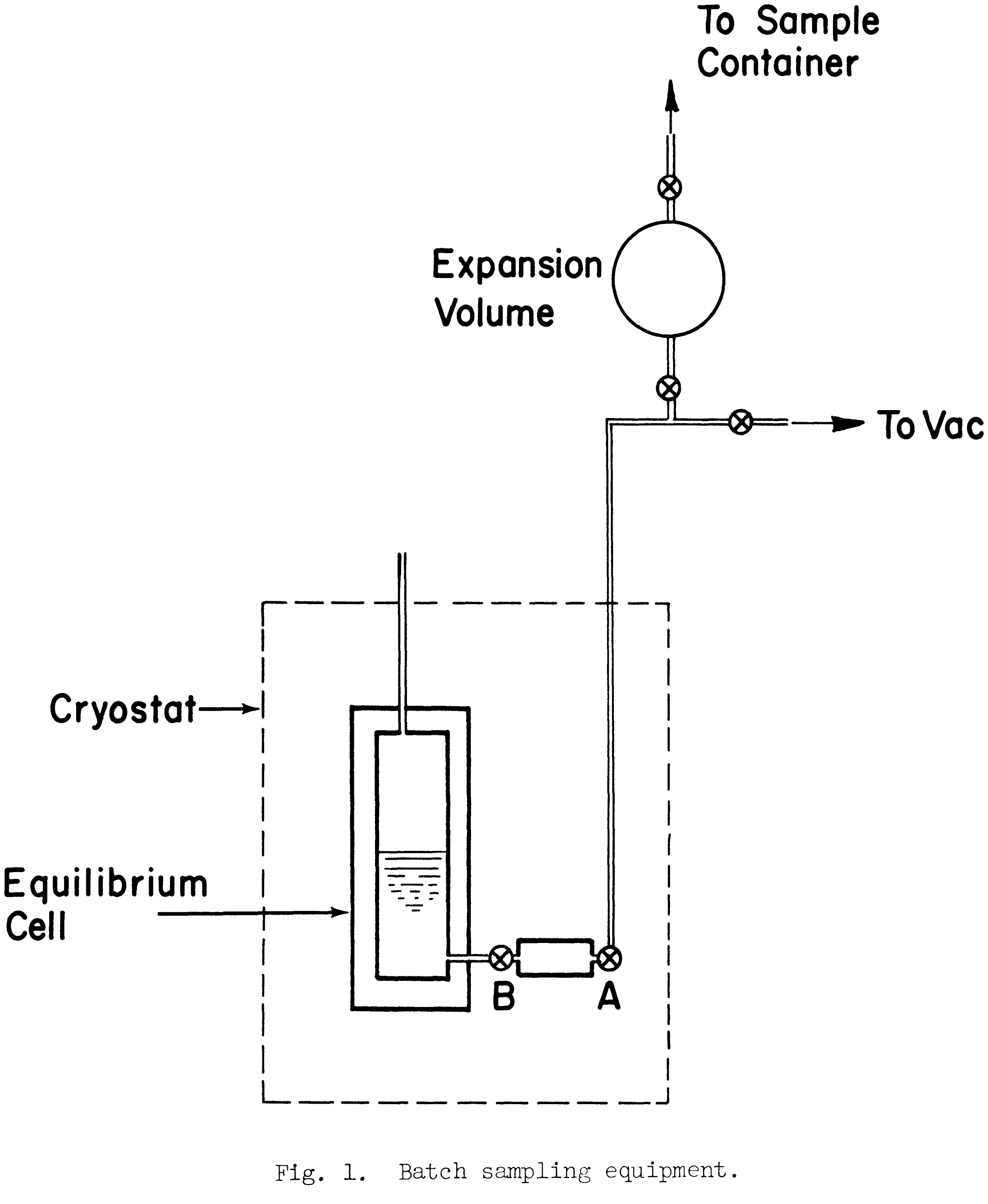


Fig. 1. Batch sampling equipment.

Giese[33] reported some difficulties with their sampling apparatus. Smith eventually obtained satisfactory results, while the apparent discrepancies in the data of Roellig and Giese are due, in part, to their problems with liquid sampling.

The batch method requires a rather elaborate set of valves which must operate satisfactorily at very low temperatures and provide a tight seal under both vacuum and pressure; also the long control rods extending into the liquid bath may introduce a significant heat leak. The procedure is cumbersome and time-consuming, and great care must be taken if accurate results are to be obtained.

3. Continuous Flow Method

The second type of liquid sampling device consists of a capillary tube, through which the liquid is withdrawn at a very low rate of flow. As the liquid flows into the warm portion of the capillary, it vaporizes and flows directly into a previously evacuated sample container. If the capillary is properly sized as to inside diameter and length, it is possible to obtain a very steady, low volume rate of flow, although the velocity of flow inside the capillary may be quite high. Under these conditions an equilibrium is quickly established and the high velocity of flow precludes any accumulation of one component as a result of fractionation.

This method was selected for use in the present work. A complete description of the equipment used will be found in a later section.

E. GAS ANALYSIS

Once representative samples of the equilibrium liquid and vapor have been obtained they may be analyzed by any suitable means, depending on the nature of the component gases. Gas chromatography and mass spectrometry are among the methods more commonly used.

Samples taken in the present work were analyzed by means of a mass spectrometer.

III. EXPERIMENTAL EQUIPMENT

A. GENERAL

Because of the difficulties inherent in carrying out experimental studies at liquid hydrogen temperatures, and because of the problems encountered by Smith,[32] and by Roellig and Giese[33] in previous investigations of the hydrogen-helium system, a careful study was made of experimental methods and equipment that have been used successfully in the past in low temperature vapor-liquid equilibrium work. Many different designs were considered, and the one finally selected includes modifications of equipment used successfully by other investigators as well as some new features which have not been previously employed.

A schematic diagram of the experimental equipment is shown in Fig. 2; a photograph of the control panel appears in Fig. 3. The basic design was taken from Dodge and Dunbar,[1] and consists of a vapor-recirculating equilibrium system with a vapor pressure controlled liquid hydrogen bath. The equipment as shown in the diagram of Fig. 2 falls into four main sections: (1) the cryostat, (2) the vapor-recirculating system, (3) the sampling system, and (4) the vapor pressure control system. Each of these sections will be discussed separately below.

Auxillary sections of the equipment include the charging system for the circulation loop, liquid nitrogen supply system, vacuum system, and vent system.

The experimental apparatus was assembled on a framework of Uni-

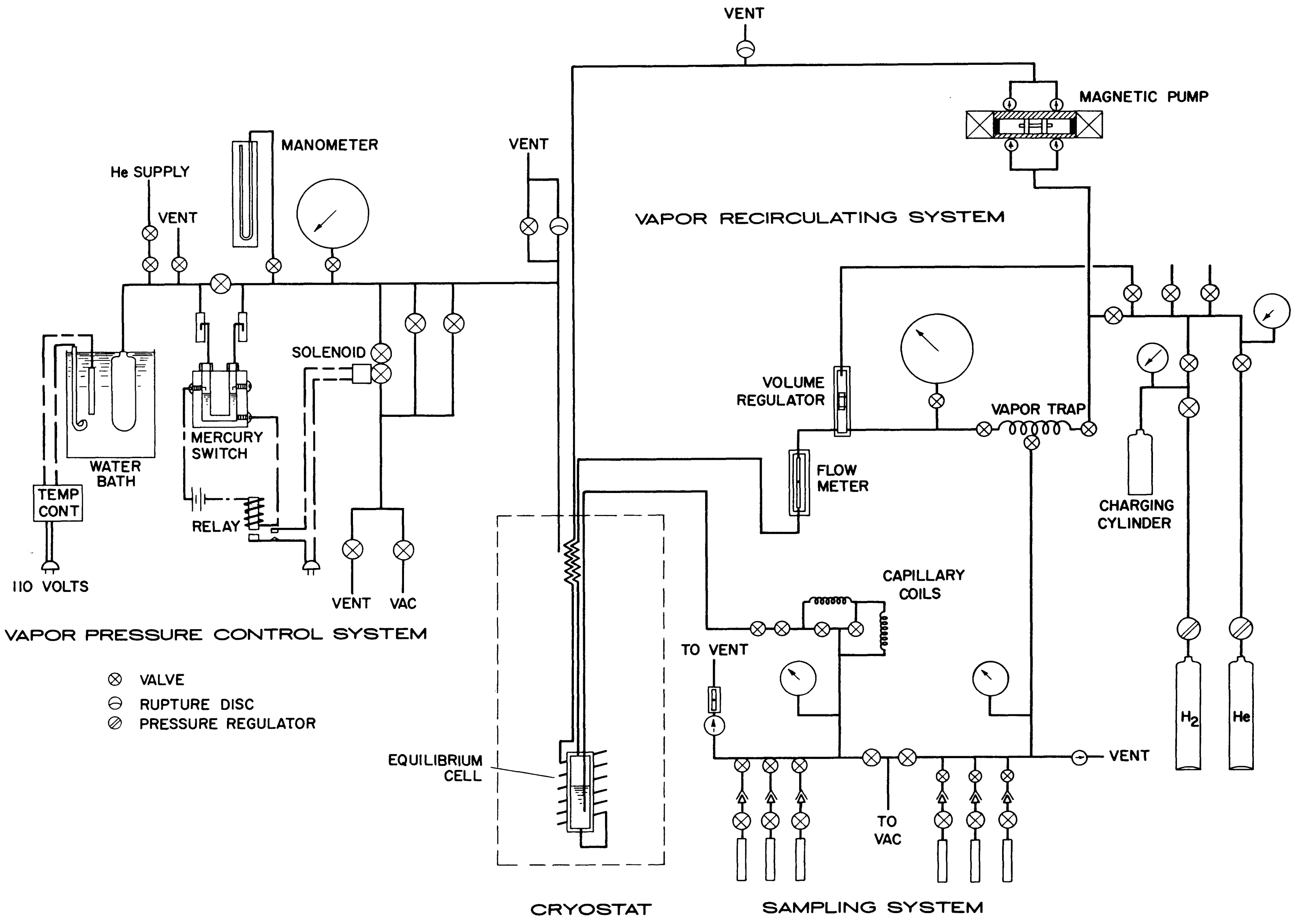


Fig. 2. Schematic diagram of experimental equipment.

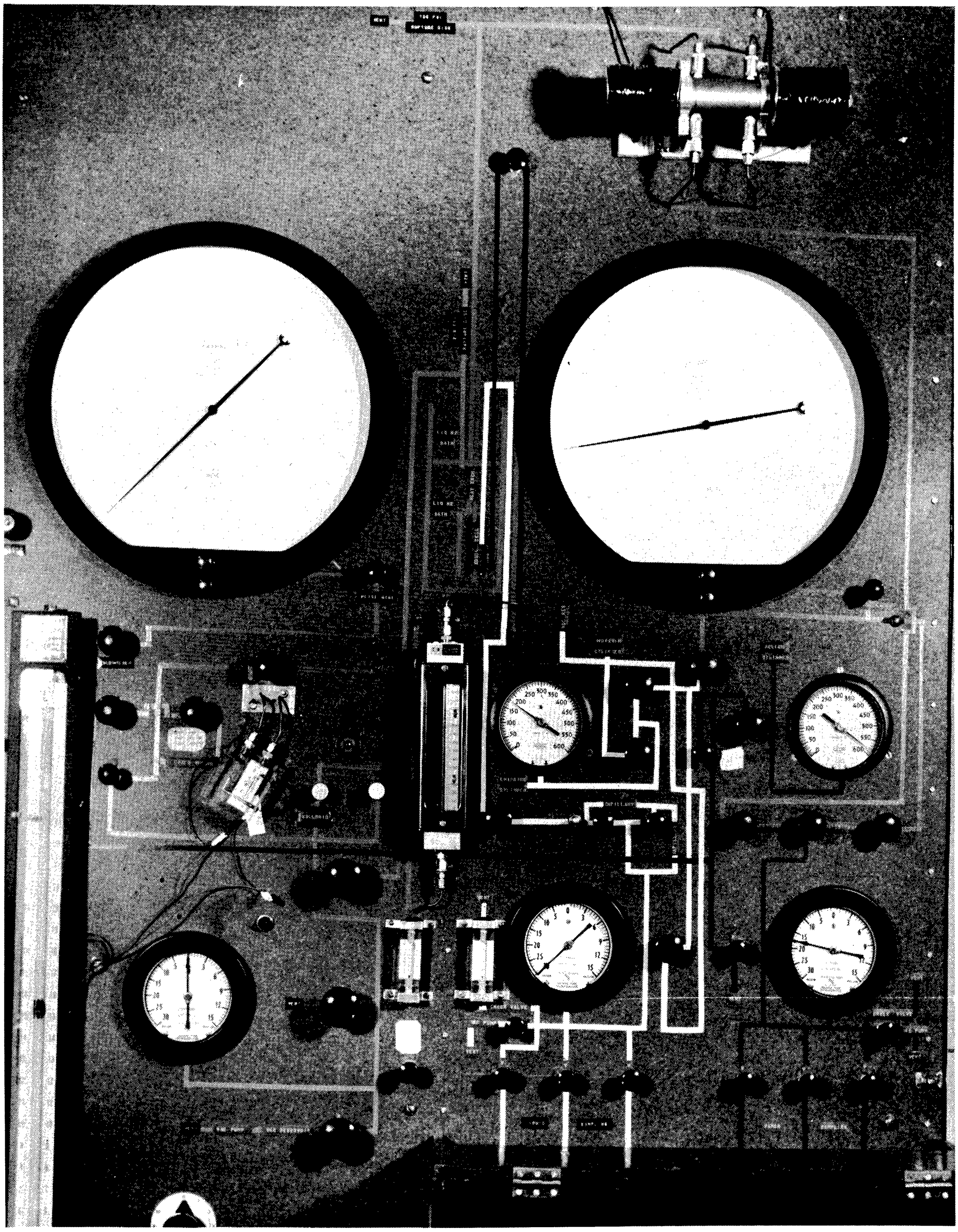


Fig. 3. View of control panel.

strut steel channels, using a sheet of quarter inch Masonite paneling for mounting the valves, gages, and other controls. The sides and back of the framework are partially covered and the top is fitted with an exhaust hood.

B. CRYOSTAT

Because of its low temperature and relatively small heat of vaporization (7500 cal/ℓ at 20.4°K), liquid hydrogen cannot be efficiently stored in conventional vacuum insulated double-walled dewards of the type used for liquid nitrogen and other higher boiling cryogenic liquids. In the past the conventional liquid hydrogen storage vessel has employed an outer jacket of liquid nitrogen in a separate vacuum insulated container. More recently the development of multiple-layer insulation,[53-56] often called "super-insulation," has made possible the construction of efficient storage vessels for liquid hydrogen without the use of nitrogen shielding. This type of insulation was chosen for the cryostat used in the present work because of the simplification it permitted in design and construction.

A cutaway drawing of the cryostat with the equilibrium cell in place is shown in Fig. 4. A view with the outer insulation partially removed is shown in Fig. 5, and the completed unit is shown in Fig. 6, with the vacuum insulated transfer line and liquid hydrogen dewar in position for filling.

Since vapor pressure control is used to maintain steady tempera-

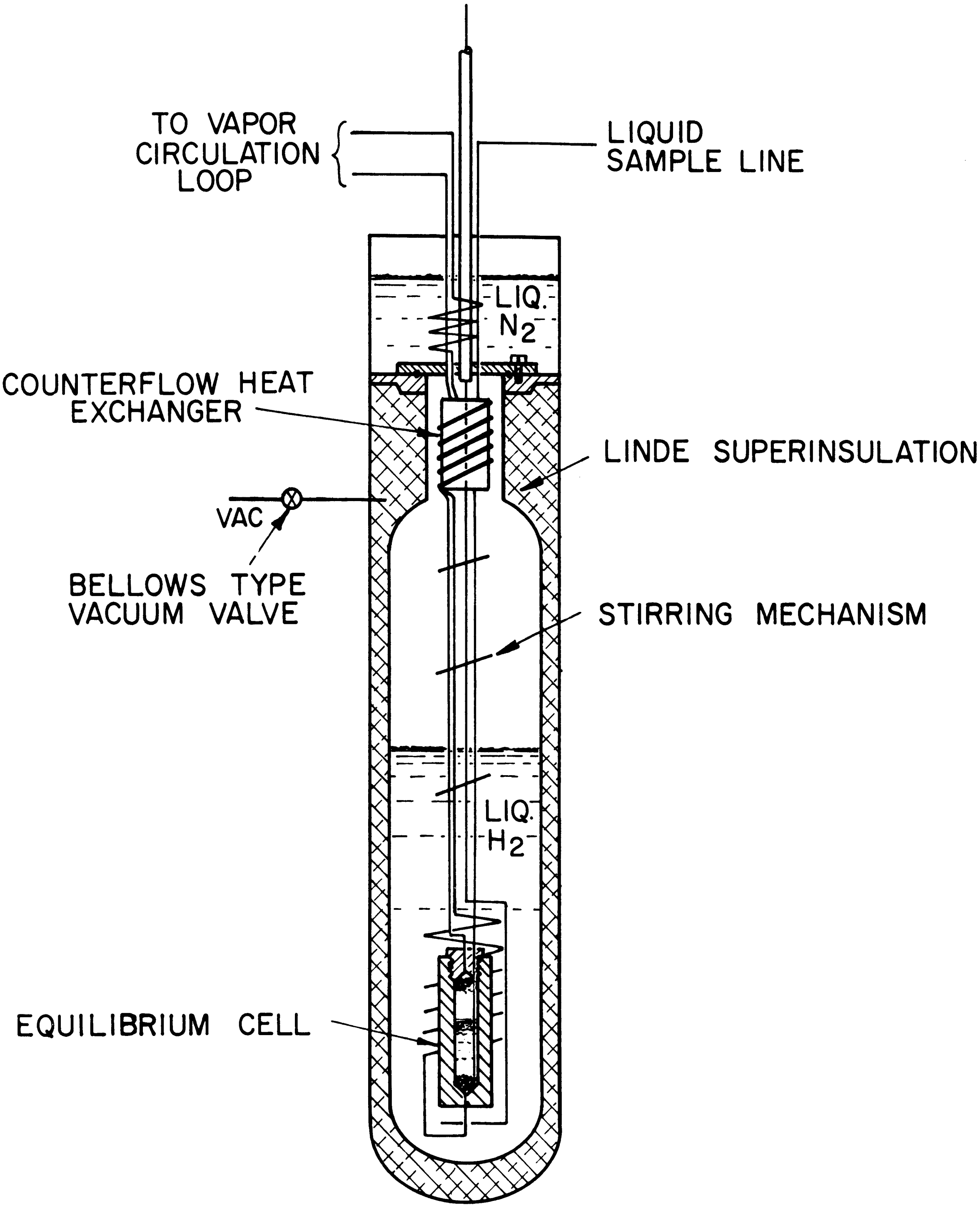


Fig. 4. Section through cryostat showing equilibrium cell.

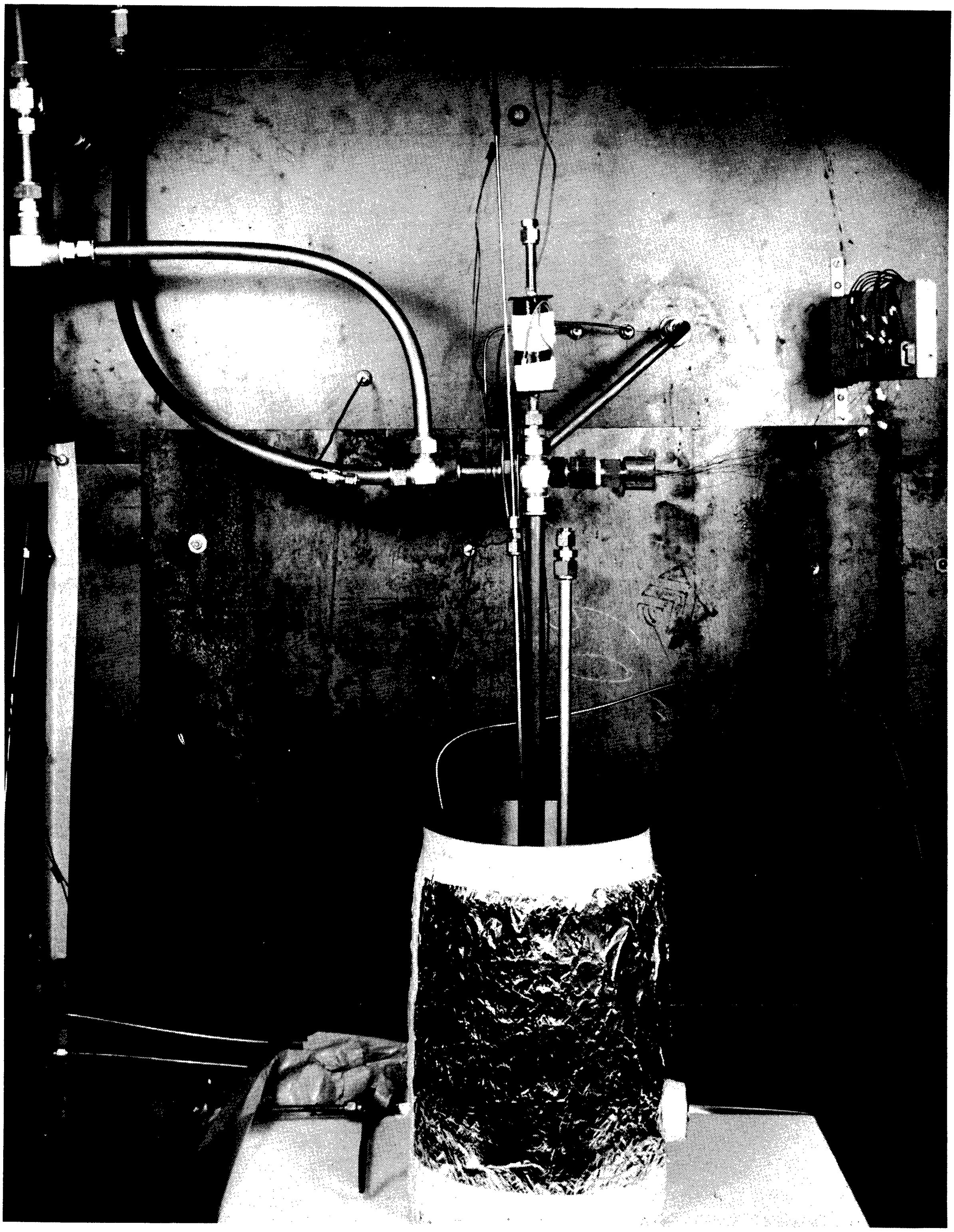


Fig. 5. View of cryostat with outer insulation partially removed.

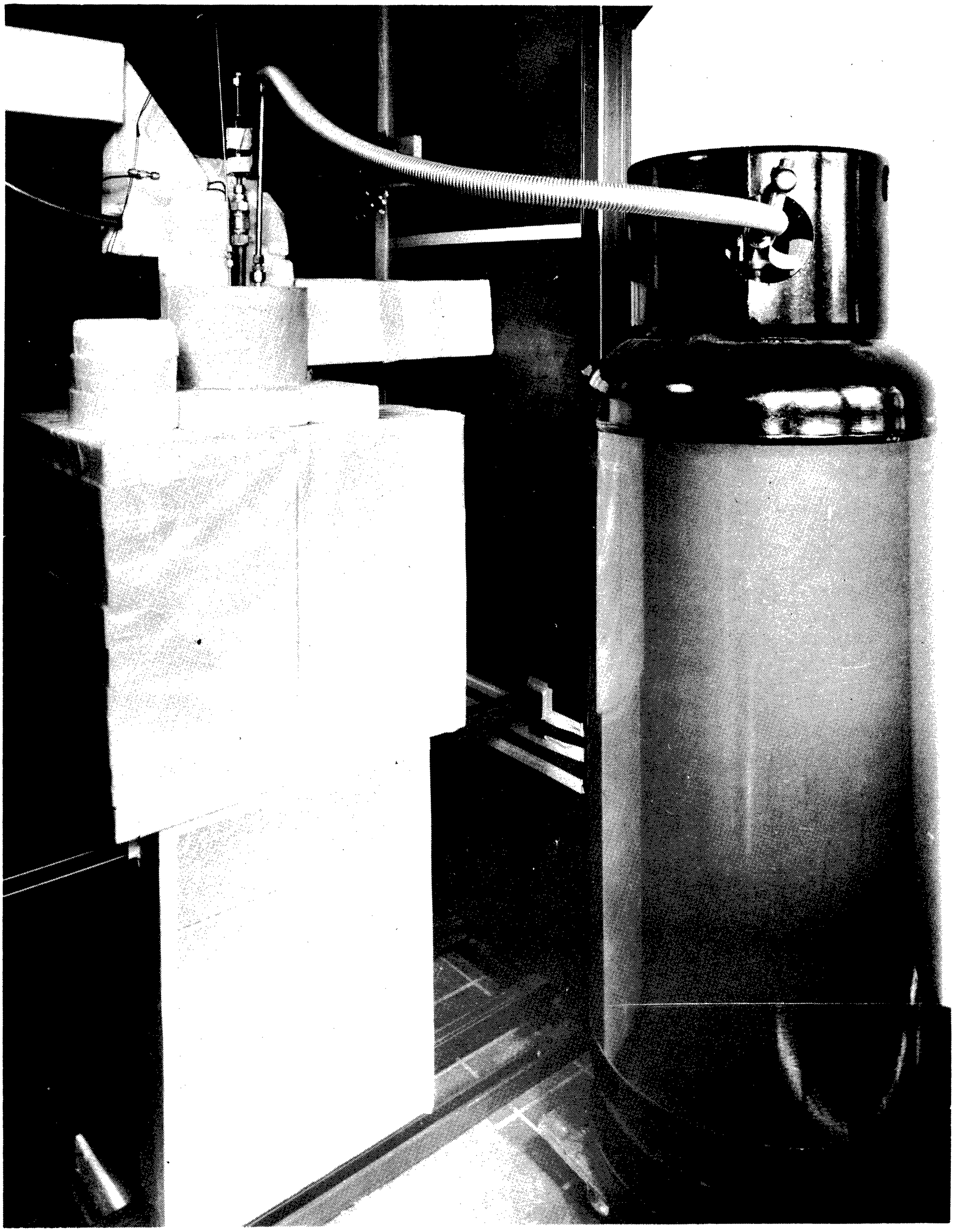


Fig. 6. View of cryostat and liquid hydrogen deward during filling.

tures, the cryostat is designed for internal working pressures up to 200 psi.

The inner and outer vessels of the cryostat are made of standard schedule five stainless steel pipe (wall thickness 0.108 in.) with standard butt-weld pipe caps for the end pieces. The inner vessel, constructed from 6 in. pipe, is suspended from the lower flange by a short length of 3 in. pipe to reduce the heat flow down the neck. The lower end of this 3 in. neck is welded into a hole cut into a 6 in. pipe cap which forms the upper part of the inner vessel.

The lower and upper flanges are machined from 3/4 and 1/2 in. thick stainless steel plate respectively. The outer edge of the lower flange is machined down to a 3/8 in. thickness to reduce the heat flow into the neck from the outer jacket. A United Aircraft Products teflon-coated stainless steel O-ring is used to seal the top flange.

Type 304 stainless steel is used throughout, including in the O-ring and flange bolts, to eliminate problems of differential contraction upon cooling.

In the assembly of the cryostat all joints are heliarc welded, with the exception of the tubes which pass through the top flange and the vacuum outlet on the outer jacket which are silver soldered.

The inner vessel was constructed first and welded to the lower flange. It was then wrapped with approximately 0.8 in. of Linde SI-4 multiple-layer insulation, and welded into the outer jacket with the final weld being made at the outer edge of the lower flange. A short length of 8 in. pipe was welded to the top of the vessel to provide a reservoir for liquid nitrogen which serves to further reduce the heat flow down the neck and to precool the circulating vapor before it reenters the cryostat.

The cryostat was fabricated to the author's design at the laboratories of the Linde Co., Tonawanda, New York. The inner vessel was pressure tested to 500 lb and both the inner vessel and the insulating space were helium leak tested.

During the installation of the cryostat the upper half of the outer vessel was wrapped with approximately 1 in. of fiberglass insulation which was covered with aluminum foil (see Fig. 5) and sealed to the vessel with plastic tape. This serves to prevent air from flowing between the insulation and the cryostat, where there would be a danger of oxygen condensing around the liquid nitrogen reservoir at the top. Approximately 6 in. of Styrofoam insulation in the form of 2 in. thick sheets was then placed around the outside of the vessel and pressed tightly around the foil-covered fiberglass, providing a seal to keep out air. The Styrofoam was then covered with a thick sheet of clear plastic (see Fig. 6). The lower half of the cryostat was wrapped with several inches of fiberglass insulation and covered with 1 in. thick sheets of Styrofoam.

For maximum efficiency the multiple-layer insulation space must be evacuated to a pressure of 0.1 micron or less. In practice it is not necessary to pump the jacket down to this pressure, since air remaining in the insulating space will condense on the outside of the inner vessel when it is filled with liquid hydrogen. In the present work the insulating space was evacuated and purged several times with carbon dioxide, and then pumped to a pressure of a few microns with a mechanical vacuum pump. This was done so that the necessary low pressure would be produced when liquid nitrogen is transferred into the cryostat to precool it. Solid carbon dioxide has a negligibly small vapor pressure at liquid nitrogen temperature. This method of condensing vacuum insulation, using carbon dioxide, has been studied by Van Gundy, et al.,[57] and found to be highly effective with multiple-layer insulation.

The completed vessel (see Fig. 6) is very compact and proved to be highly efficient. During operation it was found that liquid hydrogen was boiled off at a rate of about one liter in 6 hr, which represents a total heat leak of approximately 1200 cal/hr. This is very close to the heat leak that was calculated when the vessel was designed.

A schematic drawing of the top flange assembly is shown in Fig. 7, and a photograph in Fig. 8. A 3/4 in. O.D. copper tube is silver soldered into the center of the flange and serves as the outlet for the boil-off from the hydrogen bath. The large diameter tubing is used to allow sufficient flow area for venting the hydrogen vapor from the cryostat in case of a rupture in the outer jacket. In this event air would condense on the outside of the inner vessel, causing rapid vaporization of the contents and leading to a dangerous pressure increase unless a sufficiently large vent line is provided.

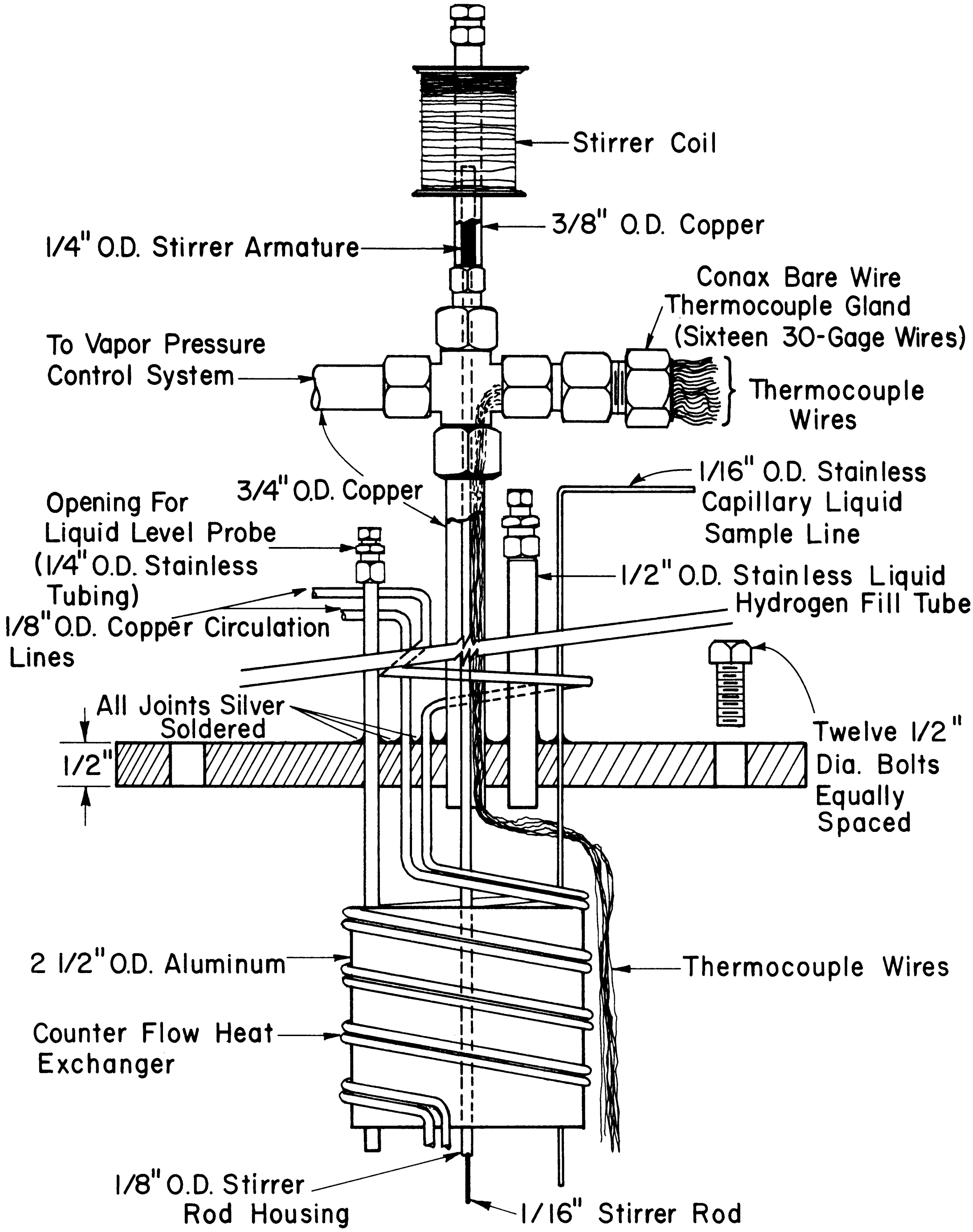


Fig. 7. Schematic drawing of top flange assembly.

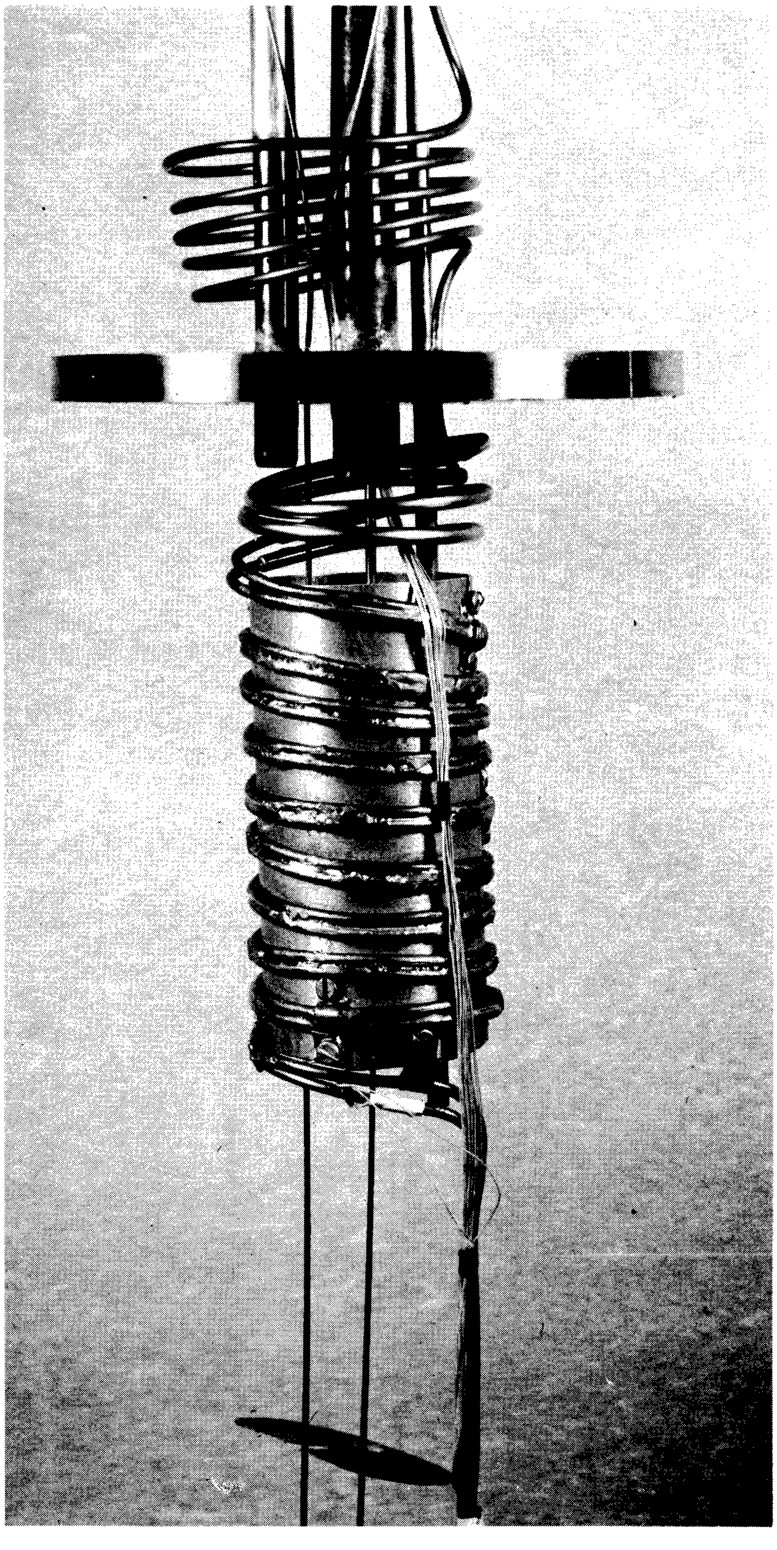


Fig. 8. View of top flange assembly and counterflow heat exchanger.

A solenoid-actuated vertical acting stirring mechanism for stirring the bath liquid passes through the center of this 3/4 in. tube. It consists of a 1/16 in. diam stainless steel rod with a 1/8 in. O.D. stainless steel housing. The housing extends to just below the neck of the inner vessel while the 1/16 in. rod runs all the way to the base of the cryostat. Stirring is produced by four circular copper discs soldered to the rod at an angle of about 30° from the horizontal. These discs may be seen in Figs. 8 and 11.

The armature of the solenoid is a 4 in. length of 1/4 in. iron rod soldered to the top of the 1/16 in. rod. It is enclosed in a length of 3/8 in. O.D. copper tubing which is attached to the outlet line of the cryostat with standard tube fittings. The solenoid coil is wound on the outside of this 3/8 in. tubing.

A mechanical-electrical timing circuit actuates the solenoid at intervals of several seconds, raising the stirrer about 3/4 of an inch; the solenoid is deactivated after about 2 sec and the stirrer falls back under its own weight. The pulsing circuit is described in a later section.

The annular space between the stirrer rod housing and the 3/4 in. tube also serves as a passage through which the thermocouple wires and resistance thermometer leads are brought out of the cryostat. They are brought out of the tube at a point above the cryostat through a bare wire thermocouple gland containing a teflon sealant.

A 1/2 in. O.D. stainless steel tube is silver soldered into the top flange and serves as an opening for inserting the vacuum insulated transfer line from the hydrogen storage dewar (see Fig. 6). The upper end of this tube is fitted with a 1/2 x 3/8 in. stainless steel Swagelok reducing union which is bored through to receive the 3/8 in. outer jacket of the transfer line. When inserted, the transfer line extends to a point in the neck of the inner vessel and is sealed at the reducing union by the 3/8 in. Swagelok fitting, using a teflon ferrule.

This method of inserting and sealing the transfer line proved very satisfactory. It is possible to evacuate the cryostat and transfer line up to the valve on the storage dewar after the transfer line has been inserted. After the cryostat is filled the transfer line is withdrawn and the opening is sealed off with a threaded cap which fits the 3/8 in. end of the union.

A 1/4 in. stainless steel tube is silver soldered into the top flange and extends to a point just below the neck; it serves as an opening for inserting a liquid level probe which is described later.

The remaining lines passing through the top flange are the vapor recirculating lines and the liquid sampling line. These are described below.

C. VAPOR RECIRCULATING SYSTEM

1. General

The vapor recirculating system (see Fig. 9) includes the equilib-

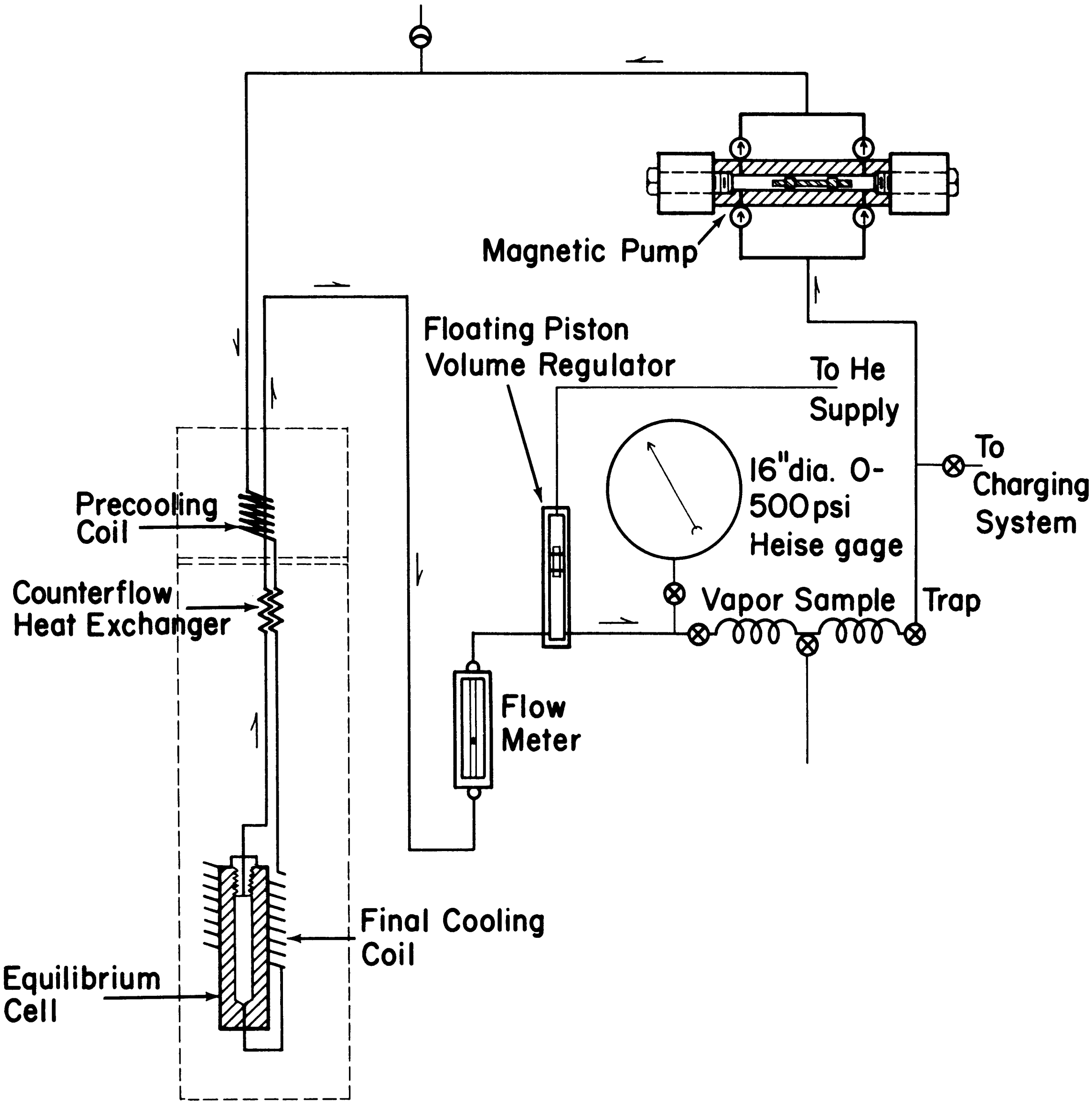


Fig. 9. Schematic diagram of vapor recirculating system.

rium cell, counterflow heat exchanger, volume regulator, vapor sample trap, magnetic pump, pressure gage, flow meter, and associated valves and tubing. One eighth inch O.D. copper tubing connects the different parts of the loop. The internal volume of the loop has been kept as small as possible so that the total amount of vapor in the loop can be recirculated in a minimum of time. The total volume of the loop, including the equilibrium cell, is estimated to be 180 cc.

2. Equilibrium Cell

The equilibrium cell (Figs. 10 and 11) was machined from a 2-1/2 in. O.D. bar of free-machining copper. It is drilled to an inside diameter of 1 in. and fitted with a screwed cap at the top; giving it an internal volume of about 55 cc. Short lengths of 1/8 in. and 3/16 in. tubing are silver soldered directly to the cell and serve as openings for inserting the 1/16 in. liquid sample line and the 1/8 in. vapor circulating lines. This allows the final soldered joint to be made along the tubing and permits disassembly and reassembly without heating the entire equilibrium cell. Before the final connections were made, the cap was screwed on and sealed around the top with soft solder.

Small lumps of copper wool were placed inside the equilibrium cell at the top and bottom. At the bottom this serves to break up the vapor bubbles as they enter, and at the top it helps to prevent liquid droplets from being carried out with the vapor.

The liquid sampling line, a 1/16 in. O.D. x 0.004 in. I.D. stainless steel capillary line, passes through the cap of the cell and reaches

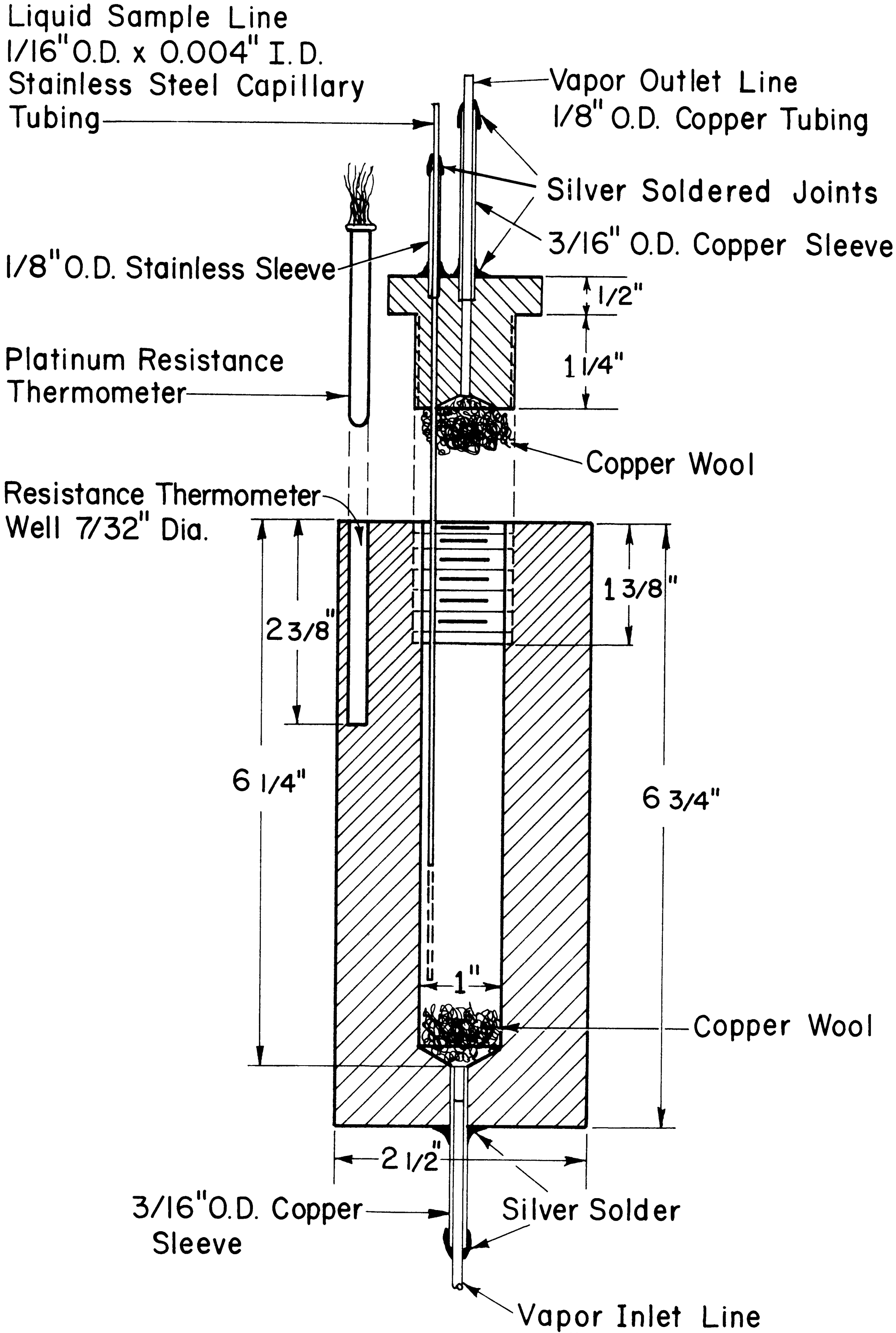


Fig. 10. Equilibrium cell.

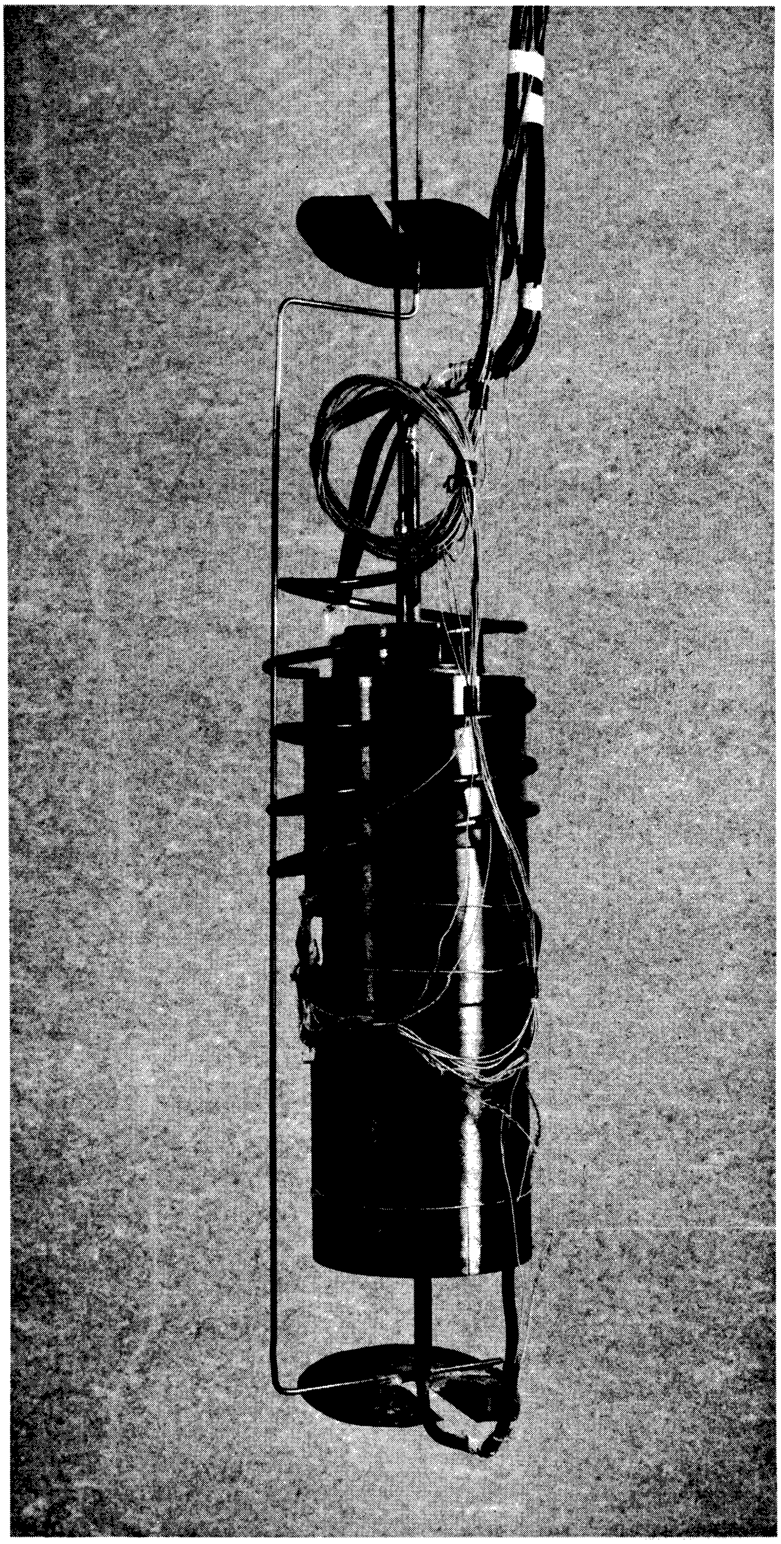


Fig. 11. View of equilibrium cell assembly.

a point just above the copper wool at the bottom. This line was silver soldered to the top flange of the cryostat where it passes through and serves as the primary support for the equilibrium cell itself.

The 1/8 in. copper tube carrying the incoming vapor is coiled around the equilibrium cell for about five turns, providing a sufficient length to insure that the return vapor is cooled to the bath temperature before it re-enters the equilibrium cell. A coil is also provided in this line at the nitrogen reservoir on top of the cryostat to precool the vapor and reduce the heat load brought about by the reciculation.

The incoming and outgoing vapor lines are wound together on a short length of 2-1/2 in. O.D. aluminum tubing to form a helical counterflow heat exchanger in the neck of the cryostat (see Fig. 8). A cover is placed over the bottom of the aluminum tubing to force the boil-off from the hydrogen bath to flow through the annular space between the neck and the heat exchanger, further reducing the heat carried in by the incoming vapor.

To keep the heat flow down the copper tubes to a minimum, a 6 in. length of stainless steel tubing has been silver soldered into each line just below the flange (see Fig. 8).

As the recirculating vapor flows out of the cryostat it passes first through a small flow meter which serves primarily to indicate whether the magnetic pump is operating and circulating the vapor at the desired rate.

3. Volume Regulator

After leaving the flow meter the vapor flows through a floating-piston volume regulator (Fig. 12). This device is connected to the circulation loop at one end, while the other end is connected, through a length of fine capillary tubing, to valves which open either to the vent or to the high pressure helium supply. By slowly withdrawing or admitting helium gas through the capillary tubing the floating piston can be moved backward or forward, causing a small change in the pressure inside the circulation loop, without changing the total composition of its contents. It is used to make slight adjustments in pressure as the mixture approaches equilibrium, and to maintain the pressure in the loop constant as the liquid sample is withdrawn.

4. Vapor Sample Trap

The vapor flows from the volume regulator to the vapor sample trap which is made of two tightly would coils of 1/4 in. copper tubing (see Fig. 16). The two coils are connected to a tee in the center, which is in turn screwed on to the inlet of the vapor sample valve A. This arrangement provides a minimum of dead space between the flow path of the gas in the loop and the valve port; this space is further reduced by inserting a copper bushing in the valve inlet. The reduced dead space is desirable as it will contain gas which is not recirculated and does not have the equilibrium composition. The valves D and E on the outside ends of the coils serve to isolate a portion of the vapor and

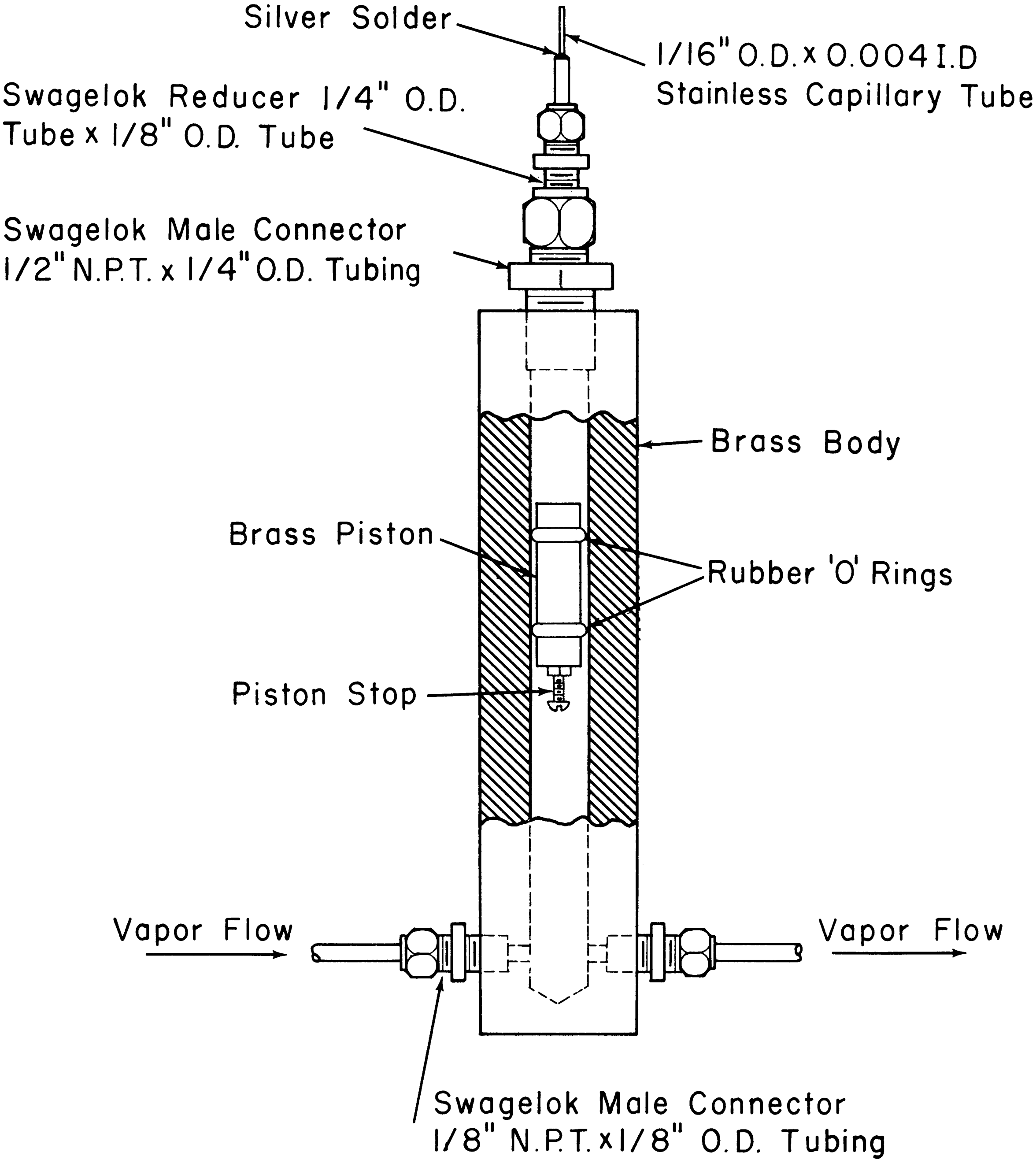


Fig. 12. Floating piston volume regulator.

permit the sample to be withdrawn without reducing the pressure in the equilibrium cell. The small diameter capillary tubing between A and B throttles the flow of vapor as the sample is withdrawn.

5. Magnetic Pump

To circulate the vapor within the loop a magnetically operated, double-acting pump has been constructed, based on a design by Sterner.[52] The completed pump is shown in Fig. 13, while a schematic diagram is shown in Fig. 9. The body of the pump was machined from a 1-1/2 in. diam round brass bar. The inside is drilled to a diameter of 3/8 in. and the ends threaded to receive the steel rods on which the coils are wound. Four small check valves with 1/8 in. pipe threads are screwed into the body as shown in the figure. The piston in the pump is made from a teflon-coated magnetic stirring bar of the type used by chemists to stir mixtures enclosed in glass vessels. Two sleeves, having diameters slightly less than that of the cylinder, are machined on the teflon, and serve as a seal for the piston. The steel rods on which the coils are wound are sealed to the body with aluminum gaskets.

The mechanical-electrical pulsing circuit for the electromagnets is built around a small d-c servomotor and cam operated switch which alternately changes the direction of current flow in the electromagnets, causing the piston to move rapidly back and forth. The resulting pumping action can be inferred from the arrangement of the check valves. The mechanical-electrical pulsing circuit is described in detail in a later section.

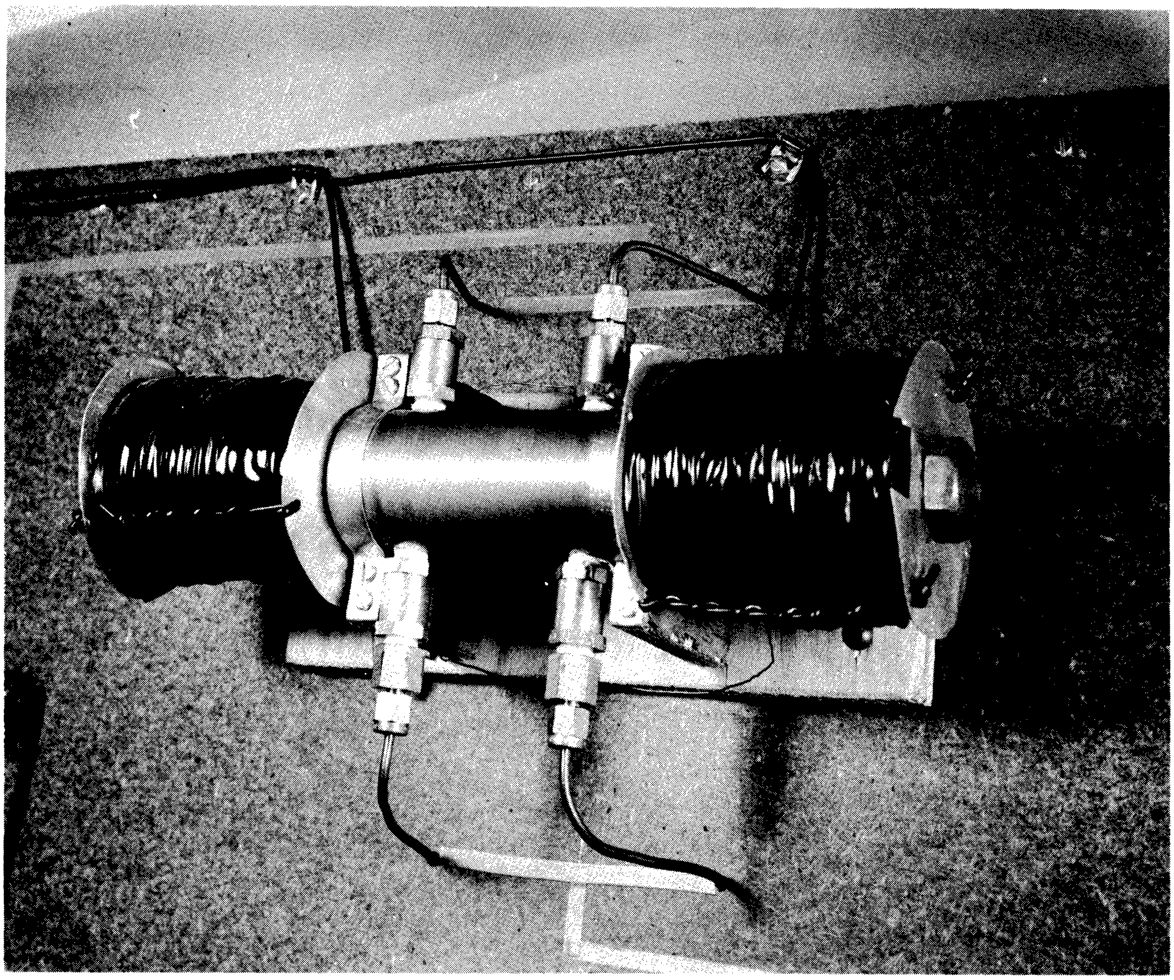


Fig. 13. View of magnetic pump.

The current flow in the electromagnets is reversed about four times per second. With a piston travel of about 1/2 in. this provides a volume flow rate of between 200 and 300 cc/min at the pump. This rate is sufficient to circulate all of the vapor in the loop in a period of several minutes and insures a rapid approach to equilibrium.

The pump performance is independent of the pressure within the loop. The pump has been used at pressures up to 500 psia; however its maximum pressure is limited only by the strength of the materials of which it is constructed. The teflon piston is self-lubricating and there are no external seals so that no substances are present to contaminate the vapor as it flows through the pump.

It has been run for a total of 300 hr or more without breakdown, and shows no signs of piston wear.

6. Charging System

Standard high pressure cylinders of hydrogen and helium gas are used to charge the circulation loop. The liquid hydrogen which forms part of the vapor-liquid mixture is condensed into the equilibrium cell by admitting pure hydrogen gas after the cell has been cooled. The quantity of hydrogen charged into the loop is estimated from the pressure drop in a 1500 cc charging cylinder included in the charging system. The charging system is connected through a valve to the vacuum system so that the charging lines and circulation loop may be evacuated before hydrogen is added.

D. TEMPERATURE CONTROL SYSTEM

1. General

Steady temperatures over the entire range of interest are obtained by controlling the vapor pressure of a bath of pure liquid hydrogen. A schematic diagram of the vapor pressure control system is shown in Fig. 14, and the controls on the front panel are shown in Fig. 15. A further description of the electrical circuit is contained in a later section.

The pressure in the cryostat is held constant by balancing it against an artificial atmosphere contained in a closed volume V (Fig. 14) maintained at constant temperature in a water bath. The pressure is balanced automatically by a solenoid valve K operated by a mercury switch S in the form of a U-tube. The mercury switch is machined from a 1 in. thick block of Plexiglas; it can be seen in Fig. 15. The mercury passages are 1/8 in. diam and the electrical contacts are provided by three No. 10-32 machine screws with small wires soldered into the tip and projecting into the mercury passages. For the contact which is made and broken frequently, platinum wire is used; it has been found that the mercury wets copper wire, causing erratic functioning at the point of contact. Small tube fittings with O-ring seals are used to seal the copper tubing to the Plexiglas.

The relay operated by the mercury switch is powered by a six volt dry cell, and it was found that a small discharge occurred at the mercury contact when the switch opened and closed. This has been min-

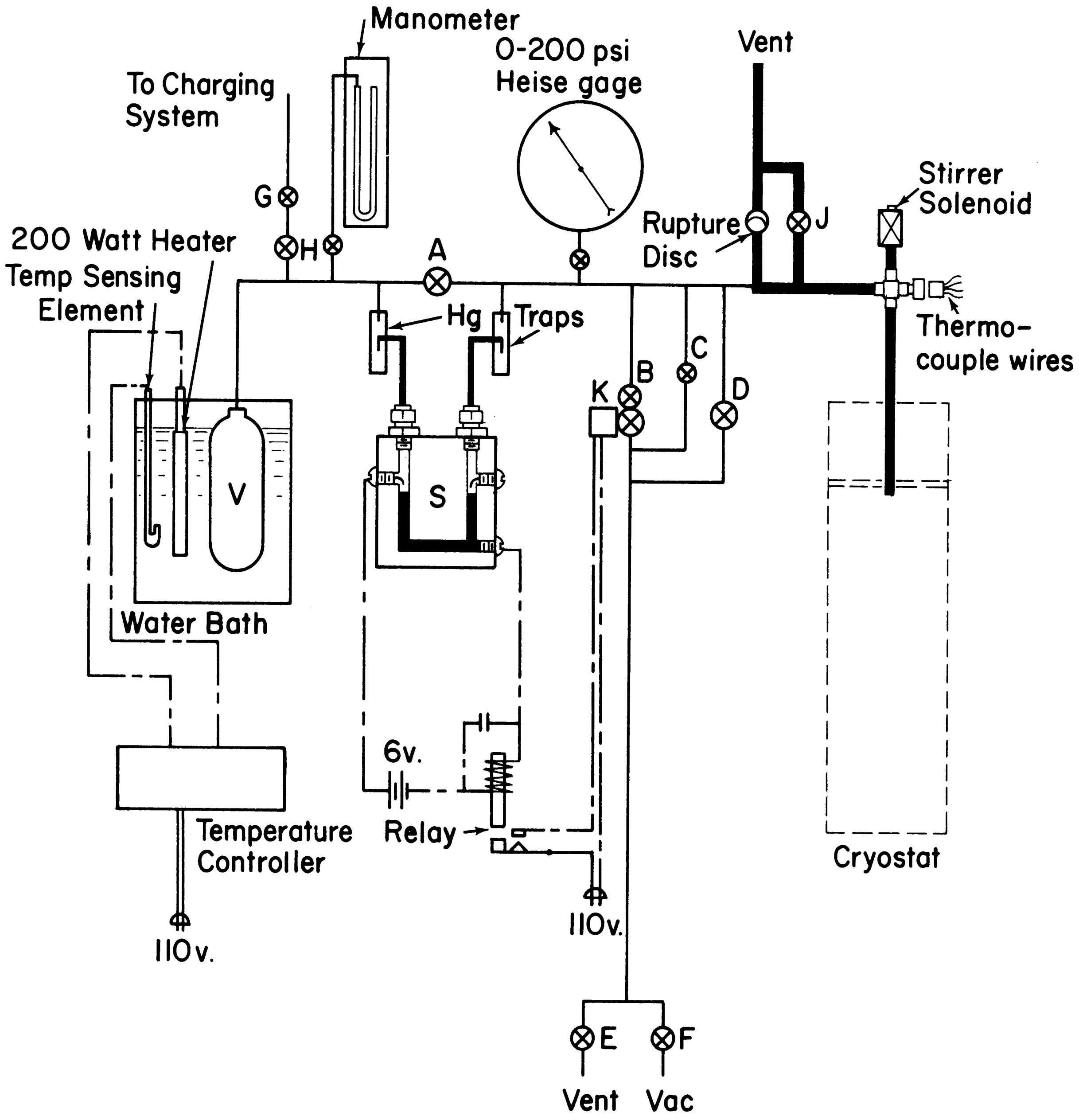


Fig. 14. Schematic diagram of vapor pressure control system.

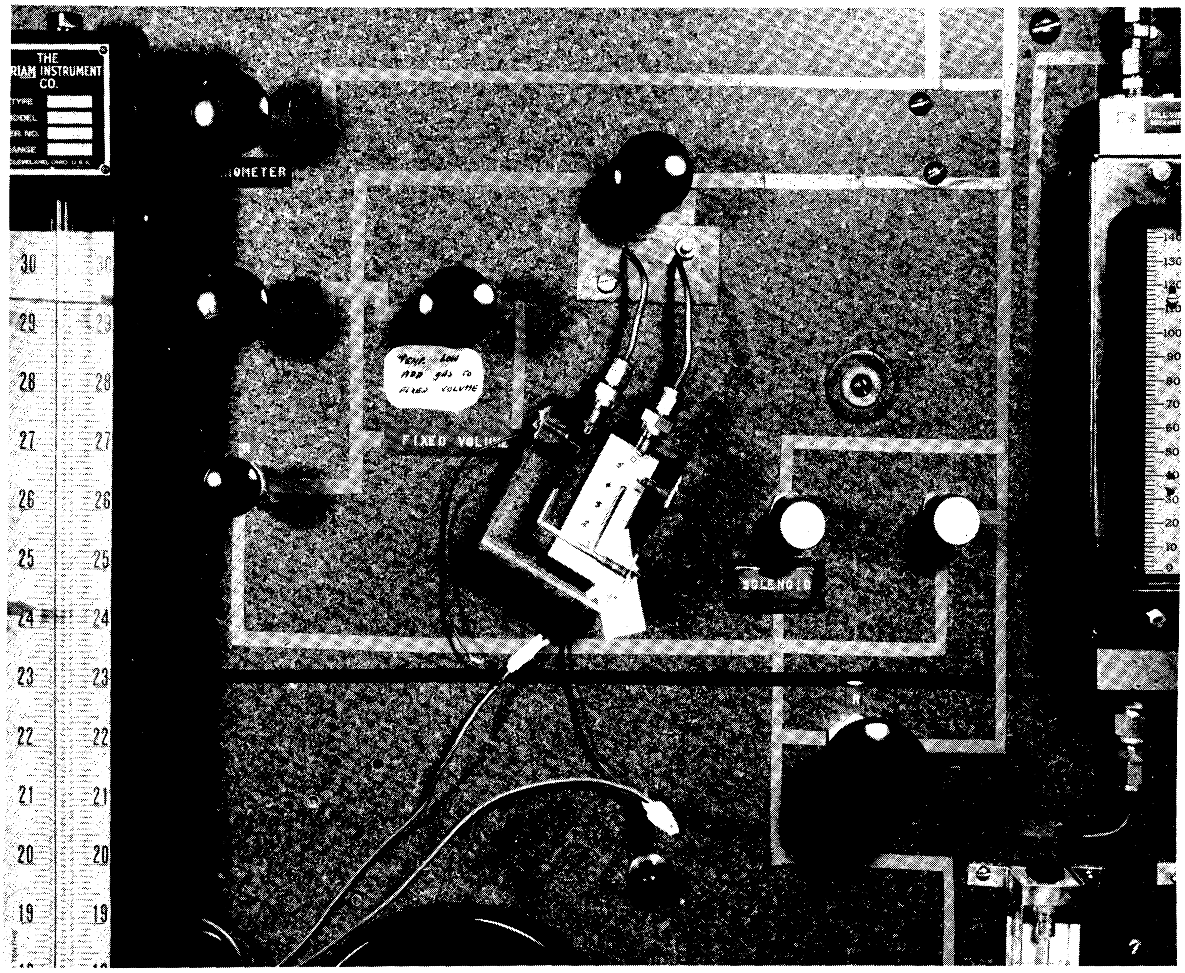


Fig. 15. View of control panel showing controls for vapor pressure control system.

imized by connecting a capacitor across the solenoid coil. To prevent the spark from coming into contact with hydrogen the space in the U-tube above the mercury is filled with vacuum pump oil of low vapor pressure. To prevent the mercury and oil from being forced into the system by a sudden pressure change, traps are placed in the lines just above the U-tube.

2. Method of Operation

The operation of the system is as follows (see Fig. 14). The desired vapor pressure of the hydrogen bath is communicated to the closed volume V by opening valve A, closing valves C,D,G,H, and J, and allowing the vapor pressure in the system to reach the desired level. Valve A is then closed and valve C, which is a very fine metering valve with a micrometer-type handle, is opened just enough to allow the hydrogen boil-off to flow out, with only a slight tendency for the pressure to rise inside the system. As the pressure rises it closes the mercury switch S, actuating the relay R which in turn activates the normally closed solenoid valve K, allowing the pressure in the system to drop; this opens the mercury switch, causing the solenoid valve to close, and the pressure starts to rise. The cycle is then repeated.

Valve B is a very fine metering valve with a micrometer-type handle, the outlet of which is screwed into the inlet of the solenoid valve; it serves to throttle the vapor flow through the solenoid valve K and prevent sharp pressure fluctuations as the solenoid opens and closes. It is important to have the smallest possible volume between the needle valve B and the port of the solenoid valve, so that undue pressure fluctuations are not caused by a flow of gas into this space after the solenoid closes.

By carefully adjusting valves B and C it is possible to maintain steady pressures in the system without frequent opening and closing of the solenoid valve. The micrometer-type handles on B and C are useful in obtaining reproducible valve settings over a wide range of openings.

By manipulating valves G and H, small quantities of gas can be added to or withdrawn from the fixed volume V, causing a small readjustment in the vapor pressure and temperature of the liquid in the cryostat. By careful setting of the controls it is possible to maintain the pressure steady to within less than a millimeter of mercury; using liquid hydrogen in the cryostat, this provides temperature control to within ±0.01°K, or better, over the entire range of interest. Through the use of valves G and H it is possible to compensate for any tendency towards temperature drift, and temperatures in the region of 20° can be held essentially constant for as long as the liquid hydrogen remains in the cryostat.

The system functions equally well at pressures below atmospheric. To obtain pressures below atmospheric (temperatures below the normal boiling temperature), valve E is closed, and valves F and D are opened, and the other controls are manipulated as before. Valve D is a large valve which allows the vapor to be pumped off rapidly to reduce the pressure in the cryostat. After the desired pressure is reached, D is partially or completely closed and valves B and C adjusted as before to maintain the pressure constant.

E. SAMPLING SYSTEM

1. Vapor Sampling

A schematic diagram of the sampling system is shown in Fig. 16, and a photograph of the sampling bank on the control panel is shown in Fig. 17.

The vapor sampling system presented no particular problems in design and construction. The vapor sample trap in the circulation loop has been described above. A short length of 1/16 in. O.D. x 0.004 in. I.D. capillary tubing is used between the vapor sampling valve A (Fig. 16) and point B to allow the vapor sample to be withdrawn slowly when the pressure in the vapor trap is relatively high. The remainder of the tubing is 1/8 in. O.D. copper tubing joined by Swagelok tube fittings.

The check valve C opens at a pressure of about 1.5 psig, preventing a pressure build-up in the glass sample bottles. It has an O-ring seal which, when coated with vacuum grease, provides a satisfactory vacuum seal and allows the entire system to be evacuated to a low pressure.

2. Liquid Sampling

The outlet of the liquid sampling bank is similar to that of the

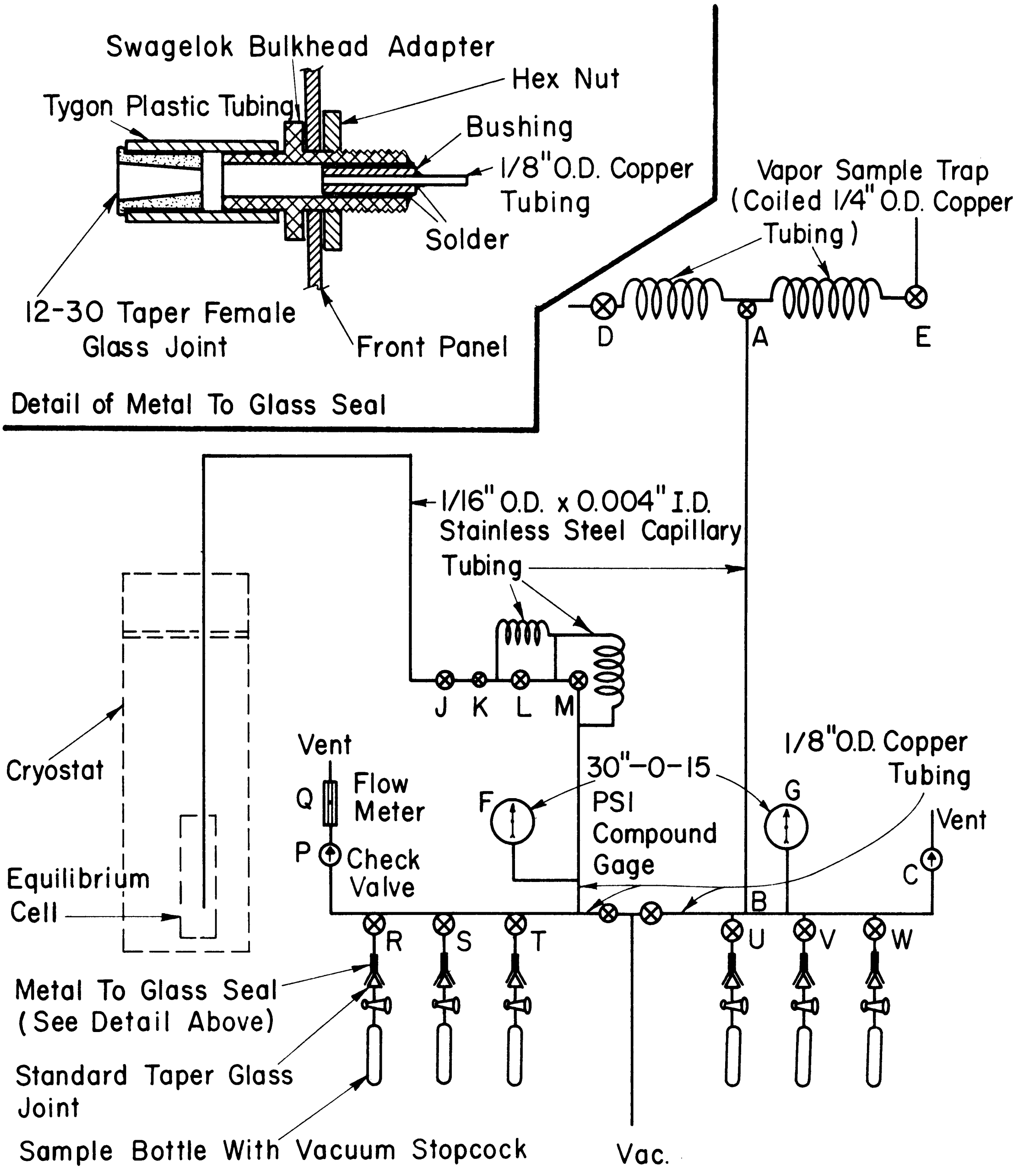


Fig. 16. Schematic diagram of sampling system.

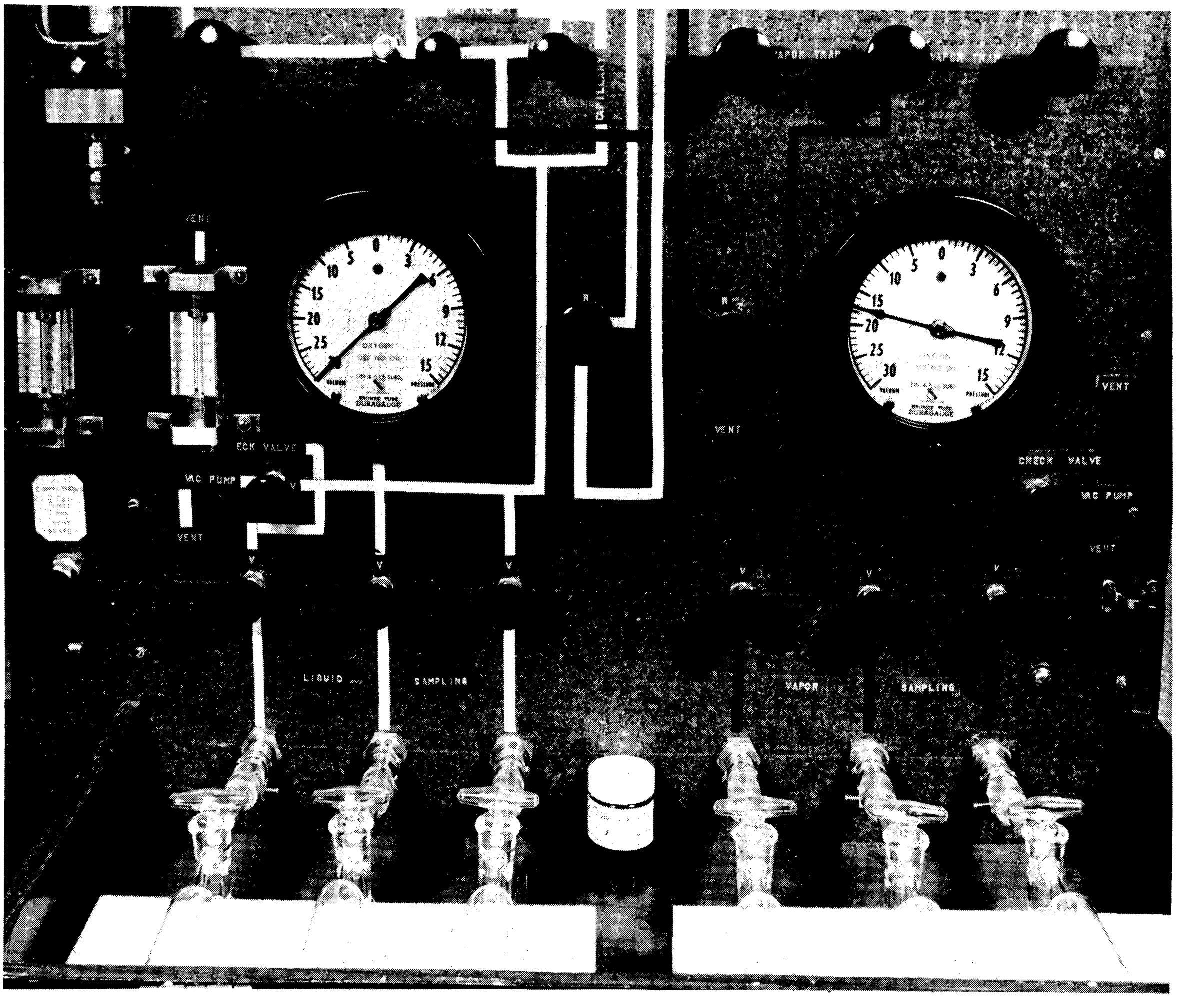


Fig. 17. View of sample bank on control panel.

vapor sampling bank. A small flow meter has been included downstream from the check valve to indicate the flow of gas through the sampling system. This was included so that the rate of flow of the sample can be estimated and the first portion to reach the sample bank can be discared. In addition, the dead space on the inlet side of the valves R, S, and T has been reduced to a minimum by inserting a bushing into the valve inlet; this was done to reduce to a minimum the quantity of gas which would be trapped in this space as the sample first flows into the lines, since this gas will flow into the bottles when the valves are opened.

The first portion of the liquid sampling line is a length of approximately 72 in. of 1/16 in. O.D. x 0.004 in. I.D. stainless steel capillary tubing. This line is soldered into the top flange of the cryostat and into the equilibrium cell and serves as the primary support for the cell. After the line comes out of the cryostat it passes to the control panel where it enters a valve J (Fig. 16), which serves as the on-off control for liquid sampling. Just downstream of this valve is a very fine metering valve K which can be used to further throttle the flow of the sample. Beyond this valve are two loops, each about 72 in. long, which can be bypassed by opening valves L and M. The variable length of the capillary tubing and the fine metering valve K provide close control over the flow of the gas, and allow the sample to be withdrawn at a very low flow rate with widely varying pressures in the equilibrium cell.

The need for 0.004 in. I.D. capillary tubing was determined by arbitrarily setting the desired rate of flow of the liquid sample and calculating the diameter and length required to produce this flow over a given range of equilibrium cell pressures.

The system has performed quite well, with multiple samples taken from the same batch of liquid having compositions whose differences are within the limits of experimental error of the mass spectrometer.

3. Sample Bottles

Samples are collected in glass bottles, fitted with Pyrex vacuum stopcocks, having an internal volume of about 20 to 30 cc, and male 12/30 standard taper joints at the outlet. A total of 60 of these bottles have been used and no problems of leakage have occurred. Six of these bottles can be seen attached to the sampling bank in Fig. 17.

The transition from metal tubing to the glass joints required for the sample bottles is made as shown in the detail in Fig. 16. The 1/8 in. copper lines from valves R,S,T,U,V, and W are soldered into a metal bushing which is in turn soldered into a 1/2 in. Swagelok bulkhead adapter attached to the front panel. The female glass joint is attached to this fitting by a short piece of tygon plastic tubing and sealed with vacuum grease. This proved to be a highly satisfactory arrangement since the plastic tubing provides a certain amount of flexibility which would be absent in a glass to metal seal of the Kovar type.

The entire sampling system, with sample bottles attached can be evacuated to a pressure of a few microns and left for a week or more without appreciable pressure increase.

F. INSTRUMENTATION

1. Temperature Measurement

The equilibrium temperature is measured with a Leeds and Northrup type 8163 platinum resistance thermometer in conjunction with a Leeds and Northrup type G-2 Mueller bridge. The bridge can be seen at the left of Fig. 18.

The null detecting equipment associated with the bridge includes a Leeds and Northrup type 2284-d galvanometer, hung in a Julius suspension, and a type 2100 lamp and scale. The lamp and scale are shown at the right of Fig. 18 and the galvanometer and suspension appear in Fig. 19.

The platinum resistance element is inserted into a hole drilled in the wall of the equilibrium cell. It can be seen in Figs. 10 and 11. Four 30 gage copper wires serve as the leads to the resistance element and are passed out of the system through the packing gland shown in Fig. 7.

To determine the temperature distribution throughout the cryostat, five differential thermocouples of gold-cobalt vs. copper have been used. This combination of metals provides a greater sensitivity (about 15 μv/degree) at liquid hydrogen temperatures than other commonly used metals.

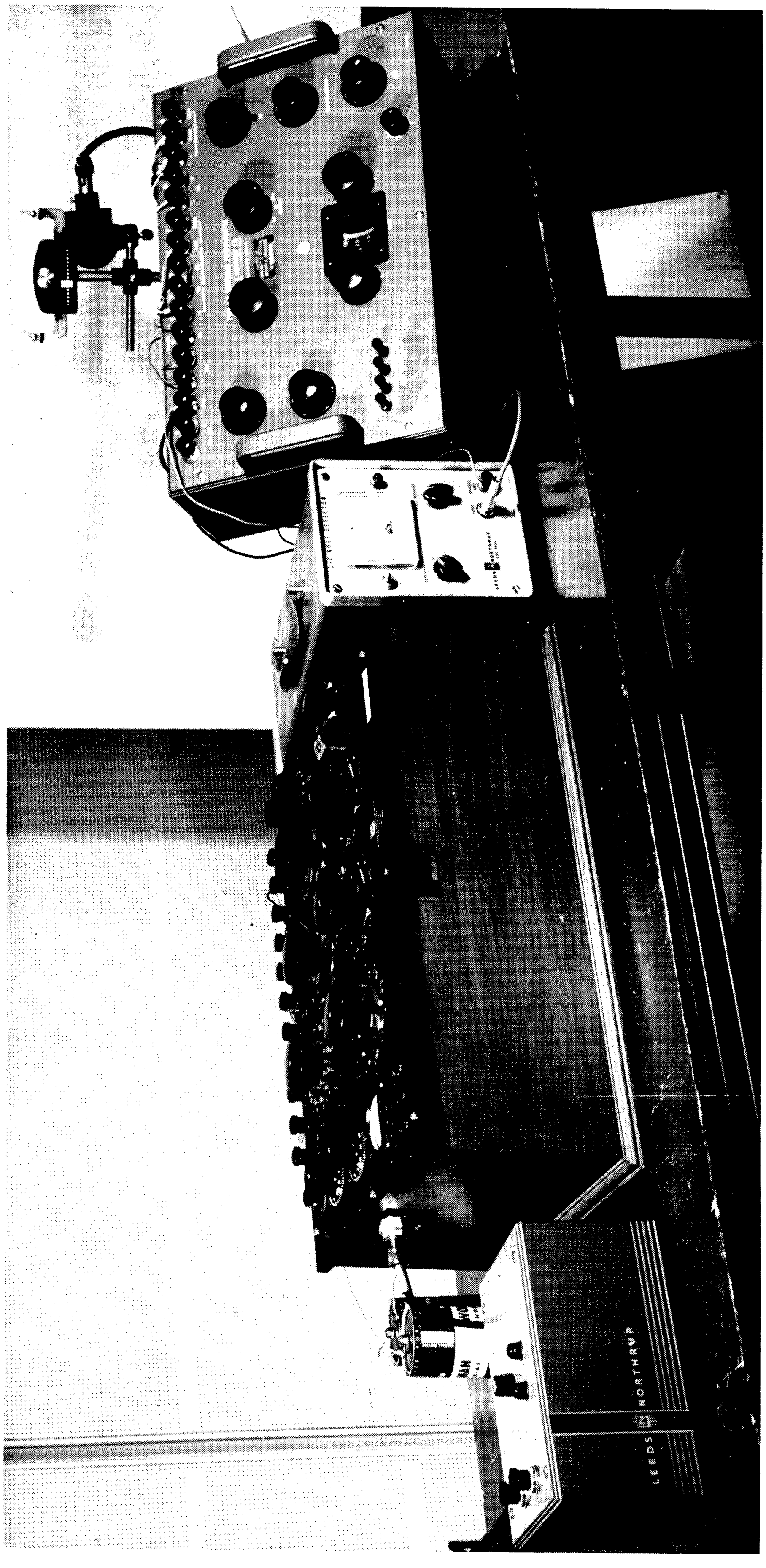


Fig. 18. Temperature measuring instruments.

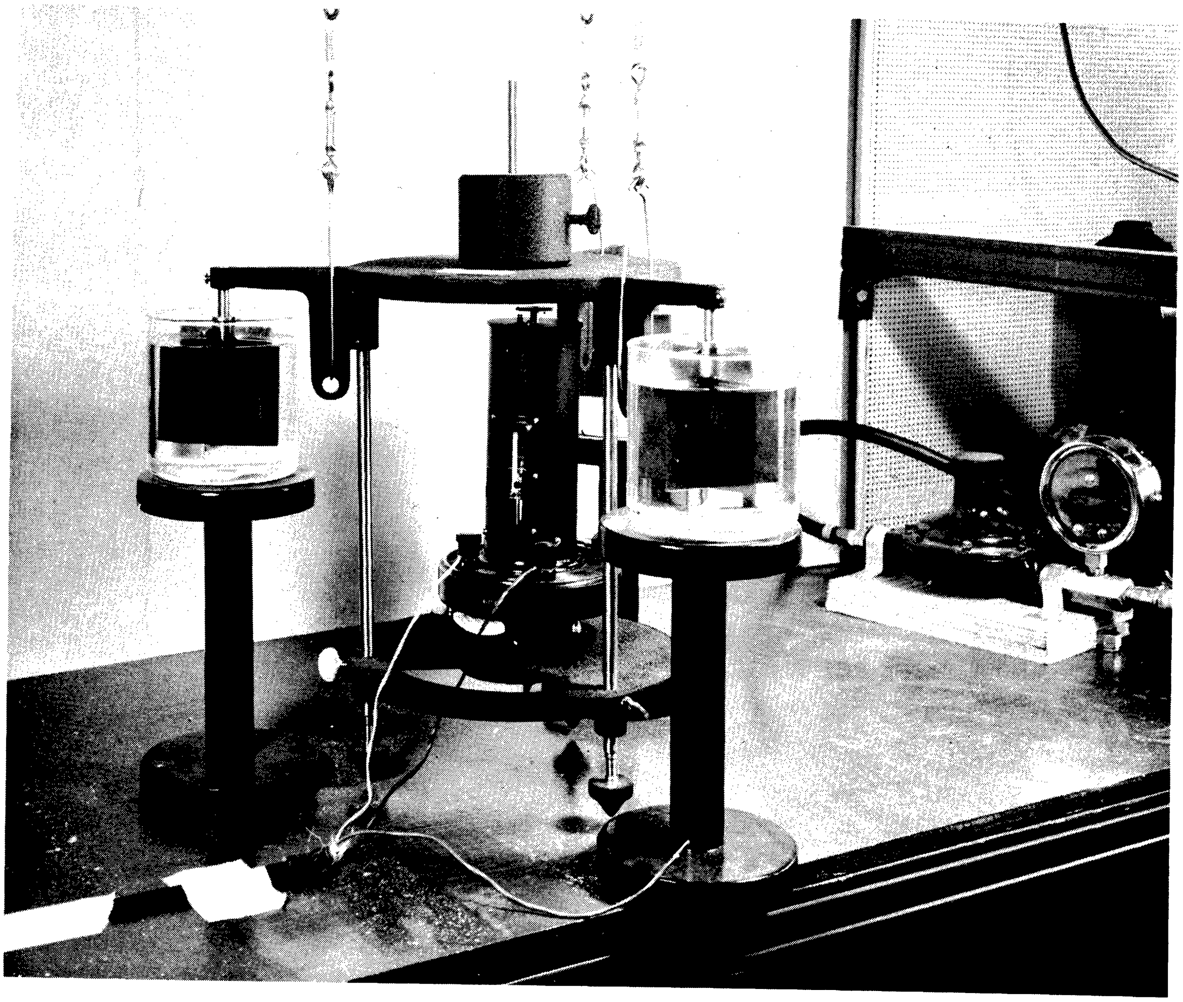


Fig. 19. Galvanometer and suspension.

The locations of these thermocouples are shown schematically in Fig. 20, and the thermocouple wires may be seen in Figs. 8 and 11. They are made of 30 gage wire and are all referenced to the platinum resistance thermometer; thus they indicate the difference in temperature between the resistance element and various points inside the cryostat. Thermocouples 1, 3, 4, and 5 are wrapped on the vapor recirculating lines, while 2 is inserted in a small hole in the wall of the equilibrium cell.

The EMF's developed by these thermocouples are measured by a Leeds and Northrup type K-3 potentiometer with a type 9834 electronic d-c null detector. The potentiometer and null detector appear at the right of Fig. 18.

2. Pressure Measurement

The equilibrium pressures in the vapor recirculating loop are measured on a 0-500 psig, 16 in., calibrated Heise gage which appears on the right of the control panel in Fig. 3.

The vapor pressure of the hydrogen in the cryostat is measured with a 0-200 psig, 16 in., calibrated Heise gage for pressures above atmospheric, and with a 0-30 in. absolute mercury manometer for pressures below atmospheric.

All other pressures are measured with conventional bourdon tube gages.

3. Liquid Level Probe

The liquid level probe is shown schematically in Fig. 21. It con-

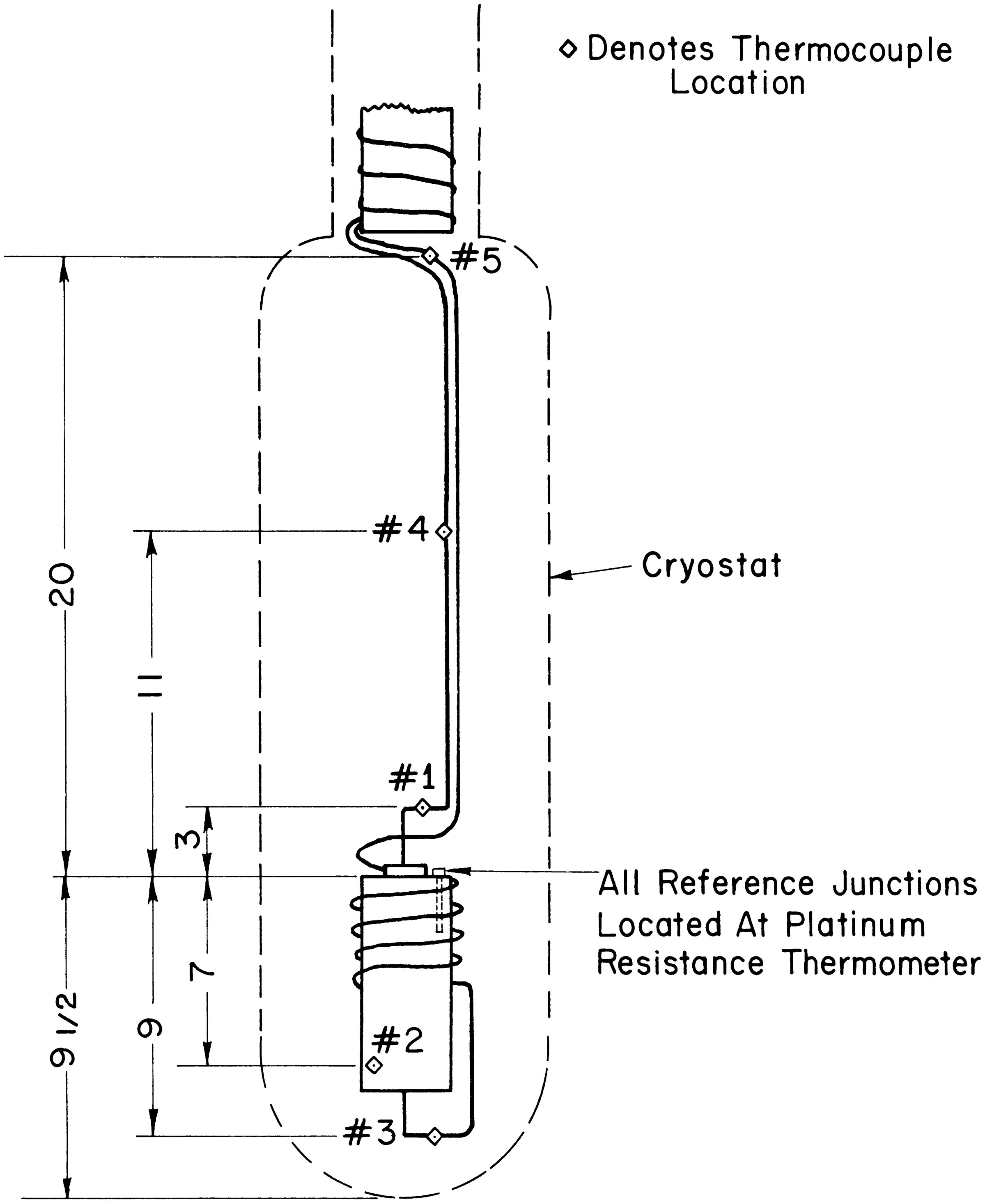


Fig. 20. Location of differential thermocouples.

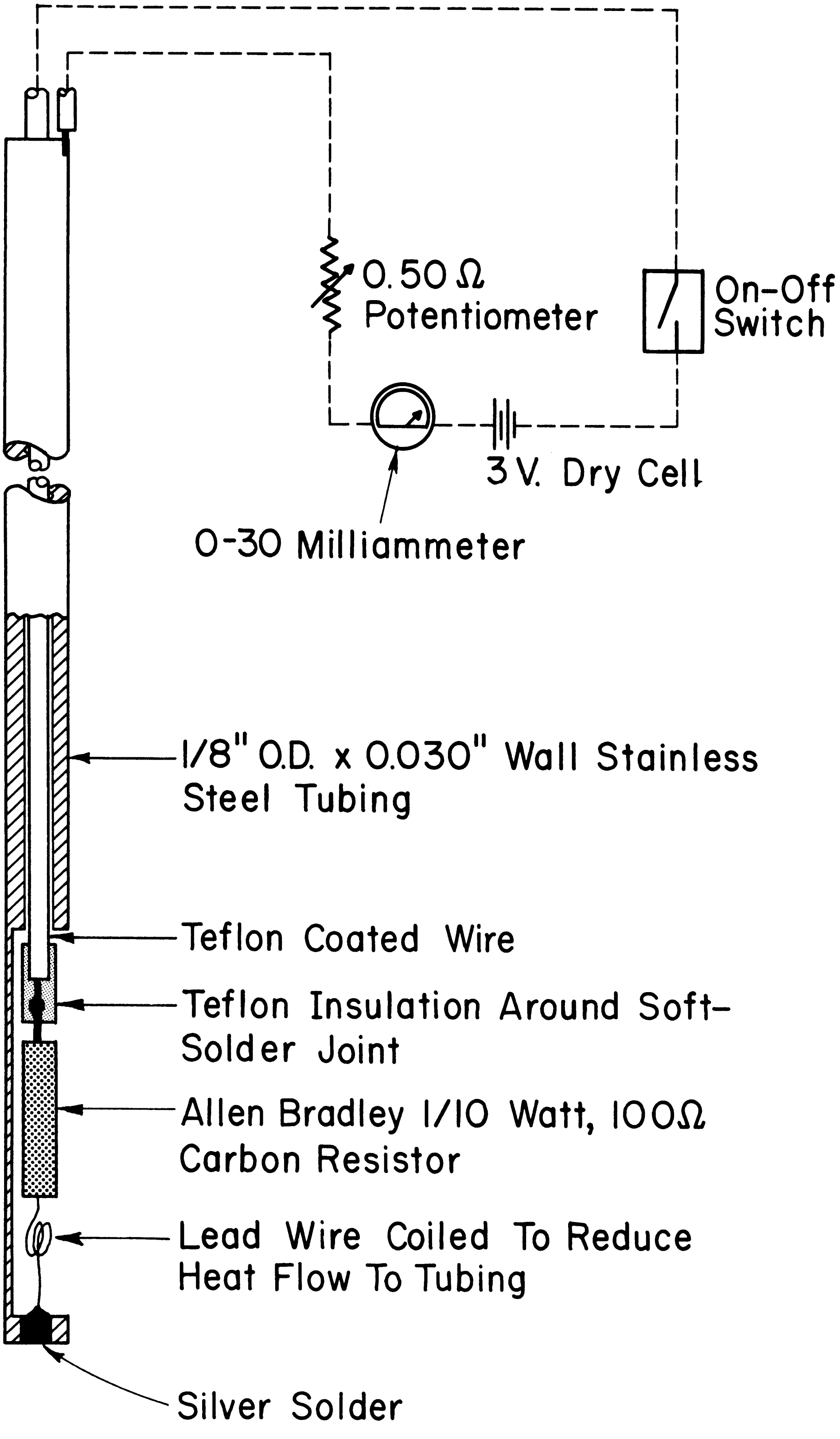


Fig. 21. Liquid level probe.

sists of a small carbon resistor attached to the end of a length of 1/8 in. O.D. x 0.030 in. wall stainless steel tubing and connected externally to a battery, a potentiometer, and a milliameter. One lead to the resistor is provided by a small teflon-coated wire passing through the inside of the tubing, with the return provided by the tubing itself.

The upper end of the 1/4 in. tube into which the probe is inserted is fitted with a 1/4 x 1/8 in. Swagelok stainless steel reducing union, bored through to allow passage of the 1/8 in. tube (see Fig. 7). The 1/8 in. tube fitting is provided with teflon ferrules which provide a seal around the probe and allow it to be moved up and down freely without leakage. In practice the liquid level is measured only upon filling, after which the probe is withdrawn, and the opening is sealed off with a threaded cap.

The probe operates on the principle of a change in the resistance of the carbon resistor with temperature. In the region below about 100°K the resistance increases rapidly with a decrease in temperature, reaching a value of about twice its room temperature value at 20°. Before the resistor enters the liquid the small current flow serves to keep its temperature well above that of the bath so that its resistance increases only slightly. When the resistor is immersed in the liquid its resistance rises sharply and a drop in current flow is registered by the milliameter. It is important to have the resistor insulated as much as possible against heat flow to the tubing, and for this purpose the lead which is soldered to the tubing is coiled several turns to increase its length.

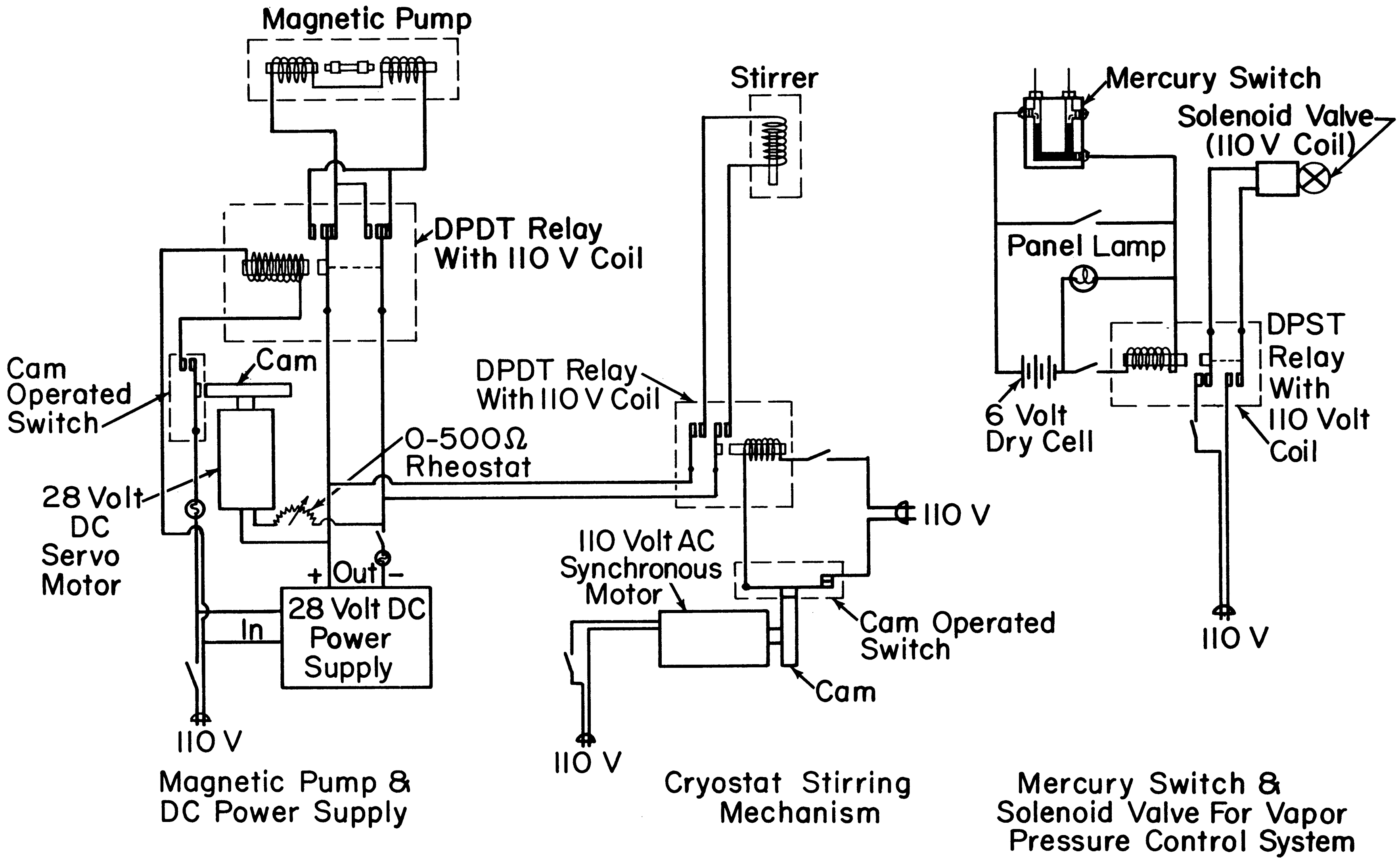
This device works quite well and determines the liquid level to within about 1/4 in. Although somewhat less sensitive at liquid nitrogen temperatures, it can also be used to determine the level of liquid nitrogen in the cryostat.

4. Electrical Circuits

The electrical circuits associated with the magnetic pump, stirring mechanism, and vapor pressure control system are shown in Fig. 22. Since the relays and switches used in these circuits produce sparks on opening and closing, it is desirable to have them situated as far as possible from that portion of the equipment containing liquid and gaseous hydrogen. All such devices are mounted on a plywood panel placed at the opposite end of the room from the main apparatus. This assembly is shown in Fig. 23, with the d-c power supply in the background. The only sparking device on the control panel is the mercury switch; the method used to isolate its spark from the hydrogen has been described above.

The d-c power supply is a 6 amp 28 v unit which operates from 115 v a-c source. It is used to supply d-c current to the electromagnets on the magnetic pump and on the stirring mechanism.

The operation of the control circuit for the magnetic pump can be seen from the diagram. During each half cycle of operation the two threaded ends of the electromagnets have the same magnetic polarity, so that at any instant the bar magnet inside the piston is attracted



Magnetic Pump & DC Power Supply

Cryostat Stirring Mechanism

Mercury Switch & Solenoid Valve For Vapor Pressure Control System

Fig. 22. Electrical circuits.

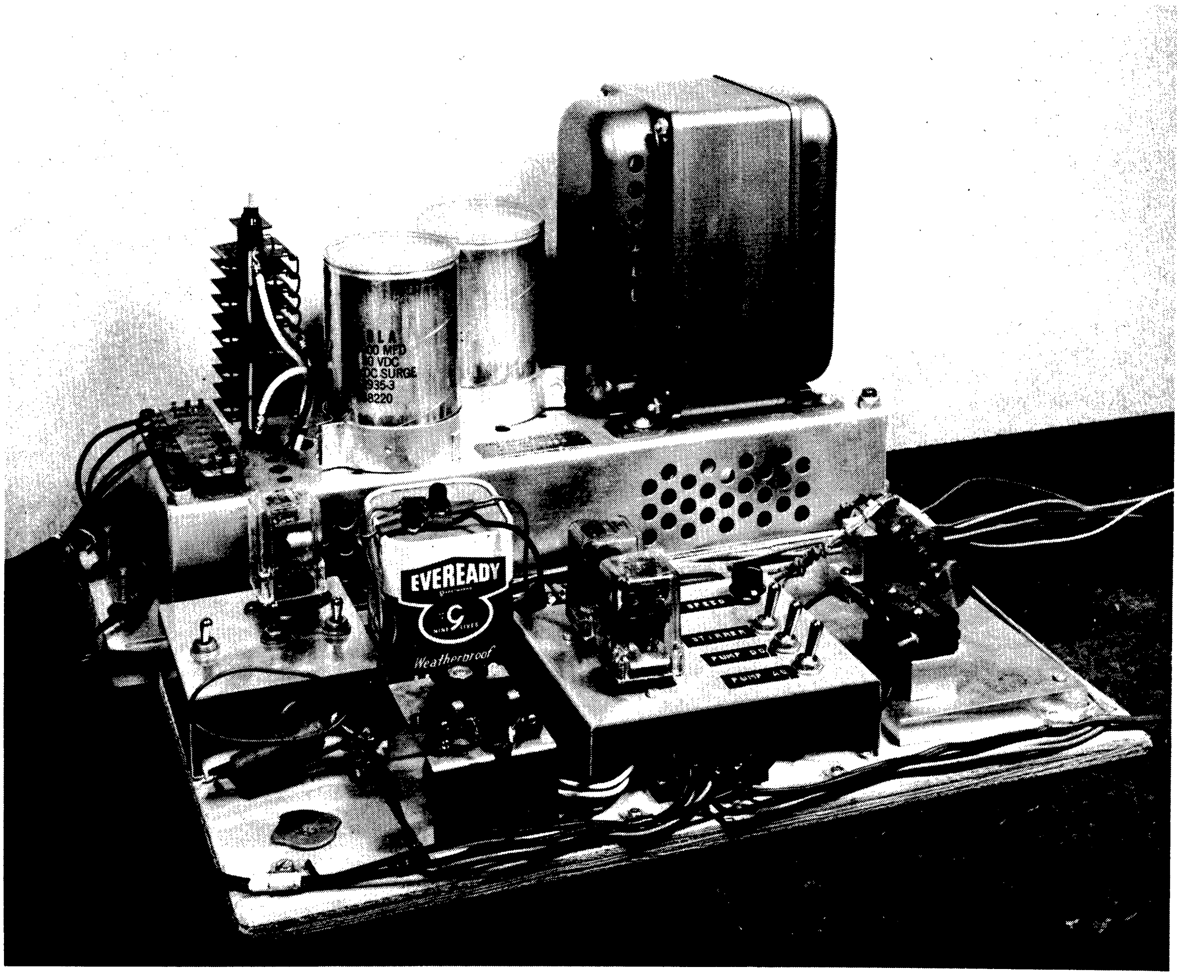


Fig. 23. View of d-c power supply and electrical control equipment.

at one end and repelled at the other. The reversal of current flow in the electromagnets changes their polarity and reverses the direction of motion of the piston. The speed of the small d-c servo motor and the resulting pump speed are varied by means of a small rheostat in series with the motor.

The circuit for the cryostat stirring mechanism works in a manner similar to that of the magnetic pump. The pulsing action in this case is provided by a 110 v synchronous a-c motor which runs at constant speed. The pulsing frequency can only be changed by changing the cam on the motor. Cams providing pulsing frequencies of 6 and 12 c/min have been used.

The operation of the electrical circuit of the vapor pressure control system has been described briefly above. The extra electrical contact on the right side of the mercury U-tube in Fig. 22 (left side in Fig. 15) was included so that a warning device, such as a buzzer, could be actuated if an unexpected pressure drop occurs in the cryostat causing the mercury to flow out of the U-tube. It could also be used in conjunction with a normally open solenoid valve to provide a greater degree of automatic control. In the present work the contact was not used.

5. Water Bath Temperature Control

The artificial atmosphere used in the vapor pressure control system is confined in a small stainless steel cylinder immersed in a water bath (see Fig. 14). An Eastern Industries precision temperature regulator with a 200 watt immersion heater is used to maintain the temperature of the bath constant, and the water is agitated by an air-operated, propeller type stirrer. This system controlled the temperature of the bath to within 0.1°C.

6. Liquid Nitrogen Level Control

The level of the liquid nitrogen at the top of the cryostat is maintained automatically by a Johns and Frame model B liquid level controller. This system includes a gas cross-charged sensing element which extends into the bath to the point where the level is to be maintained. When the level falls below the tip of the sensing element it closes a relay which actuates a three-way solenoid valve, transmitting helium gas at a low pressure to the inside of the nitrogen storage dewar. When the desired level is reached the relay opens, the gas flow is shut off, and the excess pressure in the dewar is released through an open port in the solenoid valve.

G. VACUUM SYSTEM

Two Cenco mechanical vacuum pumps with explosion proof motors are used in the experimental apparatus.

The first of these pumps is a Hyvac model which is used primarily to evacuate the sampling system. It is also connected through appropriate valves to the circulation loop and the charging system, and to the vacuum jacket of the cryostat. This pump is capable of evacuating the sample bottles to a pressure of a few microns in several minutes. The performance of the system was verified by running trace analyses on the mass spectrometer of some of the samples; these showed negligibly small quantities of air.

The second vacuum pump, a Hyvac-2 model, is used to pump a vacuum over the hydrogen bath to obtain temperatures below the normal boiling temperature of hydrogen. It is also used to evacuate and purge the cryostat and pressure control system before hydrogen is transferred into the cryostat.

Since both of these pumps sometimes discharge hydrogen gas, the outlets are fitted with short lengths of plastic tubing which conduct the gas into the vent system.

A Stokes model 276-AC Mcleod type vacuum gage is used to check the pressure in the vacuum jacket of the cryostat.

H. SAFETY EQUIPMENT

1. General

The hazards associated with the use of liquid and gaseous hydrogen may be divided into the following four categories:

a. Extreme Cold.—Liquid hydrogen is at a temperature of -423.2°F; contact with equipment at this temperature can cause severe damage to skin tissue.

b. Hazards of Pressure Build-up.—One liter of liquid hydrogen expands to a volume of over 800 ℓ of gas at room temperature and atmospheric pressure, therefore it is necessary to insure that liquid hydrogen is not trapped or isolated in any part of the apparatus and subsequently warmed.

c. Flammability.—The upper and lower limits of flammability of hydrogen in air are 75 and 4% by volume. Mixtures of solid oxygen in liquid hydrogen are also potentially explosive. Precautions must be taken not only to prevent hydrogen from escaping into the room, but also to prevent air from coming into contact with the liquid, where the oxygen in the air might condense and freeze.

d. Low Temperature Embrittlement.—Some commonly used structural materials, notably carbon steel, become brittle at liquid hydrogen temperatures.

The safety considerations followed in the design and construction of the apparatus were those recommended by the National Bureau of Standards[40] and the Linde Co.[41] Other safety references[42,43] were also consulted.

2. Materials of Construction

Those portions of the equipment at liquid hydrogen temperature include the inner vessel of the cryostat, the equilibrium cell, a portion of the tubing of the circulation loop, and part of the liquid sampling line. These parts have been described above; they are made either of type 304 stainless steel or from copper, both of which are well known for their structural stability at low temperatures. Joints have been made with soft solder, silver solder, and heliarc welding.

3. Vent System

All portions of the equipment which contain hydrogen are completely enclosed and sealed against the entry of air. A vent system has been constructed which conducts all hydrogen discharged from the system to a point above the roof outside the building. This system consists of a 1-1/2 in. cast iron pipe which runs from just above the apparatus to a point above the roof of the building. The upper end of this pipe is fitted with a conventional swing check valve to prevent the back flow of air into the system.

A low pressure supply of nitrogen gas is connected to the vent system so that the vent pipe may be purged before hydrogen is placed in the system. This purge system is connected through a flow meter on the front panel of the equipment so the flow of gas into the vent pipe can be monitored.

4. Pressure Relief Devices

To prevent a dangerous pressure build-up due to the warming of liquid hydrogen in the system, the circulation loop and the outlet line from the cryostat are fitted with rupture disc assemblies; these may be seen in Figs. 9 and 14. The rupture disc is a thin metal disc designed to burst at a predetermined pressure. It is mounted in a suitable housing and installed in the system in a manner similar to a pipe or tube fitting.

The rupture disc in the circulation loop is designed to burst at a pressure of 750 psia, and that in the cryostat outlet at 210 psia. The outlets of the rupture disc assemblies are connected to the vent system.

5. Room Ventilation

The room in which the apparatus was constructed was designed originally for use with heavier-than-air combustible gases, with the air inlet at the top of the room and discharge at the floor. This system was modified to provide for air inlet at the floor and exhaust at the ceiling.

The framework on which the apparatus is assembled is enclosed on all four sides and fitted with an exhaust hood at the top. Air is continually drawn into the enclosure through openings at the base of the sides and back. The back panel is hinged to allow easy access to the cryostat for filling (see Fig. 6).

The air from the exhaust hood and from the ducts at the ceiling of the room is withdrawn by an explosion-proof blower and discharged to the atmosphere at a point above the roof of the building. The system is capable of providing approximately 20 air changes per hour.

6. Safety Shielding

The steel framework surrounding the cryostat is lined on three sides with sheets of 1/8 in. thick steel plate which are bolted in place (see Figs. 5 and 6). An extra thickness is placed directly in front of the cryostat, providing a 1/4 in. thickness between the cryostat and the area normally occupied by the operators. The panel on the door at the rear of the assembly is made of asbestos sheet and is loosely fastened. The entire framework is held in place by means of steel channels secured to the walls of the room. This arrangement insures that the force of an explosion in the area of the cryostat would be directed toward the rear of the room, away from the operators. The windows at the rear of the room have been set in rubber mounts so that they will pop out in the event of an explosion.

7. Electrical Equipment

The solenoid valve in the pressure control system and the vacuum pump motors are explosion-proof. All sparking switches and relays have been removed as far as possible from the cryostat and placed as near floor level as possible.

The existing fluorescent lights and electrical outlets have been disconnected and replaced with explosion-proof equipment.

8. Hydrogen Storage

The cylinder of hydrogen gas used to charge the circulation loop is stored in a small aluminum shed outside the building. It is connected to the control panel through a line of 1/2 in. schedule 80 welded steel pipe. The pressure regulator is attached directly to the cylinder, and a 750 psi rupture disc assembly is connected just downstream. The outlet of the rupture disc is connected to a 1/2 in. vent line that runs up to a point above the roof of the building. This provides for the discharge of the hydrogen gas to the atmosphere in the event of a failure in the pressure regulator.

The liquid hydrogen is obtained in quantities of 150 ℓ in Linde LSH-150 super-insulated containers. Since these containers periodically release small quantities of hydrogen gas, they are stored in a small fenced enclosure just outside the building, and brought into the room only long enough to fill the cryostat at the beginning of each run.

IV. EXPERIMENTAL PROCEDURES

A. PREPARATION OF EQUIPMENT

1. Precooling

The first step in the preparation of the equipment is the precooling of the cryostat and equilibrium cell with liquid nitrogen. This is desirable as it avoids the use of large quantities of liquid hydrogen for cooling. The equilibrium cell and recirculation loop are first evacuated and purged several times with helium to insure that no air remains to freeze in the capillary lines upon cooling. Liquid nitrogen is then introduced into the inside of the cryostat and into the nitrogen reservoir at the top. The rapid vaporization of the nitrogen as it first enters serves to purge much of the oxygen from the system.

In order to cool the equilibrium cell rapidly, enough nitrogen is added to cover a portion of the cell. The level is measured with the level probe described previously. Because of the high efficiency of the multi-layer insulation in the cryostat, the nitrogen boils off very slowly after the interior is cooled to liquid nitrogen temperature (estimated rate about 0.04 ℓ/hr); thus it is desirable to have a means of quickly removing the remaining nitrogen without warming the cryostat. This is done by inserting a 1/8 in. O.D. stainless steel tube into the liquid level probe well and pressurizing the cryostat with helium, forcing the nitrogen up the tube. The helium is admitted from the charging system through the valves G and H (Fig. 14). This method permits the removal of a liter of liquid nitrogen in a few minutes.

2. Purging

Because of the danger of explosion resulting from mixtures of air and hydrogen, extreme care is taken to remove all traces of air from the system before the hydrogen is introduced. As a first step, pure helium or nitrogen gas is allowed to flow continuously through the vent system for approximately 20 min before the hydrogen is introduced; this is done through the vent purging system.

After the liquid nitrogen has been pumped out of the cryostat, the vent valve J (Fig. 14) is opened and the cryostat pressure is reduced to atmospheric. The liquid hydrogen dewar is then brought into the room and immediately connected to a common ground with the cryostat, to remove any static charge from the system. The vacuum insulated transfer line is connected first to the dewar and then to the cryostat (see Fig. 6). The Swagelok fitting with teflon ferrules used to seal the transfer line where it enters the cryostat provides a vacuum tight seal with only moderate tightening, without damaging the transfer line itself. The vent valve J is then closed, valves F, D, and A are opened, and the cryostat and vapor pressure control system are evacuated. Since the open end of the transfer line is inside the cryostat at this time, the entire transfer line is evacuated up to the valve on the hydrogen dewar, which remains closed.

The system is evacuated to a pressure of a few millimeters or less; valve F is then closed, and the pressure is raised to atmopsheric by slowly admitting helium gas through valves G and H. This procedure is repeated one or more times to insure that virtually all air is removed. Valve J is then opened and the cryostat is ready for filling.

3. Liquid Hydrogen Transfer

Liquid hydrogen is transferred into the cryostat by opening the valve in the liquid line at the top of the dewar. The slight pressure which exists inside the dewar is sufficient to effect the transfer at a rate of several ℓ/min. The liquid level is checked frequently with the level probe, and the temperatures indicated by the platinum resistance thermometer and the thermocouples are observed. The cryostat is usually filled to a depth of about 20 in. (about 10 ℓ).

When the desired liquid level is reached the valve on the dewar is closed and several minutes are allowed for the hydrogen in the transfer line to evaporate and flow out. The transfer line is then removed, first from the cryostat and then from the dewar, and the opening in the cryostat is closed with a threaded cap. The dewar ground wire is disconnected and the dewar is immediately returned to its storage area outside the building. The liquid level probe is removed and its opening is capped off.

B. RUN PROCEDURE

1. Temperature Setting and Control

The method of operation of the vapor pressure control system has been described in Section III-D. To obtain temperatures below the normal boiling temperature of hydrogen, a vacuum is pumped over the bath. No particular problems were encountered in setting the temperature in this region. As the pressure in the cryostat is lowered, the liquid boils vigorously and the temperature drops rapidly. With approximately 8 ℓ of liquid hydrogen in the cryostat, the temperature can be lowered one degree in about 10 min, using a vacuum pump having a capacity of 20 ℓ/min.

To obtain temperatures above 20.4° the vent lines are closed and the pressure is allowed to rise. It has been found that the vapor pressure rises by about 1 lb each minute, but that the temperature indicated by the platinum resistance thermometer does not rise at a corresponding rate (according to the hydrogen vapor pressure curve). This is apparently due to the fact that the bulk of the heat flow into the bath is down the walls of the cryostat; this warms a layer of liquid at the top of the bath, transmitting a correspondingly high vapor pressure to the outside, while the lower layers of liquid are warmed much more slowly as a result of the low rate of heat flow through the liquid. When the system was first placed into operation it was found that several hours were required to raise the temperature of the bath by one degree. The stirring action of the cryostat stirrer was not vigorous enough to cause thorough mixing of the liquid, and the problem was further complicated because the stirrer jammed and did not always function properly.

The problem of obtaining a rapid temperature rise was solved by inserting a length of 1/8 in. O.D. stainless steel tubing into the opening for the liquid level probe, and pumping pure hydrogen gas into the bath through the charging system. The tube extends to the base of the cryostat, so the heat is added at the lowest level. The warmed liquid at the base rises, setting up a convection flow in the bath and providing adequate mixing. The cooling and condensing of the hydrogen gas provides enough heat to raise the temperature rapidly.

Once the desired temperature is reached it is held steady by adjusting the vapor pressure control system as described previously. Although temperature differences of several tenths of a degree (measured by the differential thermocouples) exist throughout the bath as the temperature is being raised or lowered, it has been found that an essentially uniform temperature is obtained within a few minutes after the vapor pressure is held steady. This occurred even when the stirring mechanism was not operating.

Through careful setting of the controls, the vapor pressure is held within narrow limits, and the temperature remains steady with little or no attention from the operator.

There is sometimes a slight tendency for the temperature to drift, although the drift usually amounts to no more than a few thousandths of a degree in a period of 1 hr. This drift can be corrected by making small changes in the quantity of gas in the fixed volume V (Fig. 14) through valves G and H. These valves are connected together with about 8 in. of 1/4 in. copper tubing, and by opening first one valve and then the other it is possible to make small changes in the pressure in V. This causes a corresponding change in the bath vapor pressure and in the temperature of the bath liquid. The mercury switch S serves as a differential manometer for estimating the magnitude of the pressure change in V, and with a little experience the operator can virtually eliminate temperature drift.

At temperatures around 20°K and above, the temperature can be held steady to with ±.005°, or better, while at the lowest temperature at which a run was made temperatures were controlled to with ±.02°, or better.

2. Preparation of Mixture and Pressure Setting

After the temperature has been set, the hydrogen-helium mixture is charged into the circulation loop. Liquid hydrogen is first condensed into the equilibrium cell and then pressurized with helium gas.

In practice, the mass of hydrogen necessary to fill the equilibrium cell approximately half full of liquid (about 25 cc) is calculated for the given temperature; from these data the pressure drop in the 1500 cc charging cylinder required to provide this amount of liquid is determined. Hydrogen is then admitted to the loop slowly, until the dew point is reached, at which time there is a sharp break in the pressure rise. The quantity of hydrogen calculated above is then charged into the loop. (The hydrogen gas from which the liquid is condensed may be assumed to be normal hydrogen (75% orthohydrogen, 25% parahydrogen). Since the experimental data are taken within a few hours, the concentration of parahydrogen does not increase significantly, and the data obtained will represent mixtures of helium and normal hydrogen.)

Helium is added to the loop to raise the pressure to the desired level. At higher temperatures the helium must be added slowly. When it first enters the loop it forces the hydrogen into the equilibrium cell, where some of it condenses, and the pressure rises only slightly; however after a minute or two of pumping by the magnetic pump the helium begins to bubble through the liquid and the accompanying evaporation of hydrogen causes the pressure to rise. Helium is admitted in small increments until the desired pressure is reached.

As the vapor is recirculated and the two phases approach equilibrium, the pressure changes slightly. The floating-piston volume regulator is used to correct the pressure without changing the overall composition of the mixture. This permits the taking of data at the same pressures along each isotherm, and facilitates the cross plotting on temperature-composition and pressure-temperature diagrams.

At the beginning of the experimental work several runs were made to determine the approximate time required for the mixture to reach equilibrium with continuous vapor recirculation. This was done by holding the pressure and temperature constant and taking samples of each phase at different time intervals. The analyses of these samples indicated that the compositions remained essentially constant after about 10 or 15 min of recirculation. Thereafter samples were taken after about 20 to 30 min to insure that equilibrium was reached. In addition, occasional samples were taken after an hour or more and a check was made to see if the resulting compositions fell along a smooth curve through the other points.

3. Sampling

During the time allowed for the mixture to reach equilibrium, the sample bottles are evacuated. When sufficient time has elapsed the vapor recirculating pump is turned off and the valves D and E (Fig. 16) at the ends of the vapor sample trap are closed. The valve and stopcock to one of the vapor sample bottles are then opened, and valve A is opened to allow the sample to flow in. The pressure rise in the system is observed on the compound gage G, and valve A is closed when the bottle is filled to atmospheric pressure. If the valve is inadvertantly left open beyond this time, the excess pressure is released through the check valve C which opens at about 1.5 psig.

In the liquid sampling system valve J (Fig. 16) serves as the on-off control. If valves L and M are closed the vapor is forced to flow through additional lengths of fine capillary tubing which throttle the flow and allow the sample to be withdrawn slowly when the pressure in the equilibrium cell is relatively high. Valve K is a very fine metering valve used to further control the rate of flow. This fine control is desirable as it allows the sample to be withdrawn without upsetting the equilibrium inside the cell.

Since the length of capillary tubing between the equilibrium cell and the valve J contains a small amount of liquid and vapor that do not have the equilibrium compositions, the first portion of the sample to reach the sample bank is discarded by keeping valves R, S, and T closed and allowing it to flow out through check valve P which opens at about 1.5 psig. The small flow meter Q is used to determine the rate of flow of the sample and to obtain reproducible flow rates. As a general rule the vapor is allowed to flow for about 15 or 20 sec, before admitting the sample to the bottles. After the bottles are filled the valves and stopcocks are closed and the bottles removed and stored for later analysis on the mass spectrometer.

During the early experimental work as many as four or five samples were taken from the same batch of liquid, with different settings on the control valves K, L, and M, and with different purging times. The analyses of these samples showed that the rate of withdrawal and the purging time have little or no effect on the composition of the sample. Samples containing as little as 1% helium were reproducible to within a few percent of that value. Nevertheless, an attempt was made to take samples at approximately the same flow rate throughout the work.

Since the reproducibility of duplicate samples was consistently good during the early work, only one sample of each phase was taken during later runs.

4. Instrument Readings

The current flow through the resistance thermometer is maintained continually throughout the run at each temperature so the temperature can be closely monitored, and any tendency for it to drift can be detected. The usual procedure consists in setting the resistance value on the Mueller bridge, corresponding to the resistance of the platinum element for the desired temperature, and maintaining the galvanometer deflection at zero by adjusting the vapor pressure controls to correct for any drift. The necessary calibrations and adjustments are made on the bridge beforehand, and frequent checks are made during the run to detect any zero shift in the galvanometer.

The setting of the Mueller bridge and the pressure in the circulation loop are recorded at intervals of 10 or 15 min throughout each run. The EMF at each differential thermocouple is recorded just before the samples are taken at each pressure.

A zero EMF is usually observed for each of the thermocouples immersed in the liquid. This indicates a negligible temperature gradient in the bath after the vapor pressure has been held constant for a short period of time. As the liquid level falls below each thermocouple (above the equilibrium cell) it indicates a temperature above that of the resistance thermometer. This serves to give a rough estimate of the liquid level during the run.

When the liquid level falls below the resistance thermometer (indicated by a lower temperature at thermocouple No. 3) the apparatus is shut down until more liquid hydrogen is added.

The thermocouples performed satisfactorily with the exception of No. 2 which is inserted in a small hole near the base of the equilibrium cell. Very early in the experimental work this thermocouple apparently became grounded to the equipment and thereafter gave very erratic and inconsistent readings. That it was picking up a stray EMF from the equipment was indicated by the fact that its EMF oscillated back and forth when the magnetic pump was on, with precisely the same frequency at which the pump was operating. This was probably caused by a small EMF leaking from the coils of the pump.

5. Resetting the Pressure and Temperature

If the next point is to be taken at the same temperature, helium is added to the loop, or vapor is withdrawn, to bring the pressure to the desired level. The circulating pump is again turned on and the run is made as before.

As a general rule points are run at increasing pressures at each temperature, starting at a pressure just above the hydrogen vapor pressure and proceeding to the highest pressure. This procedure is particularly important at the higher temperatures, where the vapor contains a large percentage of hydrogen; under these conditions, if vapor is withdrawn from the loop to lower the pressure, there is a danger of boiling off all of the liquid. This happened in several early runs and was not discovered until the samples were analyzed.

If the next point to be taken is at another temperature, the temperature is reset by adjusting the bath vapor pressure to the necessary value. The circulation loop is opened and the remaining liquid is boiled out of the equilibrium cell, using the vacuum pump if necessary. After the temperature has been reset, the desired amount of liquid hydrogen is condensed into the cell, helium is added, and the run is made as before

C. ANALYSIS OF GAS SAMPLES

1. General

Samples taken in the present work were analyzed in the Instrumental Analysis Laboratory of the Department of Chemical and Metallurgical Engineering of The University of Michigan. The instrument used in these analyses is a Consolidated model 21-103 mass spectrometer, manufactured by the Consolidated Engineering Corp., Pasadena, California.

2. Operation of the Mass Spectrometer

The techniques of mass spectrometry as applied to quantitative chemical analysis have been well established. The following is a simplified description of the method of operation of the instrument used in this work.

A small quantity of the sample gas to be analyzed is expanded into an evacuated reservoir to a pressure of 50 t0 100 microns. This pressure is measured to within a few hundredths of a micron and recorded for later use in the final calculations. From this region, a portion of the sample flows through a small opening, called the leak, into a region of high vacuum (10^{-5} to 10^{-7} mm) where the molecules are bombarded by electrons from a heated tungsten filament. Since the pressure on either side of the leak is quite low, it can be assumed that the number of molecules of a given substance flowing through the leak is a function only of the partial pressure of that substance in the low pressure reservoir; that is, the flow of the molecules of one substance is unaffected by the presence of other types of molecules.

The electron bombardment removes electrons from the atoms of some of the molecules, producing positively charged ions having definite mass-to-charge ratios. These ions are then accelerated through an electrical field and injected into a magnetic field, where they are deflected into circular paths whose radii are a function of the mass-to-charge ratio. The separation of particles is effected by collecting, at any instant, only those particles which follow a curve of fixed radius and therefore have a specific mass-to-charge ratio. In practice, this is done by causing the ions to flow through a semicircular metal tube of fixed radius which has a small slit over the target, or collector, so that a very narrow beam is collected. By changing the magnitude of the accelerating voltage, ions with different mass-to-charge ratios are successively brought to focus on the collector; in this way any desired range of mass-to-charge ratios can be scanned.

When a beam of ions strikes the collector, each ion surrenders its charge, producing a small current flow. This current is amplified and recorded to indicate the relative abundance of the particles of a given mass-to-charge ratio reaching the collector. In the Consolidated model 21-103 mass spectrometer, the amplified current from the collector actuates a recording galvanometer which photographically records each impulse, producing a deflection proportional to the number of ions in the beam. Since the total deflection will vary considerably, the recording galvanometer makes simultaneous recordings at five different sensitivity levels, producing five peaks, some of which may fall beyond the upper limit of the graph. The highest peak which falls within the graph, for a given impulse, is then measured and multiplied by the appropriate sensitivity factor for use in the final calculations.

3. Calculations

The resulting peak height is not used as an absolute indication of the quantity of a given substance in the sample. Some substances are more easily ionized than others, so the quantities of ions of different substances reaching the collector are not proportional to the quantities of molecules of those substances in the gas sample. However, as pointed out above the rate of flow of molecules of a given substance through the leak is a function only of the partial pressure of that substance in the low pressure reservoir. This makes it possible to use the peak heights produced by pure samples as standards of comparison. These peak heights are converted into component sensitivities for each substance, usually expressed in divisions (units of linear distance on the graph) of peak height per micron, by dividing the peak height by the pressure of the pure sample in the low pressure reservoir. The peak heights produced on the graphs of the samples being analyzed are then divided by the component sensitivities to obtain the partial pressures of each substance in the mixture. These partial pressures are added to obtain the total pressure, and the mole percent is computed as the ratio of partial pressure to total pressure.

These calculations may be briefly summarized. Let us assume that a binary mixture of components A and B is to be analyzed. Pure samples of A and B are run through the instrument in the normal manner and the component sensitivities are calculated as

$$\text{Component sensitivity} = \frac{\text{peak height of pure sample}}{\text{pressure of pure sample}} .$$

The sample mixture is then run, the peak heights for each substance are measured, and the partial pressures are calculated from the relation

$$\text{Partial pressure} = \frac{\text{peak height of component in mixture}}{\text{component sensitivity}} .$$

The partial pressures are added, and used to compute the mole percent as

$$\text{Mole percent}_A = \frac{\text{partial pressure}_A}{\text{Total pressure}} .$$

In practice these calculations may become quite complicated, especially when the molecules of a single substance are split up and ionized in different ways by the electron bombardment, producing many different mass-to-charge ratios for that substance. The problem is further complicated if some of the peaks are made up of contributions from two or more substances whose ions have different masses and charges, but the same mass-to-charge ratio.

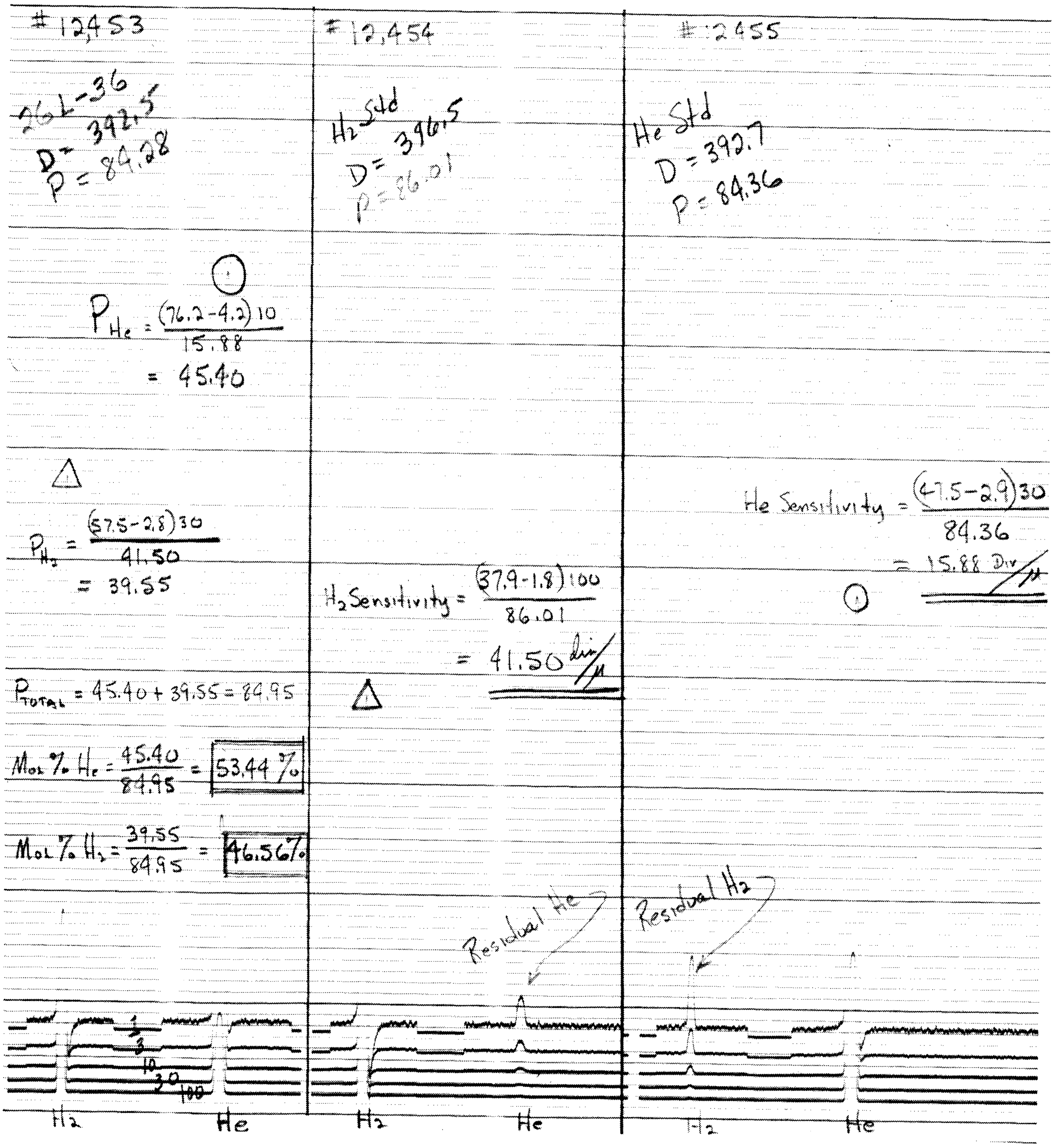
In the present work no problems of this type were encountered. The peaks produced by hydrogen and helium are unicomponent peaks; that is, they are caused by only one component.

4. Sample Calculations

A randomly selected set of mass spectra from this work is shown in Fig. 24. It includes, from left to right, a typical gas sample, a hydrogen standard, and a helium standard. The calculations are shown on the graph.

The number at the top of each column is from the log of the Instrumental Analysis Laboratory and is the identification number used in the laboratory referencing system. All graphs are on permanent file in the laboratory. The reference numbers for each sample analyzed in this work have been included in the tabulation of experimental data in Appendix A, so that the original spectra may be consulted.

The information just below these numbers identifies the sample—in this case (from left to right) sample No. 26-L-36, a hydrogen standard, and a helium standard. Just below this line are the dial readings from the sample reservoir pressure gage and the corresponding pressure. The



12,453

~~26L-36~~

D = 392.5

P = 84.28

①

$P_{He} = \frac{(76.2-4.2)10}{15.88}$

= 45.40

△

$P_{H_2} = \frac{(57.5-2.8)30}{41.50}$

= 39.55

$P_{TOTAL} = 45.40 + 39.55 = 84.95$

Mol % He = $\frac{45.40}{84.95}$ = $\boxed{53.44\ \%}$

Mol % H_2 = $\frac{39.55}{84.95}$ = $\boxed{46.56\%}$

12,454

H_2 Std

D = 396.5

P = 86.01

H_2 Sensitivity = $\frac{(37.9-1.8)100}{86.01}$

= 41.50 div/μ

△

12455

He Std

D = 392.7

P = 84.36

He Sensitivity = $\frac{(47.5-2.9)30}{84.36}$

= 15.88 Div/μ

①

Fig. 24. Typical mass spectra.

dial reading is converted to a pressure reading (in microns) by the relation $P = D^2/K$, where K = 1828.

The dark lines across the bottom of the graph are the recording galvanometer traces; the sensitivity factor for each trace is written at the bottom of the left column. Interruptions can be seen in these traces in the form of peaks which have been labeled at the bottom. The highest peak that falls within the graph is used for the calculations. Hydrogen peaks used are enclosed in triangles and helium peaks in circles. The galvanometer trace associated with a given peak is determined by counting the number of peaks below it; the lowest peak is always from the lowest trace, and each successive peak from the next higher one.

In the helium standard (right column) the peak has been measured at 47.5 divisions above the baseline of the graph; however, it is associated with the second trace from the bottom which is 2.9 divisions above the baseline, giving a net peak height of 44.6 divisions. This number is multiplied by the galvanometer sensitivity factor (30 in this case) and divided by the pressure (84.36 microns) to give a helium sensitivity of 15.88 divisions per micron. The hydrogen sensitivity is calculated in a similar manner.

For the sample, the net peak height is multiplied by the galvanometer sensitivity factor and divided by the component sensitivity factor to get the parital pressure for each component. The sum of the calculated pressures may be checked against the total pressure measured in the instrument and recorded at the top of the graph. In this case the discrepancy is less than 1%. This comparison will detect any gross errors in peak height measurements.

The small peaks labeled "residual He" and "residual H_2" in the hydrogen and helium standards are a part of the instrument background; they are caused by the presence of small quantities of gas which have not been removed from the ionizing chamber by the ion-type vacuum pump used in this instrument. These peak heights (modified by the appropriate galvanometer sensitivity factor) may be assumed to be superimposed upon the peak heights in each mixture being analyzed. They are significant when one component is present in small concentrations, in which case the residual peak height is subtracted from the component peak height before the calculations are made.

D. OPERATIONAL DIFFICULTIES

In general the apparatus functioned satisfactorily, and no serious breakdowns occurred during this work. The principal problem encountered was that of raising the bath temperature above 20.4° rapidly, without boiling off too much of the liquid. This was done by pumping pure hydrogen gas into the liquid as described above.

The problems with the bath stirring mechanism and with thermocouple No. 2 have been mentioned above. Neither of these items was essential to the proper functioning of the apparatus.

One peculiar problem, not associated with a failure in the equipment, was encountered during the runs at the two lowest temperatures

(17.07 and 15.50°K). At these temperatures, at a pressure below 500 psia, the density of the vapor phase (which is mostly helium), becomes equal to that of the liquid phase (mostly hydrogen). At higher pressures the vapor phase is more dense and the mixture is apparently inverted in the equilibrium cell, with the liquid floating on top of the vapor. Smith[32] observed this phenomenon in his studies of the system and concluded that it occurred at pressures slightly above 500 psia in the temperature range over which he was working (17.4-21.8°).

Before runs were made at the lower temperatures in the present work, calculations were made to estimate the pressure at which this inversion should occur, using data on hydrogen and helium densities from Chelton and Mann.[59] These calculations indicated that at temperatures around 15.0° this inversion would take place at a pressure of about 350 psia, and at higher pressures with increasing temperatures.

When the run was made at 17.07°, the apparatus functioned normally for pressures up to 400 psia; however when an attempt was made to set the pressure at 500 psia there were two indications that the inversion pressure had been exceeded. First, the pressure in the circulation loop began to oscillate, with a period of several minutes, between about 480 psia and 505 psia; these oscillations leveled off to about 6 lb after 30 min. Secondly, there was a sharp increase in the rate of boil-off of the liquid hydrogen in the cryostat, requiring a readjustment in the valve settings in the vapor pressure control system. Neither of these phenomena had been observed previously. Assuming that the inversion had taken place, the probable explanations are as follows. The pumping action of the magnetic pump draws liquid up the outlet line of the equilibrium cell, and it vaporizes as it reaches a warmer portion of the equipment. This causes a gradual pressure rise, which continues until the evaporated liquid has traversed the circulation loop and re-entered the equilibrium cell where it condenses and (presumably) returns to the liquid by floating up through the vapor at the bottom. The increase in boil-off of the bath liquid can be explained as a result of the additional heat supplied by the condensation of the circulating mixture as it re-enters the cryostat.

During the 15.50° run, data were taken in the normal manner at 300 psia, but the phenomena described above occurred when an attempt was made to set the pressure at 400 psia.

At the two points mentioned above, where the phases were inverted, samples were taken in the usual manner, but the compositions obtained from their analyses were entirely inconsistent with the other results, and the data were discarded.

No further attempts were made to take data at pressures above the inversion point, since the inaccessible region covered only a small portion of the total area of interest. It appears that in subsequent studies of this system provisions will have to be made in the apparatus to enable data to be taken in the region where the inversion occurs. With an apparatus of the type used in this work this could be done very simply with the following three modifications to the present design: (1) add an additional capillary sampling line in the equilibrium cell to withdraw samples from near the top of the cell, (2) add a coil of copper tubing in the present vapor outlet line of the equilibrium cell at a point just above the cell, and (3) install a valve assembly in the circulation loop to allow the direction of flow of the vapor passing through the equilibrium cell to be reversed.

A simplified schematic diagram of a modified vapor recirculating system is shown in Fig. 25. For normal operation, valves A and B are open and C and D are closed; for reverse flow A and B are closed and C and D opened. When the phases are inverted in the cell, vapor would be withdrawn from the bottom, circulated through the external loop as before, and returned to the top of the cell to bubble down through the liquid. The functions of the other modifications are apparent.

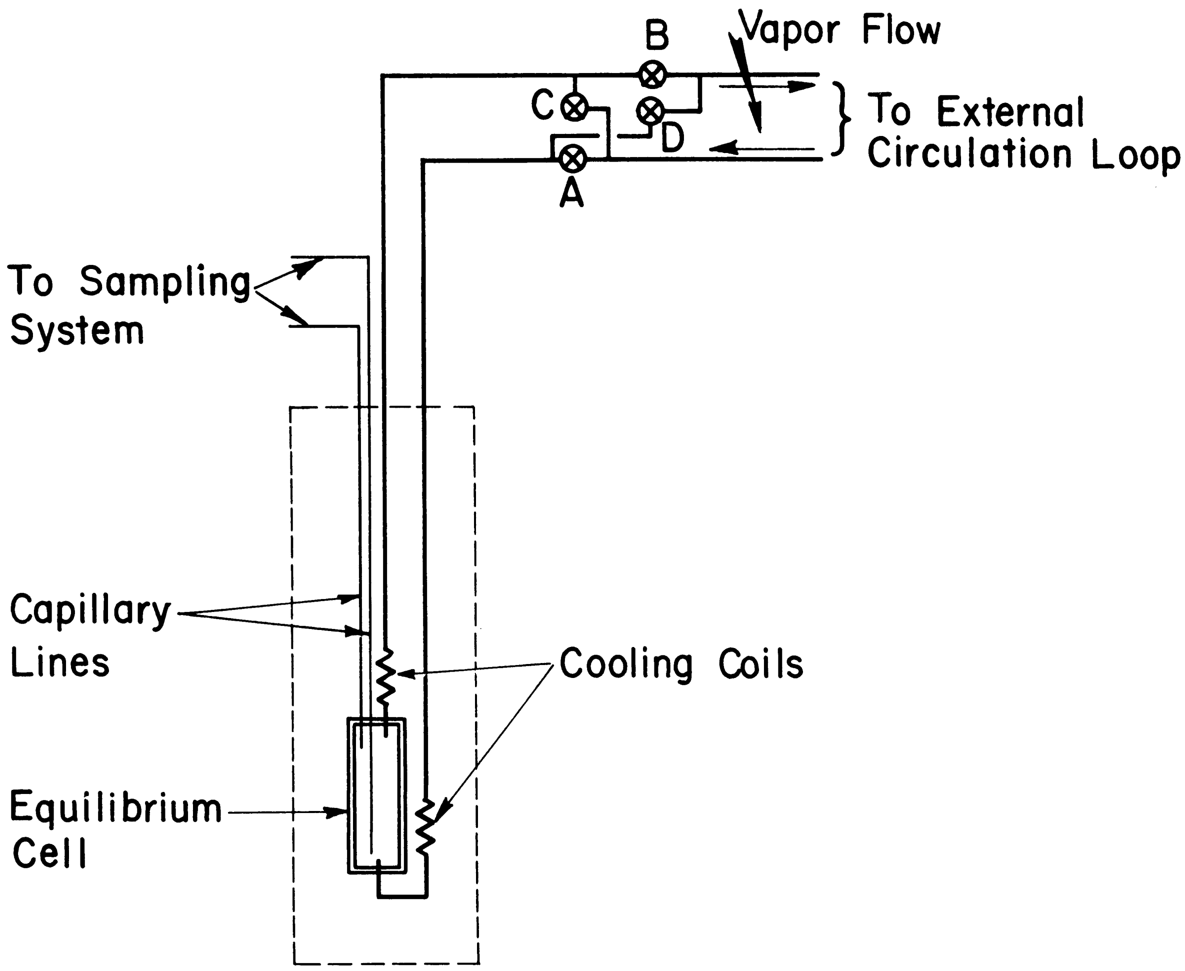


Fig. 25. Schematic diagram of modified vapor circulating system.

V. EXPERIMENTAL ERRORS

A. TEMPERATURE MEASUREMENT

1. Resistance Thermometer

The Leeds and Northrup type 8163 platinum resistance thermometer used in this work was calibrated by the National Bureau of Standards to an accuracy of 0.0001 ohm; the data furnished from this calibration consists of tabulated values of resistance vs. temperature for the platinum element. In the range of interest for the present work the values are tabulated at intervals of 0.1°K, and it is estimated that linear interpolation introduces errors not in excess of 0.0004°. A resistance change of 0.0001 ohm in the resistance element corresponds to temperature changes of about 0.005° at 15°, and 0.002° at 30°K.

The Leeds and Northrup type G-2 Mueller bridge is capable of accurately measuring resistances to within 0.0001 ohm when used with a type 2284-d reflecting glavanometer. A resistance change of 0.0001 ohm corresponds to a galvanometer deflection of about 1 mm, so it is possible to detect temperature changes ranging from 0.002 to 0.005°, depending on the temperature. However, since the International Temperature Scale is defined only to the nearest 0.01°, the temperatures reported here are rounded off to that accuracy.

2. Thermocouples

The construction of the thermocouples has been described previously.

Since they are used as differential thermocouples, producing small EMF's, they have not been calibrated. The temperature-EMF data used to convert the thermocouple readings to temperature is taken from Bunch and Powell.[62]

The Leeds and Northrup type K-3 potentiometer used in conjunction with these thermocouples has a sensitivity of ±(0.5 μv + 0.015% of the reading). Since the largest EMF's recorded were around 800 μv, the accuracy of all EMF's reported can be assumed to be 0.5 to 0.6 μv.

The gold-cobalt vs. copper thermocouples have a sensitivity varying from about 12.5 μv/degree at 15° to 21.3 μv/degree at 30°. Thus the temperatures measured by these thermocouples are accurate to within about ±0.04° at the lowest temperature and ±0.02° at the highest temperature.

3. Validity of Recorded Temperatures

The temperature indicated by the platinum resistance thermometer is assumed to be that of the mixture inside the equilibrium cell. This seems justified for the following reasons: (1) the platinum element is inserted in a hole drilled in the wall of the equilibrium cell and is therefore in intimate contact with the cell itself; (2) the thermal conductivity of copper at liquid hydrogen temperatures is several times its room temperature value, while its specific heat is about 1/10 of its room temperature value; and (3) the differential thermocouples just above and below the equilibrium cell consistently indicated EMF's of zero when both the cell and the thermocouples were immersed in the liquid. The temperature of the equilibrium cell may therefore be assumed to be essentially free of gradients.

Thermocouple No. 3 is located on the vapor inlet line of the equilibrium cell at a point about 1/2 in. from the bottom of the cryostat. Its reading would indicate any temperature difference between the vapor entering the cell and the cell itself. Whenever the reading at this thermocouple exceeded ±0.5 μv (the limiting sensitivity of the galvanometer) the experimental work was stopped; this occurred only when the liquid level began to drop below the top of the equilibrium cell, in which case the temperature at No. 3 would fall below that of the resistance thermometer. Throughout the experimental work the recirculating vapor entering the equilibrium cell was at a temperature which differed from that of the mixture in the cell by no more than ±0.03°K.

Thermocouples No. 1 and No. 4 are located on the vapor outlet lines of the equilibrium cell (see Fig. 20). They were placed at these points to determine if, at any time, the temperature of the outgoing vapor fell below that of the equilibrium cell; if this occurred it would mean that the vapor might partially condense as it flows out, giving it a limiting composition equal to that of the lower temperature. The only case in which a measurably lower temperature was recorded at either thermocouple was during the run of several points at 15.5°. The maximum reading at thermocouple No. 1 in this case was -2.3 μv, indicating a temperature difference of about 0.2°. A check of the temperature-composition plot of the experimental data shows that this could cause a limiting error in the vapor composition of about 0.03 mole percent, while the effect of the liquid composition would be negligible.

Thermocouple No. 5 is located on the vapor inlet line just below the counterflow heat exchanger (Fig. 20). It was placed there primarily to determine the effectiveness of the heat exchanger in lowering the temperature of the incoming vapor, and its readings are not critical in the evaluation of the experimental results.

Thermocouple No. 2 is located in a small hole near the base of the equilibrium cell on the opposite side of the cell from the platinum resistance element. Very early in the experimental work it apparently became grounded to the cell and thereafter gave erratic and inconsistent readings. However, because of the evidence cited above to indicate that the equilibrium cell was at a uniform temperature, the proper functioning of this thermocouple is not considered essential for accurate temperature measurement.

B. TEMPERATURE CONTROL

It has been pointed out above that the platinum resistance thermomenter and associated equipment used in this work are capable of detecting temperature changes of as little as 0.005°, or less, over the range of interest. In general, the temperature was controlled to within these limits except during the runs at 15.50° and 17.07°, during which the temperature varied by about ±0.02°. The reason for the poorer control during these runs is that the mercury switch in the vapor pressure control system was inoperative, and the bath pressure was controlled manually by observing the pressure on the 0-30 in. mercury manometer. The slopes of the isobaric data plots on the temperature-composition diagram shows that the change in composition with temperature in this region is quite small for both phases, so that a temperature error of 0.02° would cause an error in composition of 0.05 mole percent or less.

The control of the vapor pressure of the bath offers another means of estimating the maximum temperature fluctuations in the bath. In general the vapor pressure of the bath is slightly higher than that corresponding to the temperature indicated by the platinum resistance thermometer. This is apparently due to a slight temperature gradient at the top of the liquid caused by the flow of heat down the walls of the cryostat and the heat introduced by the recirculating vapor. Nevertheless, the bulk of the liquid is essentially free of temperature gradients, and once the pressure is set, the temperature remains constant.

The magnitude of the pressure fluctuations in the cryostat can be determined from the motion of the mercury in the U-tube mercury switch (Fig. 14), which functions as a differential manometer. With careful setting of the controls, the linear motion of the mercury in the U-tube is observed to be less than about 1 mm, and the accompanying pressure fluctuations are slightly less since the U-tube is tilted to produce a greater linear travel for a given pressure change. A check of vapor pressure data for hydrogen[45] indicates that this provides temperature control consistent with that indicated by the resistance thermometer.

C. PRESSURE MEASUREMENT

The only pressure which must be accurately measured is that of the equilibrium mixture in the circulation loop. This is measured with a 0-500 psig calibrated 16 in. Heise gage, having an accuracy of 0.1% of full scale reading over the entire scale. The equilibrium pressures reported here are accurate to within ±0.5 psi.

D. ATTAINMENT OF EQUILIBRIUM

Equilibrium is assumed to be reached when the compositions of the two phases no longer change with time. During the early work the time required was determined to be on the order of 10 to 15 min, and thereafter 20 to 30 min was allowed for each mixture to reach equilibrium.

E. GAS PURITY

The hydrogen gas used in making up the equilibrium mixtures is Matheson ultra-pure grade hydrogen having total impurities of less than 10 ppm.

The helium used in the mixture is special analyzed helium, donated by the U. S. Bureau of Mines Helium Research Center, Amarillo, Texas. It has total impurities less than 12 ppm.

F. SAMPLING

Errors introduced in sampling, especially those associated with the fractionation of the liquid, are prominently mentioned in many papers on low temperature vapor liquid equilibria. Fractionation, if it occurs, would be expected to cause considerable scatter in the data and to make reproducibility difficult. The capillary continuous sampling system used in the present work gave consistently reproducible results which show relatively little scatter. The data agree quite well with that of Smith[32] (see Chapter VI) who used a different method of sampling.

G. MASS SPECTROMETER ANALYSIS OF GAS SAMPLES

In the routine analysis of gas samples on the mass spectrometer, the following three sources of error are considered.[60]

1. Change in instrument calibration,
2. Impurities in the calibrating gases, and
3. Presence in the mixture of materials not included in the analysis.

The latter problem has no effect on the analysis when unicomponent peaks are used in the calculations. In the present work, for example, the presence of a trace of air in the sample will not affect the accuracy of the analysis, since the peak heights will still give the correct hydrogen to helium ratio. In this case the air would represent an impurity added to the mixture after it was with drawn from the system, so it would not be considered a part of the sample in any case.

The calibrating gases used in the analyses are known to be of high purity. No appreciable error is considered to have been introduced because of impurities in these gases.

It is know that the sensitivity of the instrument to hydrogen may change with time. To reduce this source of error to a minimum, hydrogen standards were run frequently, usually at the beginning and end of each day's run on the mass spectrometer. The hydrogen sensitivities at the beginning and end of each day were then calculated, and a linear change with time was assumed to have occurred throughout the day between these values. This is a standard procedure in minimizing errors due to changes in instrument calibration.

The total of all errors in the mass spectrometer analysis of the sample may be expressed as an error in the mole percent calculated for a given component. The manufacturer of the Consolidated model 21-103 mass spectrometer quotes[61] the following maximum errors from all causes:

% Component (Mole %)	Maximum Deviation (Mole %)	Maximum % Deviation
100.0	±1.0	± 1.0
10.0	±0.10	± 1.0
1.0	±0.05	± 5.0
0.10	±0.01	±10.0

During a period of several months just prior to the time the samples taken in this work were analyzed, the mass spectrometer underwent a very thorough inspection and calibration. Carefully prepared samples of known composition were run and errors in the analyses were consistently within the limits listed above. These limits of accuracy are assumed to apply to the analyses of samples taken in this work.

VI. EXPERIMENTAL RESULTS

A. GENERAL

The experimental results reported here consist of vapor and liquid phase compositions at eleven different temperatures, covering the range 15.50 to 32.50°K, and at pressures from hydrogen saturation pressure to 500 psia. The data are for mixtures or normal hydrogen (75% orthohydrogen, 25% parahydrogen) and helium.

B. PRESENTATION OF DATA

The results of the experiment are summarized in Table I and Figs. 26-31. In general, points were taken along each isotherm at pressure intervals of 25 psi up to 200 psia, and at the higher pressures 250, 300, 400, and 500 psia. The three points run at 31.60° were taken in an attempt to locate the critical point for that isotherm.

Figure 26 is an isothermal pressure-composition diagram, representing the projection on the P-x coordinate plane of curves cut in the P-T-x surface by planes of constant temperature. A portion of this diagram, on which most of the liquid lines cross each other, is shown on an expanded scale in Fig. 27.

Figure 28 is a plot of the data on a temperature-composition diagram. These curves are projections on the T-x coordinate plane of curves cut in the P-T-x surface by planes of constant pressure. Because the data were taken at the same pressures at each temperature,

TABLE I

SUMMARY OF EXPERIMENTAL DATA

Temperature (°K)	Pressure (psia)	Liquid		Vapor	
		Mole % He	Mole % H_2	Mole % He	Mole % H_2
15.50	49.5	---	---	93.78	6.22
	75.0	0.29	99.71	95.51	4.49
	100.0	0.46	99.54	96.31	3.69
	125.0	0.51	99.49	96.77	3.23
	150.0	0.55	99.45	97.02	2.98
	175.0	0.64	99.36	97.14	2.86
	200.0	0.71	99.29	97.29	2.71
	250.0	0.82	99.18	97.41	2.59
	300.0	0.87	99.13	97.48	2.52
17.07	56.5	0.36	99.64	89.67	10.33
	75.0	0.43	99.57	91.86	8.14
	100.0	0.57	99.43	93.30	6.70
	125.0	0.72	99.28	94.12	5.88
	150.5	0.80	99.20	94.64	5.36
	175.0	0.89	99.11	95.03	4.97
	200.0	1.00	99.00	95.15	4.85
	250.0	1.14	98.86	95.56	4.44
	300.0	1.31	98.69	95.82	4.18
	400.0	1.51	98.49	95.90	4.10
20.40	35.0	0.34	99.66	53.60	46.40
	50.0	0.41	99.59	65.45	34.55
	75.0	0.61	99.39	75.40	24.60
	100.0	0.84	99.16	80.30	19.70
	125.0	1.05	98.95	83.20	16.80
	150.0	1.30	98.70	84.80	15.20
	175.0	1.54	98.46	86.03	13.97
	200.0	1.67	98.33	87.13	12.87
	250.0	2.05	97.95	88.41	11.59
	300.0	2.36	97.64	88.97	11.03
	400.0	2.96	97.04	90.08	9.92
	500.0	3.39	96.61	90.35	9.65
23.00	50.0	0.38	99.62	37.00	63.00
	75.0	0.75	99.25	53.44	46.56
	100.0	1.15	98.85	62.90	37.10
	125.0	1.36	98.64	67.87	32.13
	150.0	1.72	98.28	71.75	28.25
	175.0	2.15	97.85	74.35	25.65

TABLE I (Continued)

Temperature (°K)	Pressure (psia)	Liquid		Vapor	
		Mole % He	Mole % H_2	Mole % He	Mole % H_2
	200.0	2.39	97.61	76.30	23.70
	250.0	2.91	97.09	78.78	21.22
23.00	300.0	3.55	96.45	80.55	19.45
	400.0	4.58	95.42	82.34	17.66
	500.0	5.46	94.54	83.30	16.70
	81.0	0.67	99.33	22.60	77.40
	100.0	0.97	99.03	33.50	66.50
	125.0	1.43	98.57	43.37	56.63
	150.0	1.92	98.08	49.77	50.23
26.00	200.0	2.86	97.14	56.90	43.10
	250.0	3.64	96.36	62.67	37.33
	300.0	4.76	95.24	65.65	34.35
	400.0	6.64	93.36	68.58	31.42
	500.0	8.48	91.52	70.02	29.98
	127.0	0.91	99.09	14.03	85.97
	151.0	1.50	98.50	21.92	78.08
	175.0	2.20	97.80	27.75	72.25
	200.0	3.07	96.93	32.93	67.07
29.00	250.0	4.59	95.41	39.54	60.46
	300.0	6.21	93.79	43.70	56.30
	400.0	9.63	90.37	47.95	52.05
	500.0	13.35	86.65	49.20	50.80
	300.0	7.29	92.71	30.32	69.68
30.60	400.0	13.24	86.26	32.60	67.40
	450.0	17.95	82.05	30.36	69.64
	176.5	1.49	98.51	11.28	88.72
	199.0	2.51	97.49	15.59	84.41
	250.0	4.78	95.22	22.58	77.42
	300.0	7.49	92.51	26.57	73.43
31.00	325.0	8.73	91.27	27.55	72.45
	350.0	11.03	88.97	27.85	72.15
	375.0	12.93	87.07	27.59	72.41
	400.0	15.64	84.36	25.78	74.22
	413.0	20.87	79.13	21.85	78.15

TABLE I (Concluded)

Temperature (°K)	Pressure (psia)	Liquid		Vapor	
		Mole % He	Mole % H_2	Mole % He	Mole % H_2
31.50	177.0	1.27	98.73	7.67	92.33
	200.0	2.30	97.70	11.94	88.06
	225.0	3.61	96.39	15.64	84.36
	250.0	4.83	95.17	18.35	81.65
	275.0	6.26	93.74	20.30	79.70
	300.0	8.18	91.82	21.37	78.63
	325.0	10.47	89.53	21.49	78.51
	351.0	16.59	83.41	17.58	82.42
31.90	174.5	0.81	99.19	4.00	96.00
	200.0	2.07	97.93	8.31	91.69
	220.0	3.17	96.83	11.75	88.25
	238.5	4.29	95.71	13.86	86.14
	250.5	4.99	95.01	14.82	85.18
	261.5	---	---	15.62	84.38
	275.5	6.87	93.13	16.19	83.81
	289.5	8.71	91.29	16.35	83.65
	300.0	10.10	89.90	15.88	84.12
	308.5	12.02	87.98	---	---
32.50	188.5	0.98	99.02	3.12	96.88
	200.0	1.68	98.32	4.80	95.20
	220.0	3.10	96.90	7.45	92.55
	242.0	5.09	94.91	---	---
	250.0	5.99	94.01	---	---
	258.0	6.75	93.25	---	---

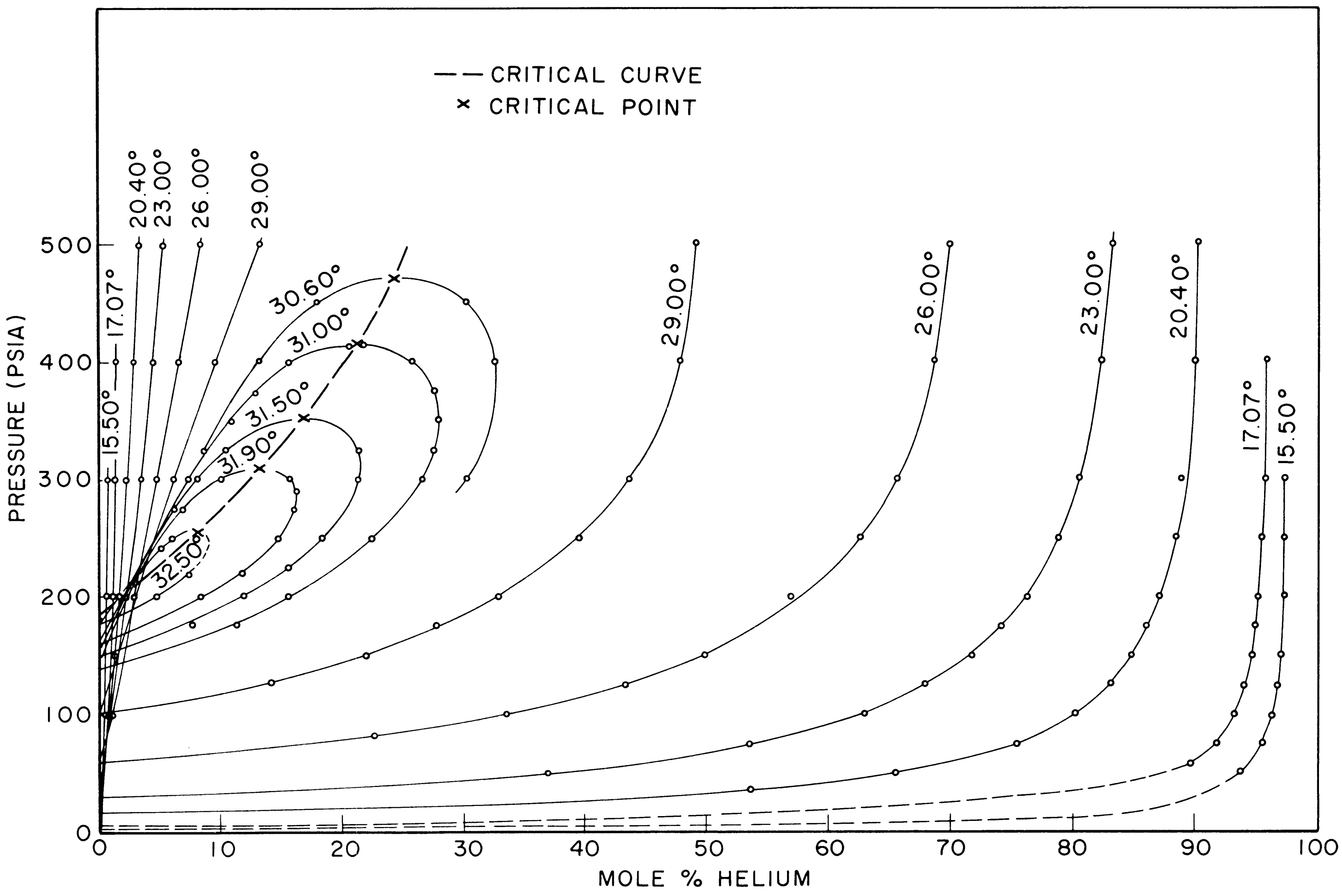


Fig. 26. Isothermal pressure-composition diagram.

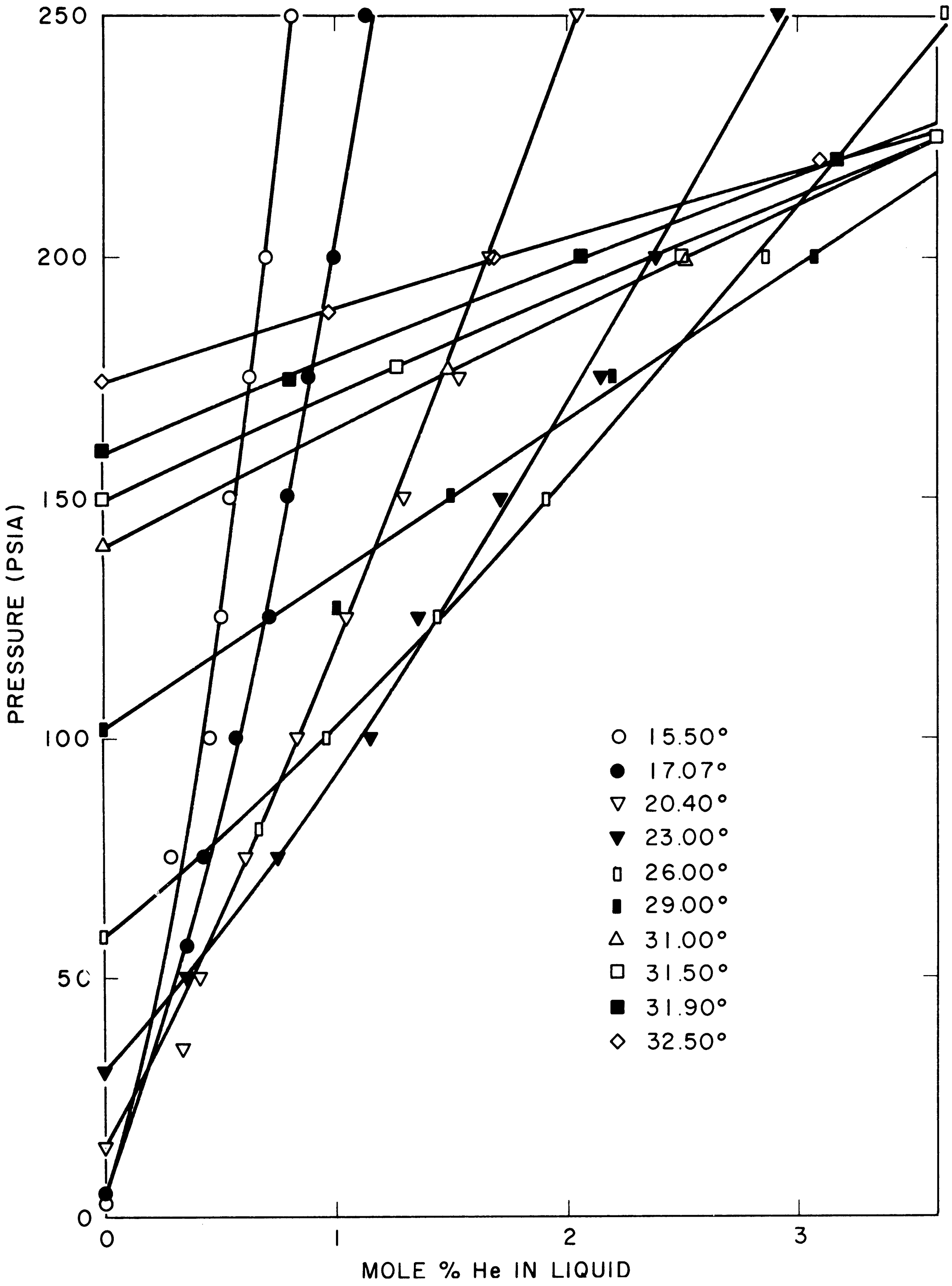


Fig. 27. Isothermal pressure-composition diagram showing liquid region on expanded scale.

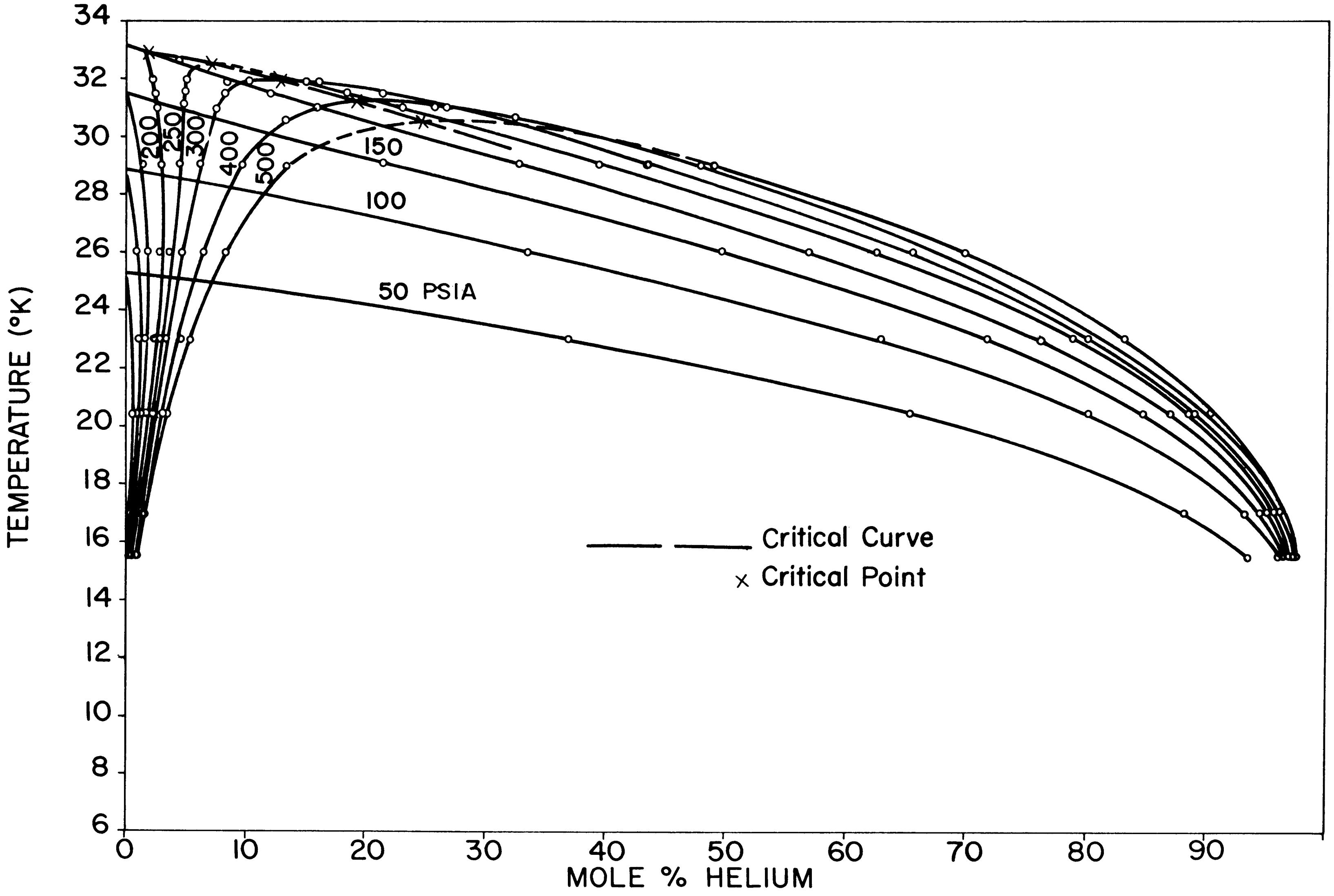


Fig. 28. Isobaric temperature-composition diagram.

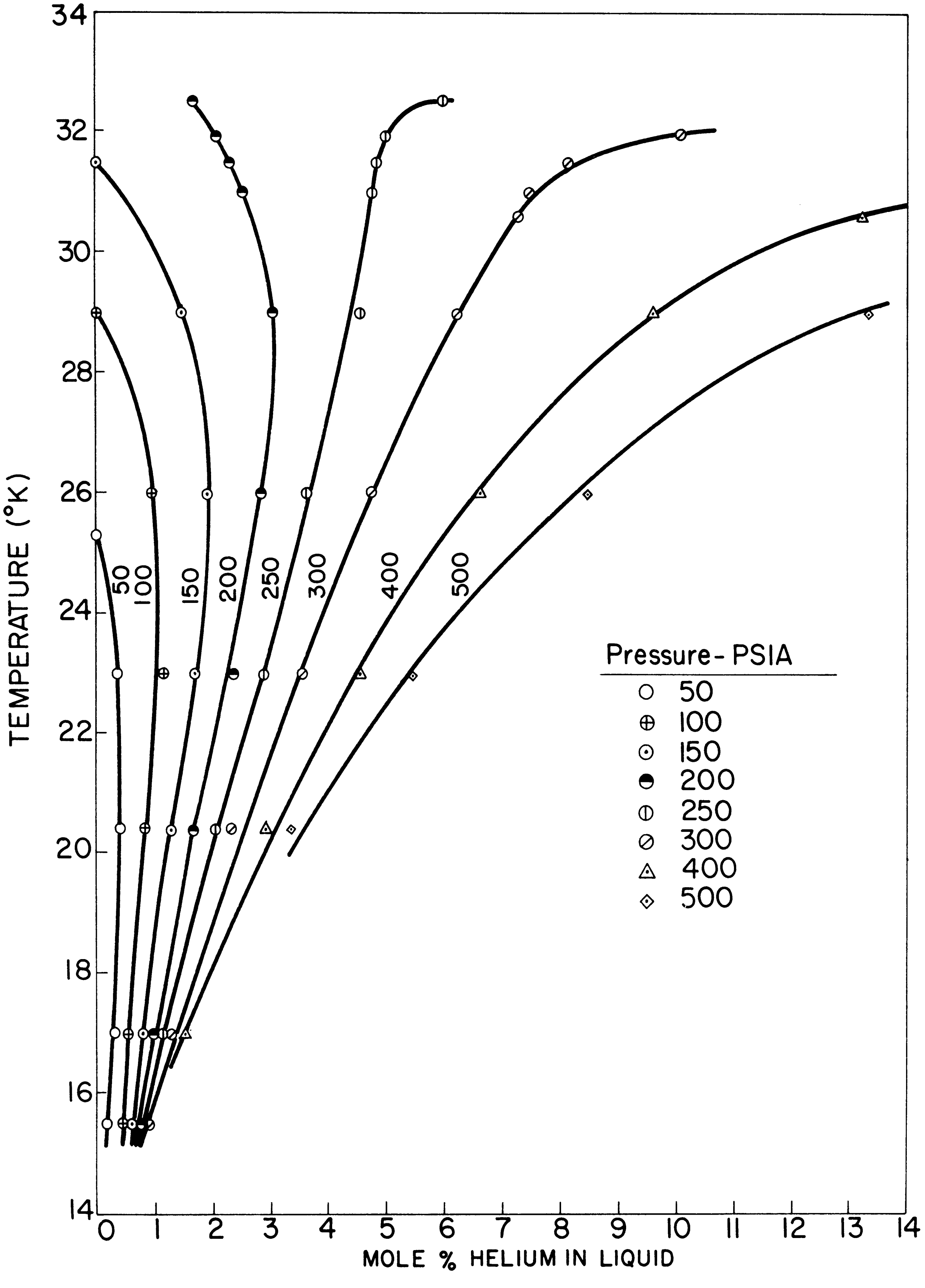


Fig. 29. Isobaric temperature-composition diagram showing liquid region on expanded scale.

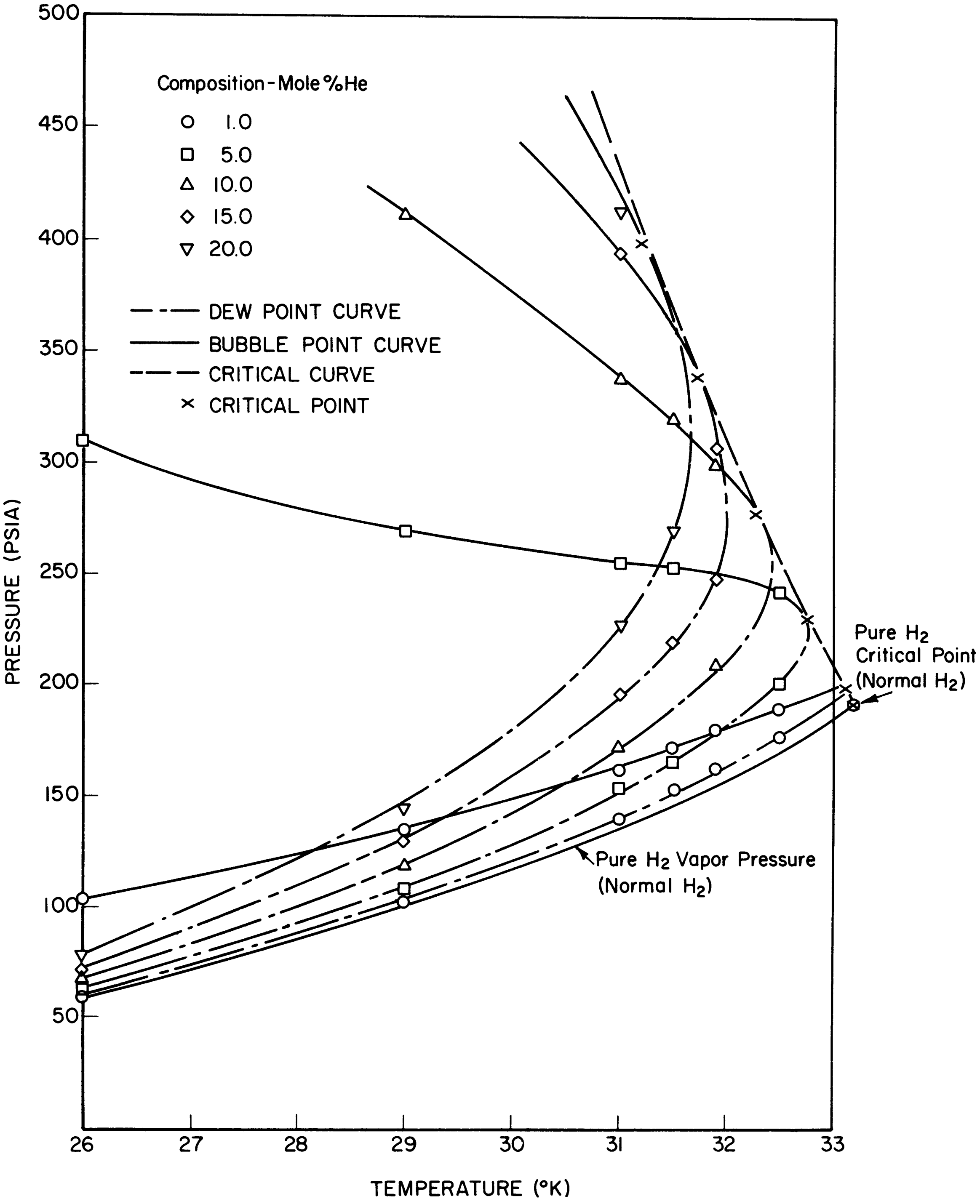


Fig. 30. Pressure-temperature diagram.

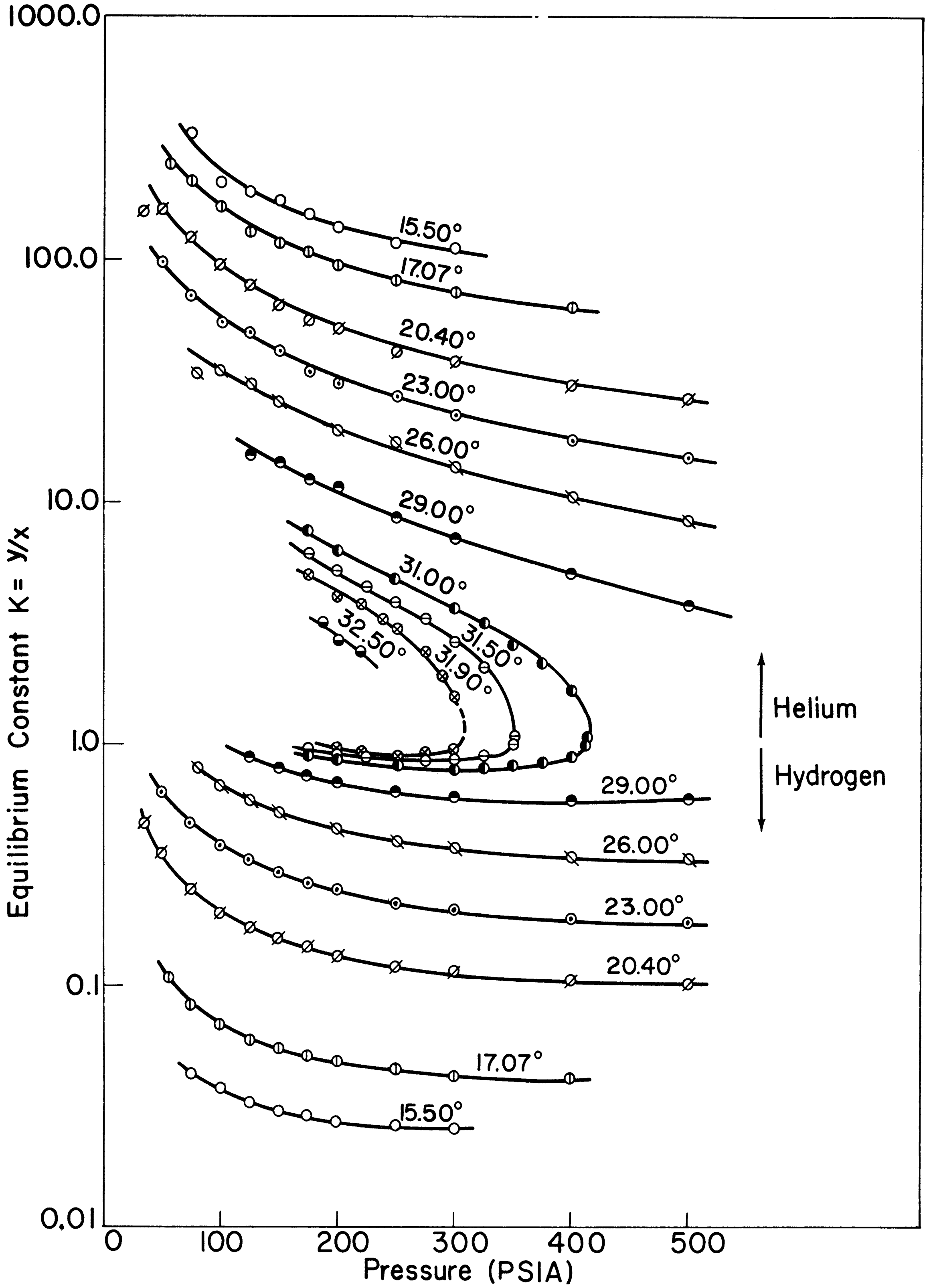


Fig. 31. Equilibrium K values.

very little interpolation of the P-x isotherms was required to plot the curves in Fig. 28. Figure 29 shows the liquid region of the temperature-composition diagram on an expanded scale.

Figure 30 shows a cross-plot of the data from Figs. 26 and 28 on a pressure-temperature diagram. These curves are lines cut in the P-T-x surface by planes of constant composition.

Figure 31 is a plot of equilibrium constants K vs. pressure. The constant K is defined as the ratio of the mole fraction of a component in the vapor to its mole fraction in the liquid.

C. DISCUSSION

The behavior of this system, as shown by the curves in Figs. 26-30, is similar to that of other systems involving components whose critical points are far apart. Similar behavior is exhibited, for example, by the systems nitrogen-helium,[24,63] and nitrogen-hydrogen.[16]

In the P-x diagram of Fig. 26 and the T-x diagram of Fig. 28, each curve is divided into two branches, representing the equilibrium liquid and vapor compositions. At fixed pressure and temperature (represented by a horizontal line in either diagram) the two co-existing phases lie at the ends of a horizontal line between the two curves. The region between the curves represents mixtures consisting of two phases, while points outside are in a single phase region. The two branches of each equilibrium curve on these diagrams merge at a point at which the two phases become indistinguishable. These points are called critical points and their locus on the P-T-x surface is called the critical curve. It projects as a smooth curve on each of the three coordinate planes of the P-T-x diagram. In general, the critical curve will appear on the pressure-temperature plot as an envelope (sometimes called the critical envelope) which is tangent to each of the curves of constant composition; thus critical points will always appear as maxima or minima on the curves in the P-x and T-x diagrams. A further discussion of this subject may be found in the book by Ruhemann.[16]

Each of the closed loops in Fig. 26 includes a region of retrograde condensation. This is that portion of the curve which lies to the right of a vertical line through the critical point of the loop. For example, if a low pressure gas mixture containing 25% helium is compressed isothermally at 31.0°, condensation will occur first at a pressure of about 275 psia. Condensation will continue upon further compression up to about 380 psia; however at higher pressures the liquid will begin to evaporate and will disappear completely around 405 psia, leaving a single vapor phase as in the beginning.

In Fig. 27 the scatter in the liquid region of low helium content is greatly magnified. In general, the deviation of points from a smooth curve does not exceed 0.1 mole percent, which for most points does not exceed the limits of accuracy of the mass spectrometer in this region.

In Figs. 28 and 29, the data exhibit reverse-order solubility in the liquid region. This is defined as an increase in the solubility of a constituent with increasing temperature, at constant pressure, and is characterized by a positive slope of the liquid lines on the T-x diagram.

The area on the P-x diagram of Fig. 26 in which the liquid lines cross represents a region in which a minimum occurs in the bubble point curves in the P-T diagram. Thus a minimum would be expected in the bubble point curves for mixtures with up to 4% helium. (The minimum in the 1% line in Fig. 30 is out of the range of the diagram to the left.)

The critical curve shown in Figs. 26, 28, and 30 has been estimated from a study of the trend of the data on the P-x, T-x, and P-T plots. Because of the flatness of the P-T-x surface in the vicinity of the critical curve, it is difficult to locate critical points accurately. No visual observation of phenomena in the critical region was possible in this experiment, due to the nature of the apparatus.

The best estimate of the location of the critical curve is obtained from the P-x plot of Fig. 26. For the 31.00° and 31.50° isotherms, experimental points were obtained which permitted the loops to be completely closed without extrapolation, and this served to define the general shape of all loops at nearby temperatures.

Several runs were made at the higher temperatures in an attempt to complete those loops which close at pressures below 500 psia. With an apparatus of the type used in this work, the problem is somewhat difficult. At a given temperature, say 31.5°, pure hydrogen is charged into the cell and a predetermined amount of liquid is condensed. At this point the contents of the cell are represented by the point in Fig. 26 at which the 31.5° loop touches the left edge of the diagram. Helium is added to the loop and the pressure rises, and a curve of total composition vs. pressure for the mixture extends into the loop. With further addition of helium, the pressure and total helium content increase; however the path followed by the line representing total composition is not accurately known, and a two-phase mixture will exist only as long as the curve remains inside the loop. It may happen that it passes out of the loop and into a single phase region before the critical pressure is reached. This would mean either that all of the liquid had evaporated (exit on the vapor side), or that the cell became swamped with liquid (exit on the liquid side). During the run at 32.5° the cell apparently became swamped with liquid at a pressure above 220 psia, since the samples taken at higher pressure showed the same composition for liquid and vapor, although the compositions fell along a smooth curve with the liquid data at lower pressures. The same phenomenon was observed at 31.9° and 308.5 psia.

In general there is reasonable agreement between the critical curves obtained on each of the three diagrams (P-x, T-x, and P-T). The critical points indicated on these diagrams are estimated to be accurate to within ±10 psi, ±0.2°K, or ±0.2 mole percent.

VII. ANALYSIS OF EXPERIMENTAL RESULTS

A. COMPARISON WITH PREVIOUS WORK

1. General

The work of Smith[32] and of Roellig and Giese[33] on the vapor-liquid equilibrium of the hydrogen-helium system has been mentioned previously. A comparison of their results with the present work is shown in Figs. 32-35.

2. Comparison With Data of Smith

Of the three isotherm studied by Smith, only that at 20.4° was duplicated in the present work. A comparison with Smith's results at this temperature is shown in Figs. 32 and 33. The agreement is quite good. Smith's work shows somewhat more scatter, especially in the vapor phase compositions.

To obtain a comparison with Smith's work at 17.4° and 21.8°, data at these temperatures were obtained for the present work by graphical interpolation of the temperature-composition diagrams of Figs. 34 and 35. A plot of this data on a large scale was used for this interpolation. The comparison is shown in Figs. 34 and 35. The agreement is not as good as that at 20.4°. A study of the data indicates that smooth curves through Smith's data agree reasonably well with isotherms of the present work which are about 0.3 to 0.4°K lower than the temperatures reported by Smith. This discrepancy may be due to the method of

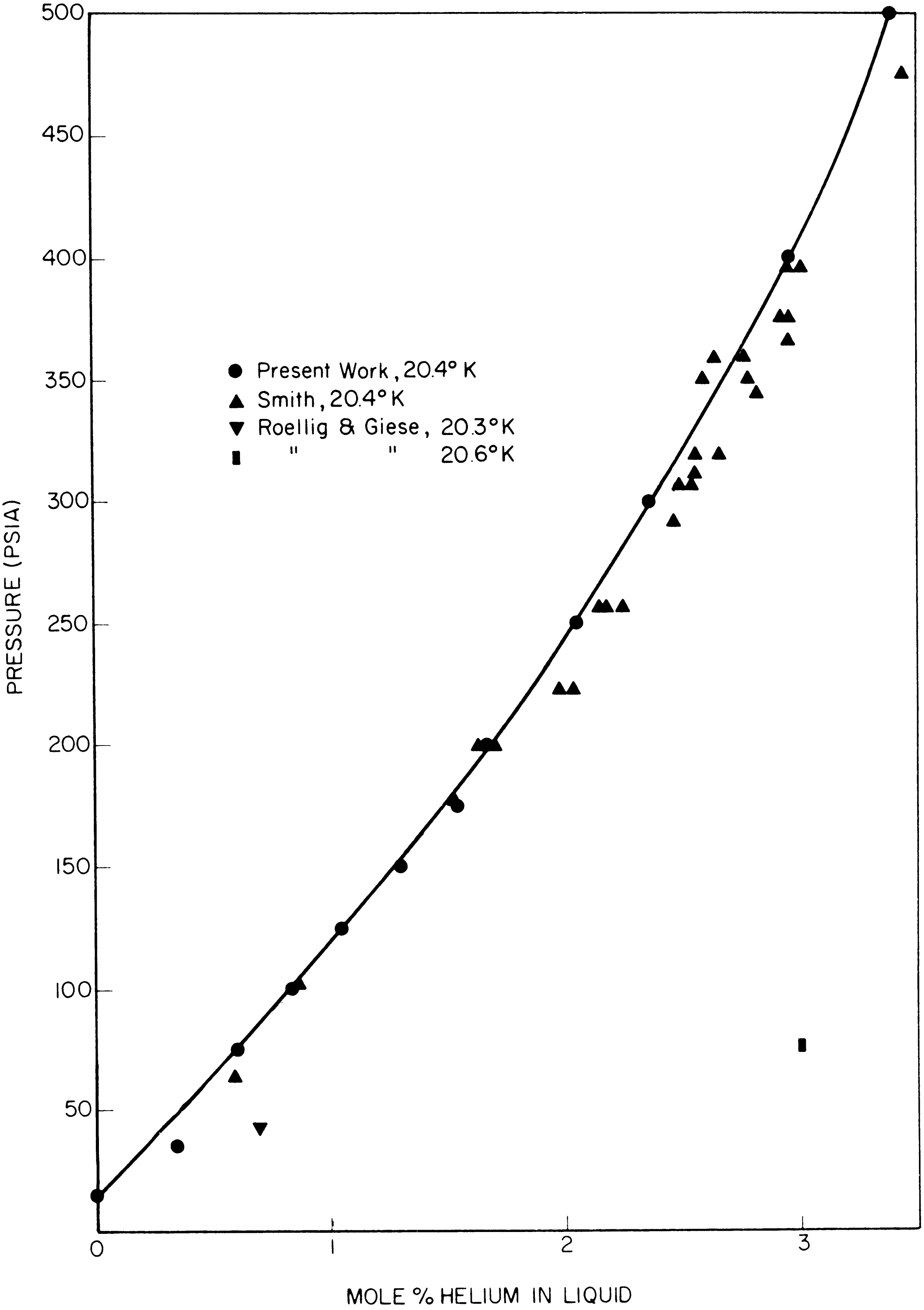


Fig. 32. Comparison with previous work, liquid data at 20.4°K.

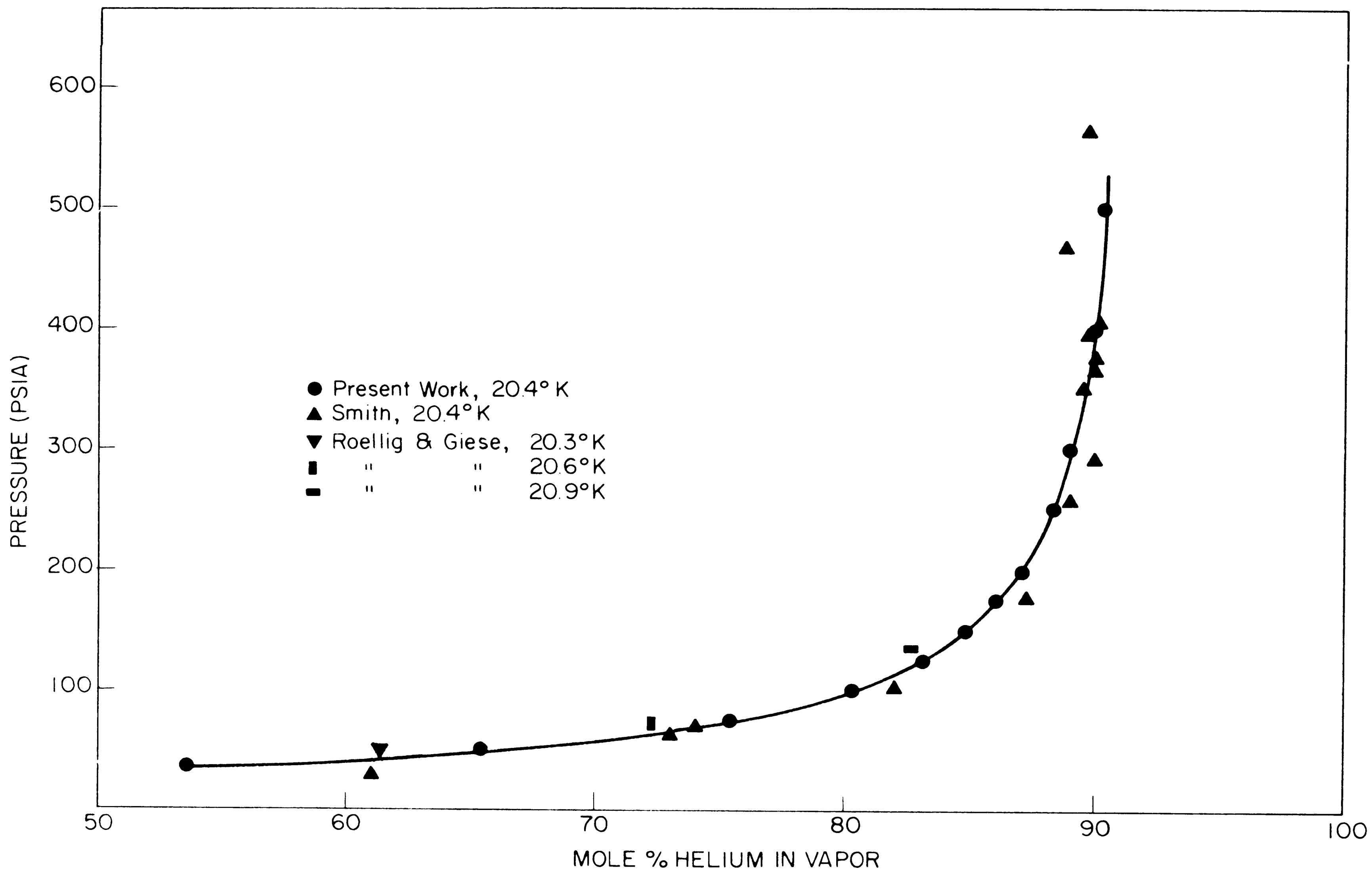


Fig. 33. Comparison with previous work, vapor data at 20.4°K.

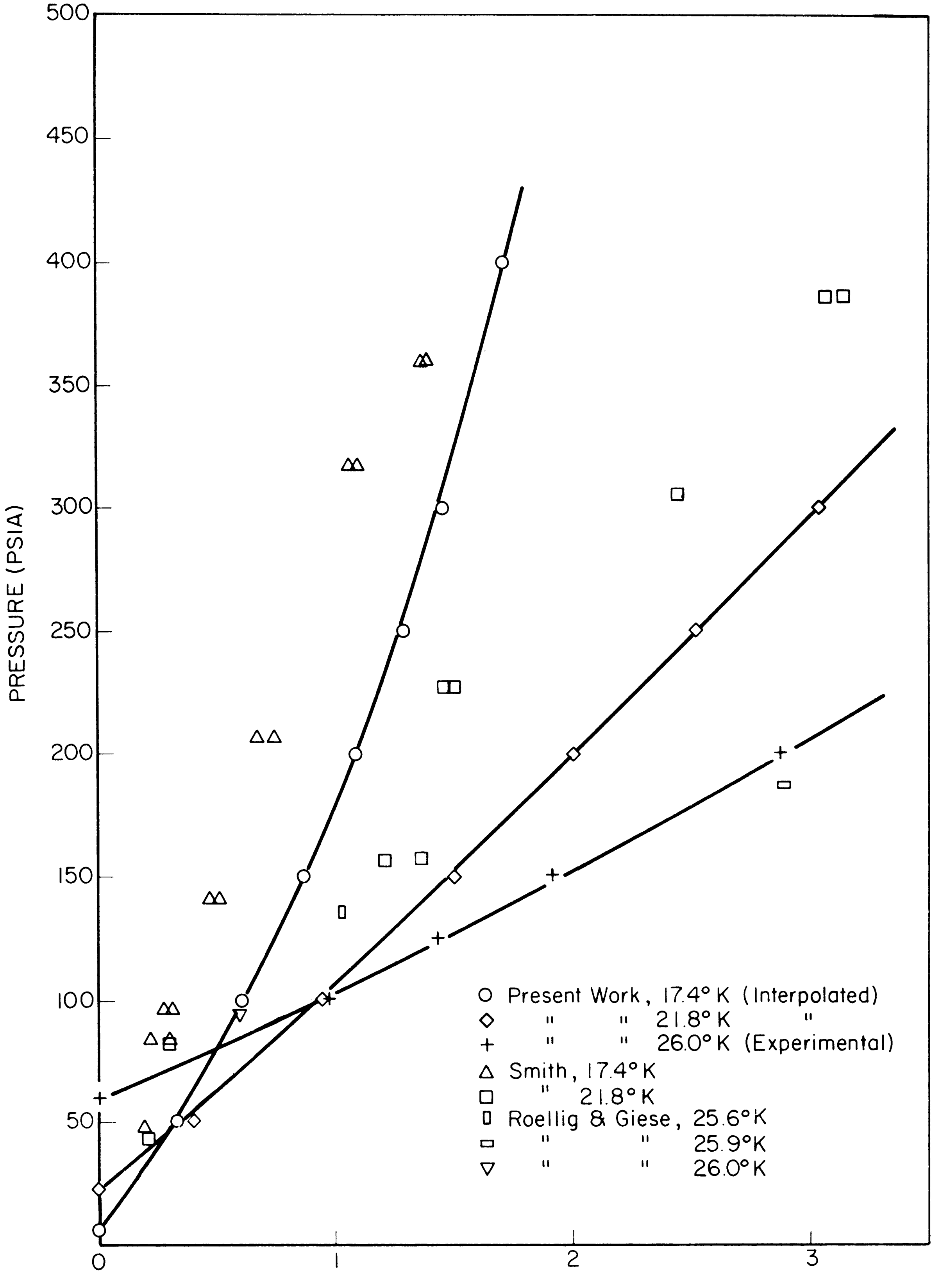


Fig. 34. Comparison with previous work, liquid data at 17.4, 21.8, and 26.0°K.

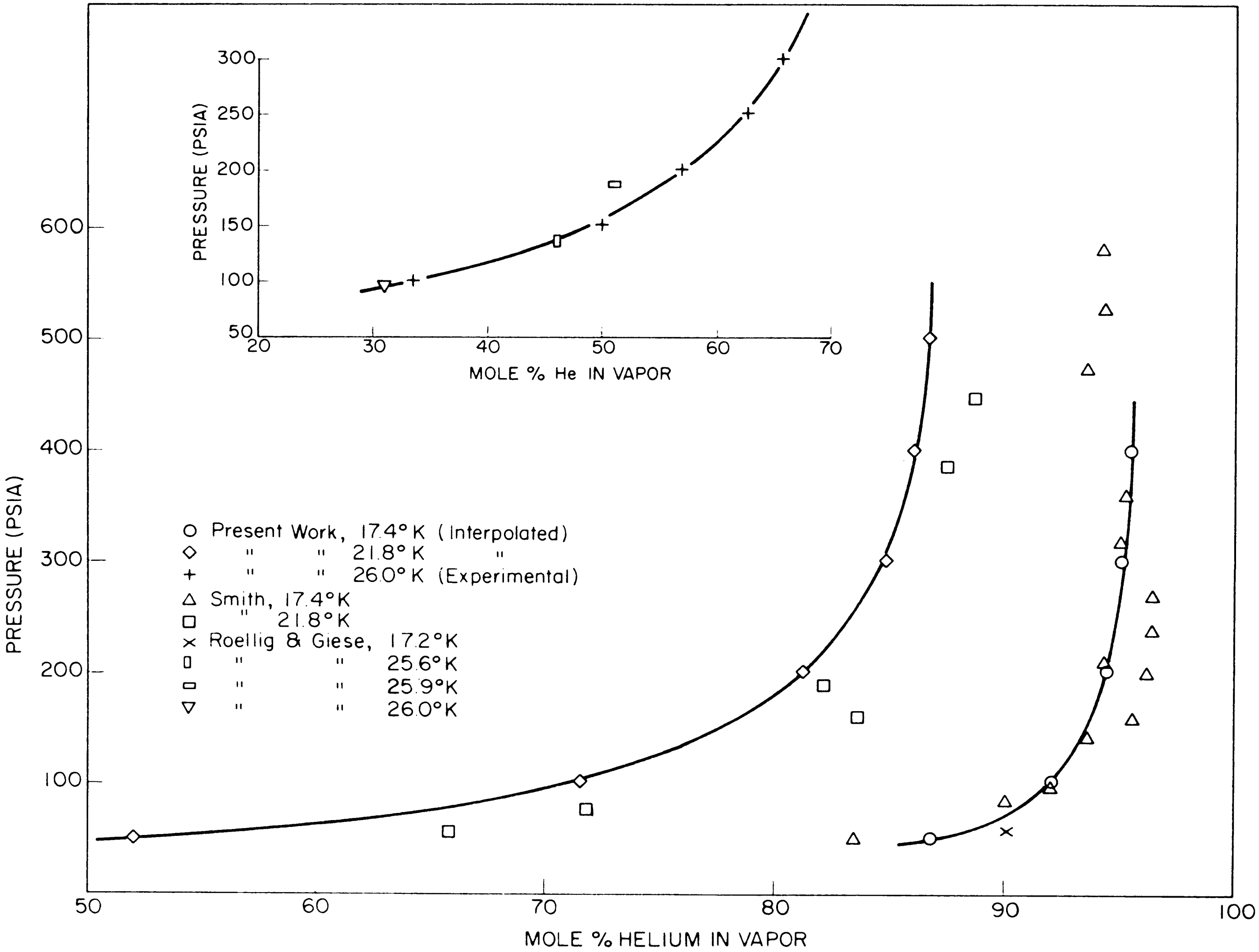


Fig. 35. Comparison with previous work, vapor data at 17.4, 21.8, and 26.0°K.

temperature measurement used by Smith. He reported temperatures measured with a single copper-constantan thermocouple referenced in an ice bath. The sensitivity of copper-constantan thermocouples at liquid hydrogen temperatures is about 5 μv/degree, and the total EMF (reference junction at 0°C) is over 6000 μv. An error of 1 μv would introduce a temperature error of about 0.2°K. Accurate temperature measurement would require very precise calibration of the thermocouple and very accurate measurement of the EMF. To determine the temperature to within ±0.01°, as reported by Smith, the EMF would have to be measured to within ±0.05 μv, or ±0.008% of the total. Even then, the results would be questionable. Scott[45] states that the best copper-constantan thermocouples are rarely free of stray EMF's due to inhomogeneities to better than 1 or 2 μv in 5000.

3. Comparison With Data of Roellig and Giese

Comparison with the data of Roellig and Giese cannot be made directly. They reported nine separate points, giving only the temperature, partial pressure of helium in the vapor, and mole percent helium in the liquid. Total pressure and vapor phase composition can be determined for each point by reversing the calculations they used to obtain the values reported.

To make the comparison given here, the values of temperature calculated by Eckert and Prausnitz[35] have been used with the data of Roellig and Giese. Roellig and Giese measured temperatures indirectly, using experimentally determined liquid and vapor phase compositions and assuming Raoult's law valid for the liquid and ideal gas behavior for the vapor. They obtained a value for the vapor pressure of hydrogen and took the temperature from the hydrogen vapor pressure curve. Eckert and Prausnitz observed that the assumption of Raoult's law and ideal vapor leads to significant errors in the temperature. Using a rigorous thermodynamic equation in place of the ideal relation, they recalculated the temperatures, assuming only that liquid hydrogen is in compressible and that the Lewis-Randall rule can be used to determine the fugacity of hydrogen in the liquid. The resulting temperatures differ from those of Roellig and Giese by as much as 2.7°K. While these temperatures are probably more accurate than those arrived at by Roellig and Giese, they will still reflect any errors in the determination of the phase compositions.

The data are listed in Table II, showing both temperatures for each point. Vapor phase compositions and total pressure were calculated by this author from the published data of Roellig and Giese.

The liquid phase compositions for the two temperatures 20.6 and 20.9° (calculated by Eckert and Prausnitz) are plotted in Fig. 32. The lack of agreement is apparent. The three liquid points at 26.0, 25.6, and 25.9° are plotted in Fig. 34, and agree reasonably well with the 26.0° isotherm of this work.

TABLE II

DATA OF ROELLIG AND GIESE

Temp, °K Roellig and Giese	Temp, °K Eckert and Prausnitz	Pressure (psia)	Liquid Mole %		Vapor Mole %	
			He	H_2	He	H_2
16.3	16.1	30.9	1.26	98.74	88.7	11.3
17.7	17.2	61.4	3.80	96.20	89.8	10.2
19.8	18.6	114.3	11.05	88.95	89.9	10.1
20.7	20.3	42.5	0.69	99.31	61.1	38.9
21.6	20.6	74.6	3.01	96.99	72.3	27.7
22.3	20.9	135.8	8.35	91.65	82.7	17.3
26.8	26.0	96.8	0.59	99.41	31.1	68.9
27.3	25.6	137.6	1.03	98.97	46.2	53.8
28.6	25.9	187.0	2.89	97.11	51.0	49.0

The vapor phase compositions for the above five points, along with that of the 17.2° point are shown in Figs. 33 and 35. Thes show excellent agreement with the present work.

Roellig and Giese concluded from their limited data that the solubility of helium in the liquid increases with a decrease in temperature—just the opposite of the behavior observed in this work.

B. THERMODYNAMIC TREATMENT

1. Previous Work

The original work of Smith[32] on the hydrogen-helium system includes a review of some thermodynamic relations used to calculate the fugacities of components in vapor and liquid mixtures.

Smith applied several of these methods to the calculation of the fugacities of each component in the vapor, and compared the results to ideal behavior described by Henry's law and Raoult's law. His calculations are somewhat difficult to follow. He first calculated the helium vapor phase fugacity by the Lewis-Randall rule; and then calculated the fugacity of the mixture, using a two constant virial equation of state. He used these results to calculate the vapor phase fugacity of hydrogen, using an equation relating component fugacities to mole fractions and total fugacity. He did not take the obvious step of calculating the fugacity of hydrogen in the liquid and comparing it to the calculated vapor phase fugacity.

Brazinsky and Gottfried[37] have pointed out that Smith's vapor phase hydrogen fugacities are in poor agreement with the liquid phase fugacities calculated from the Lewis-Randall rule. They concluded that the disagreement was due to incorrect values of the second virial coefficient for hydrogen-helium mixtures used by Smith. They recalculated the hydrogen vapor phase fugacities, using better values for the virial constants, and obtained reasonable agreement between these values and the liquid fugacities calculated from the Lewis-Randall rule. Eckert and Prausnitz[35] have pointed out however that this is a very insensitive test, as five- or ten-fold changes in the helium content of the liquid will not affect the results.

2. Other Theoretical Considerations

The test performed by Brazinsky and Gottfried is a comparison of the calculated vapor and liquid phase fugacities of a single component at separate pressure-temperature points; these should be equal for a system in equilibrium. Another type of commonly used consistency test is based on the Gibbs relation between partial modal free energies of the components in a single phase:

$$SdT - VdP + x_A d\bar{G}_A + x_B d\bar{G}_B = 0 \qquad (1)$$

Many variations of this relation have been developed and used, in both differential and integral forms, to correlate and predict vapor-liquid equilibrium data. Perhaps the most commonly used form is the Gibbs-Duhem equation, valid at constant pressure and temperature:

$$x_A (d\bar{G}_A)_{T,P} + x_B (d\bar{G}_B)_{T,P} = 0 \qquad (2)$$

This relation may also be written in terms of fugacities or activity coefficients:

$$x_A (d\ell n\bar{f}_A)_{T,P} + x_B (d\ell n\bar{f}_B)_{T,P} = 0 \qquad (3)$$

$$x_A (d\ell n\gamma_A)_{T,P} + x_B (d\ell n\gamma_B)_{T,P} = 0 \qquad (4)$$

Smith integrated the relation (3) over a range of pressures at constant temperature, using his calculated vapor phase fugacities. He stated that the results agreed to within 10%, although they are not included in his work.

The differential relations (3) and (4) along with several semi-empirical integrated forms associated with the names of Margules, Van Laar, Scatchard, Redlich, etc., have been used frequently for predicting correlating the behavior of binary systems. Ibl and Dodge,[64] Thijssen,[65] and Adler, et al.,[66] and others have pointed out that the Gibbs-Duhem equation is not an exact relation when applied to binary systems, since, at constant temperature and pressure, the equilibrium phase compositions are invariant; they have developed more exact relations which can be applied either to isothermal or to isobaric data. Other papers[67-69] published within the last 10 years have also dealt with this subject.

Most of the relations developed for treating isothermal or isobaric data require some knowledge of the partial molal properties of each component in the mixture. Such data are difficult to evaluate for the hydrogen-helium system, especially for the liquid phase. The problem is further complicated by the fact that the generalized reduced property tables developed by Hougen, Lyderson, et al., have been found to show a poor correlation for both hydrogen and helium; this rules out the use of psuedo-reduced critical constants for estimating mixture properties.

At the present time it appears that the use of equations of state for hydrogen and helium and their mixtures would offer the best means of obtaining a rigorous thermodynamic consistency test for the data presented here. Such an investigation is beyond the scope of this work.

APPENDIX A

EXPERIMENTAL DATA

The tables below include a summary of all experimental data recorded during this work. The following notations are used in the table headings:

Run: First number and letter give day and month (L for July, A for August); second and third numbers are sample bottle numbers for liquid and vapor, respectively. These numbers are recorded on the graphs of the mass spectrometer analyses which are on file in the Department of Chemical and Metallurgical Engineering Instrumental Analysis Laboratory.

T_0: Temperature indicated by platinum resistance thermometer, °K.

T_1: Temperature at Thermocouple No. 1, °K.

T_2: Temperature at Thermocouple No. 2, °K.

T_3: Temperature at Thermocouple No. 3, °K.

T_4: Temperature at Thermocouple No. 4, °K.

T_5: Temperature at Thermocouple No. 5, °K.

TCL: Temperature control limits, ±°K.

Pres: Equilibrium pressure, psia.

Time: Total time of vapor recirculation.

MSL: Instrumental Analysis Laboratory log number for liquid sample analysis.

Liq: Mole percent helium in liquid

MSV: Instrumental Analysis Laboratory log number for vapor sample analysis.

Vap: Mole percent helium in vapor.

Run	T_o	T_1	T_2	T_3	T_4	T_5	TCL	Pres	Time	MSL	Liq	MSV	Vap
10L-30-29	20.40	20.4	20.4	20.4	22.0	46.7	.005	50	27	12,228	0.41	92,237	65.45
10L-7-8	20.40	20.4	20.4	20.4	24.0	48.2	.005	100	30	12,214	0.84	12,234	80.30
10L-15-11	20.40	20.4	20.4	20.4	24.5	44.1	.005	200	35	12,216	1.67	12,235	87.13
10L-20-2	20.40	20.4	20.4	20.4	25.0	43.8	.005	300	60	12,218	2.36	12,231	88.97
10L-13-12	20.40	20.4	20.4	20.4	25.7	43.6	.01	400	28	12,221	2.96	12,236	90.08
10L-27-14	20.40	20.4	20.4	20.4	27.2	47.4	.01	500	30	12,224	3.39	12,339	90.35
11L-48-36	23.00	23.0	23.0	23.0	41.5	57.0	.004	50	42	12,246	0.38	12,253	63.00
11L-46-35	23.00	23.0	23.0	23.0	38.4	54.3	.004	100	39	12,245	1.15	12,252	62.90
11L-38-31	23.00	23.0	23.0	23.0	41.5	57.0	.004	200	48	12,241	2.39	12,248	76.30
11L-40-32	23.00	23.0	23.0	23.0	42.1	61.1	.004	300	34	12,242	3.55	12,249	80.55
11L-42-33	23.00	23.0	23.0	23.0	39.6	54.5	.004	400	39	12,243	4.58	12,250	82.34
11L-44-34	23.00	23.0	23.0	23.0	39.6	52.9	.004	500	34	12,244	5.46	12,251	83.30
19L-51-35	26.00	26.0	--	26.0	26.0	47.5	.003	100	33	12,305	0.97	12,319	33.50
19L-50-34	26.00	26.0	--	26.0	26.0	44.7	.003	200	30	12,304	2.86	12,318	56.90
19L-48-32	26.00	26.0	--	26.0	26.0	43.3	.003	400	31	12,302	6.64	12,316	68.58
19L-47-31	26.00	26.0	--	26.0	26.0	42.3	.003	500	61	12,301	8.48	12,315	70.02
23L-24-8	29.00	29.0	--	29.0	29.0	49.3	.002	151	48	12,343	1.50	12,353	21.92
23L-25-9	29.00	29.0	--	29.0	29.2	48.6	.002	200	47	12,344	3.07	12,354	32.93
23L-26-10	29.00	29.0	--	29.0	30.1	48.8	.002	250	30	12,345	4.59	12,355	39.54
23L-27-11	29.00	29.0	--	29.0	30.2	48.4	.002	300	32	12,346	6.21	12,356	43.70
23L-28-12	29.00	29.0	--	29.0	31.1	47.4	.002	400	33	12,347	9.63	12,357	47.95
23L-29-13	29.00	29.0	--	29.0	31.5	46.5	.002	500	39	12,348	13.35	12,358	49.20
23L-30-15	31.00	31.0	--	31.0	34.2	63.5	.002	199	32	12,349	2.51	12,359	15.59
23L-46-31	31.00	31.0	--	31.0	33.9	52.4	.002	300	35	12,350	7.49	12,360	26.57

Run	T_o	T_1	T_2	T_3	T_4	T_5	TCL	Pres	Time	MSL	Liq	MSV	Vap
25L-53-1	15.50	15.5	--	15.5	29.4	49.8	.02	49.5	33	--	--	12,413	93.78
25L-54-2	15.50	15.5	--	15.5	29.8	52.8	.02	75	25	12,403	0.29	12,414	95.51
25L-55-3	15.50	15.5	--	15.5	30.0	54.0	.02	100	23	12,404	0.46	12,415	96.31
25L-56-4	15.50	15.5	--	15.5	30.0	54.3	.02	125	23	12,405	0.51	12,416	96.77
25L-57-5	15.50	15.4	--	15.5	30.0	54.6	.02	150	22	12,406	0.55	12,417	97.02
25L-58-6	15.50	15.4	--	15.5	29.8	54.9	.02	175	23	12,407	0.64	12,418	97.14
25L-59-7	15.50	15.4	--	15.5	29.8	54.8	.02	200	26	12,408	0.71	12,419	97.29
25L-60-8	15.50	15.4	--	15.5	28.9	54.2	.02	250	30	12,409	0.82	12,420	97.41
25L-24-9	15.50	15.3	--	15.5	28.3	53.4	.02	300	25	12,410	0.87	12,421	97.48
25L-49-34	17.07	17.0	--	17.1	23.2	46.1	.02	56.3	50	12,377	0.36	12,390	89.67
25L-50-35	17.07	17.1	--	17.1	25.3	51.0	.02	75	27	12,378	0.43	12,391	91.86
25L-51-36	17.07	17.1	--	17.1	25.7	51.8	.02	100	30	12,379	0.57	12,392	93.30
25L-52-37	17.07	17.1	--	17.1	25.3	44.7	.02	125	28	12,380	0.72	12,393	94.12
25L-16-38	17.07	17.1	--	17.1	25.5	51.6	.02	150.5	30	12,381	0.80	12,394	94.64
25L-17-39	17.07	17.1	--	17.1	25.8	51.3	.02	175	26	12,382	0.89	12,395	95.03
25L-18-40	17.07	17.1	--	17.1	25.8	51.3	.02	200	25	12,383	1.00	12,396	95.15
25L-19-41	17.07	17.1	--	17.1	25.7	50.2	.02	250	27	12,384	1.14	12,423	95.56
25L-20-42	17.07	17.1	--	17.1	25.3	50.5	.02	300	27	12,385	1.31	12,424	95.82
25L-21-43	17.07	17.1	--	17.1	25.0	49.6	.02	400	27	12,386	1.51	12,425	95.90
26L-26-11	20.40	20.4	--	20.4	21.0	48.6	.004	35	50	12,431	0.34	12,443	53.60
26L-27-12	20.40	20.4	--	20.4	21.1	48.7	.004	75	22	12,432	0.61	12,444	24.60
26L-28-13	20.40	20.4	--	20.4	21.1	48.8	.004	125	20	12,433	1.05	12,445	83.20
26L-29-14	20.40	20.4	--	20.4	21.8	49.1	.004	150	20	12,434	1.30	12,446	84.80
26L-30-15	20.40	20.4	--	20.4	22.3	49.3	.004	175	19	12,435	1.54	12,447	86.03
26L-46-31	20.40	20.4	--	20.4	22.5	49.4	.004	250	20	12,436	2.05	12,448	88.41
26L-51-36	23.00	23.0	--	23.0	23.8	54.4	.004	75	20	12,441	0.75	12,453	53.44
26L-50-35	23.00	23.0	--	23.0	23.7	53.0	.004	125	20	12,440	1.36	12,452	67.87
26L-49-34	23.00	23.0	--	23.0	23.6	51.5	.004	150	20	12,439	1.72	12,451	71.75
26L-48-33	23.00	23.0	--	23.0	24.0	50.3	.004	175	22	12,438	2.15	12,450	74.35
26L-47-32	23.00	23.0	--	23.0	24.5	50.1	.004	250	49	12,437	2.91	12,449	78.78

Run	T_o	T_1	T_2	T_3	T_4	T_5	TCL	Pres	Time	MSL	Liq	MSV	Vap
30L-56-7	31.00	31.0	--	31.0	34.5	48.4	.002	176.5	25	12,493	1.49	12,497	11.28
30L-57-8	31.00	31.0	--	31.0	35.2	49.8	.002	250	27	12,494	4.78	12,498	22.58
30L-58-9	31.00	31.1	--	31.0	36.5	50.6	.002	325	26	12,495	8.73	12,499	27.55
30L-59-10	31.00	31.2	--	31.0	37.0	51.1	.002	350	22	12,496	11.03	12,500	27.85
30L-60-11	31.00	31.3	--	31.0	37.4	51.4	.002	375	24	12,497	12.93	12,501	27.59
30L-26-12	31.00	31.5	--	31.0	37.8	51.7	.002	400	23	12,498	15.64	12,502	25.78
30L-21-43	31.50	31.5	--	31.5	33.1	46.4	.002	177	20	12,470	1.27	12,482	7.67
30L-22-44	31.50	31.5	--	31.5	33.2	46.7	.002	200	20	12,471	2.30	12,483	11.94
30L-23-45	31.50	31.5	--	31.5	33.5	47.2	.002	225	17	12,472	3.61	12,484	15.64
30L-24-1	31.50	31.5	--	31.5	33.8	47.4	.002	250	20	12,473	4.83	12,485	18.35
30L-25-2	31.50	31.5	--	31.5	34.3	48.0	.002	275	20	12,474	6.26	12,492	20.30
30L-52-2	31.50	31.5	--	31.5	34.6	48.8	.002	300	20	12,489	8.18	12,493	21.37
30L-53-4	31.50	31.5	--	31.5	34.9	48.9	.002	325	20	12,490	10.47	12,494	21.49
30L-54-5	31.50	31.5	--	31.5	35.1	49.0	.002	351	20	12,491	16.59	12,495	17.58
30L-28-14	29.00	29.0	--	29.0	33.7	47.2	.002	127	23	12,489	0.91	12,504	14.03
30L-27-13	29.00	29.0	--	29.0	31.8	44.2	.002	175	20	12,490	2.20	12,503	27.75
30L-16-37	31.90	31.9	--	31.9	33.0	49.4	.002	174.5	25	12,465	0.81	12,476	4.00
30L-17-38	31.90	32.0	--	31.9	32.6	45.0	.002	200	34	12,466	2.07	12,477	8.31
30L-18-39	31.90	32.0	--	31.9	32.3	44.3	.002	220	26	12,467	3.17	12,478	11.75
30L-19-40	31.90	32.0	--	31.9	32.1	43.6	.002	238.5	27	12,468	4.29	12,479	13.86
30L-20-41	31.90	31.9	--	31.9	31.9	43.0	.002	250.5	28	12,469	4.99	12,480	14.82
30L-*-42	31.90	31.9	--	31.9	31.9	42.9	.002	261.5	19	--	--	12,481	15.62

*Liquid sample line plugged.

Run	T_o	T_1	T_2	T_3	T_4	T_5	TCL	Pres	Time	MSL	Liq	MSV	Vap
3A-16-1	32.50	32.6	--	32.5	35.0	67.2	.002	188.5	24	12,530	0.98	12,547	3.12
3A-19-2	32.50	32.6	--	32.5	34.8	60.7	.002	200	17	12,531	1.68	12,548	4.80
3A-17-3	32.50	32.6	--	32.5	34.5	54.0	.002	220	20	12,532	3.10	12,599	7.45
3A-18-4	32.50	32.6	--	32.5	34.2	51.5	.002	242	22	12,533	5.09	12,550	5.24
3A-20-5	32.50	32.5	--	32.5	34.0	49.5	.002	250	22	12,534	5.99	12,551	6.27
3A-21-6	32.50	32.5	--	32.5	34.0	48.0	.002	258	23	12,535	6.75	--	--
3A-22-7	31.90	31.9	--	31.9	32.8	43.8	.002	275	18	12,536	6.87	12,553	16.19
3A-23-8	31.90	31.9	--	31.9	33.6	44.3	.002	289.5	26	12,537	8.71	12,554	16.35
3A-24-9	31.90	31.9	--	31.9	34.5	44.9	.002	300	23	12,538	10.10	12,555	15.88
3A-25-10	31.90	31.9	--	31.9	34.8	45.2	.002	308.5	23	12,539	12.02	12,556	12.07
3A-27-12	31.00	31.6	--	31.0	33.8	42.3	.002	413	40	12,541	20.87	12,557	21.85
3A-28-13	30.60	31.8	--	30.6	32.6	44.1	.002	300	20	12,542	7.29	12,558	30.32
3A-29-14	30.60	32.6	--	30.6	34.0	45.3	.002	400	29	12,543	13.24	12,559	32.60
3A-30-15	30.60	33.0	--	30.6	34.9	46.6	.002	450	23	12,544	17.95	12,560	30.36
3A-46-36	26.00	27.3	--	26.0	29.6	39.6	.003	81.	20	12,518	0.67	12,523	22.60
3A-47-37	26.00	27.9	--	26.0	32.0	44.9	.003	125.	22	12,519	1.43	12,524	43.37
3A-48-38	26.00	28.3	--	26.0	36.0	49.9	.003	150	21	12,520	1.92	12,525	49.77
3A-49-39	26.00	29.7	--	26.0	37.5	52.8	.003	250	23	12,521	3.64	12,526	62.67
3A-50-40	26.00	30.5	--	26.0	38.9	54.7	.003	300	23	12,522	4.76	12,527	65.65

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