THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING

Department of Mechanical Engineering

FINAL REPORT

LIQUID-VAPOR EQUILIBRIUM IN THE SYSTEM HYDROGEN-HELIUM

R.E. Sonntag

R.W. Crain, Jr.

W.B. Streett

G.J. Van Wylen

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PREFACE

This report constitutes the final report on Contract No. 8-5256, National Aeronautics and Space Administration, George C. Marshall Space Flight Center, Huntsville, Alabama.

The first phase of the investigation, equilibrium in the system normal hydrogen-helium was conducted as a doctoral thesis by Mr. William B. Streett. A complete description of the apparatus and results obtained have been reported previously, Report No. 05664-1-T. That report may be consulted for details not included here.

The second phase of the investigation, equilibrium in the system $20.4^{\circ}K$ equilibrium hydrogen-helium was conducted by Mr. Richard W. Crain, Jr., and Mr. Sudhir Savkar, who also assisted in the first study. Both phases of the investigation were 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 his staff in the Department of Chemical and Metallurgical Engineering Instrumental Analysis Laboratory for their work in the mass spectrometer analyses of the samples. The assistance of Mr. Jack Brigham and the members of the staff of the Automotive Engineering Laboratory is also appreciated.

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 the high-purity analyzed helium by the U.S. Bureau of Mines Helium Research Center, Amarillo, Texas, is also gratefully acknowledged.

June, 1964   G.J. Van Wylen

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I. INTRODUCTION

A. GENERAL

The present investigation was undertaken to determine phase compositions in the liquid-vapor system hydrogen-helium in the range 15.5-32.5°K at pressures from hydrogen saturation to 500 psi.

Knowledge of the solubility of helium in liquid hydrogen is of particular importance, inasmuch as liquid hydrogen is commonly transferred by pressurization with helium gas. Such information is also of interest in bubble-chamber studies, where it may be possible to utilize hydrogen-helium mixtures to investigate the interaction of high-energy particles with helium nuclei. The hydrogen-helium system is also of interest from a theoretical standpoint, since the two components are the elements with the two lowest critical temperatures, both of which exhibit large quantum effects, and further because of the different ortho-para modifications of hydrogen.

Prior to the present investigation, two studies have been made on the liquid-vapor system hydrogen-helium, both covering only a limited experimental range. Both of these investigations apparently used normal hydrogen (75% ortho, 25% para, the room temperature equilibrium composition) since no mention was made of conversion.

The first of these is a Ph.D. thesis done by S. R. Smith[1] at Ohio State University in 1952. Smith reported experimental values of vapor and liquid phase compositions at three temperatures 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[2] 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[3] 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 $2.7^{\circ}K$.

In addition to the two reports of experimental work on hydrogen-helium vapor-liquid equilibrium, two additional reports[4,5] 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.

B. PRESENT INVESTIGATION

The principal investigation undertaken on this project deals with the system normal hydrogen-helium, and was the subject of the doctoral thesis by

W. B. Streett[6]. This work has been reported previously in considerable detail[7,8]

and will be merely reviewed in the present report. Upon completion of that

phase of the investigation, it was felt necessary to study this system using

$20.4^{\circ}K$ equilibrium hydrogen (0.21% ortho, 99.79% para) instead of normal hydrogen,

in order to determine the nature and extent of any differences between the two

systems. It was not deemed necessary to make as thorough a coverage as in the

first phase of the work, since the prime concern here is with differences

between the two systems. Consequently, while eleven isotherms were investigated

for normal-hydrogen (15.5, 17.07, 20.4, 23.0, 26.0, 29.0, 30.6, 31.0, 31.5, 31.9,

$32.5^{\circ}K$), only six were repeated for equilibrium hydrogen (20.4, 23.0, 26.0,

29.0, 31.0, $31.5^{\circ}K$) at pressures from hydrogen saturation to 500 psia.

II. EXPERIMENTAL APPARATUS AND INSTRUMENTATION

A. GENERAL

The experimental apparatus and instrumentation used in the present investigation have been discussed in considerable detail in reference 7, "Liquid-Vapor Equilibrium in the System Normal Hydrogen-Helium", W. B. Streett, R. E. Sonntag, and G. J. Van Wylen, report 05664-1-T, September, 1963. This equipment will be reviewed here, along with a description of modifications and additions made for studying the system equilibrium hydrogen-helium. Reference 7 should be consulted for additional details regarding the basic equipment.

As seen in the schematic diagram Figure 1, the experimental apparatus can be divided into four basic areas: (1) cryostat; (2) vapor recirculation system; (3) vapor pressure temperature control system; (4) liquid and vapor phase sampling; each will be discussed separately below.

B. CRYOSTAT

A cross-sectional view of the cryostat is shown in Figure 2. It was necessary to design the cryostat of stainless steel, since vapor pressure control was used for the liquid hydrogen bath, with cryostat pressure approaching 200 psi. The inner and outer vessels are made of schedule five type 304 SS pipe (0.108 inch wall) with standard butt-weld pipe caps for the end pieces. The inner vessel is constructed of 6 inch pipe, and has a 3 inch pipe neck as indicated in the diagram, in order to reduce heat flow into the cryostat. The cryostat capacity is approximately 15 liters. The flange was machined from 3/4 inch stainless steel, reduced to 3/8 inch at the outer perimeter to reduce heat conduction to the inner vessel. The top plate is machined from a 1/2 inch stainless plate, and sealed with a teflon-coated stainless steel O-ring.
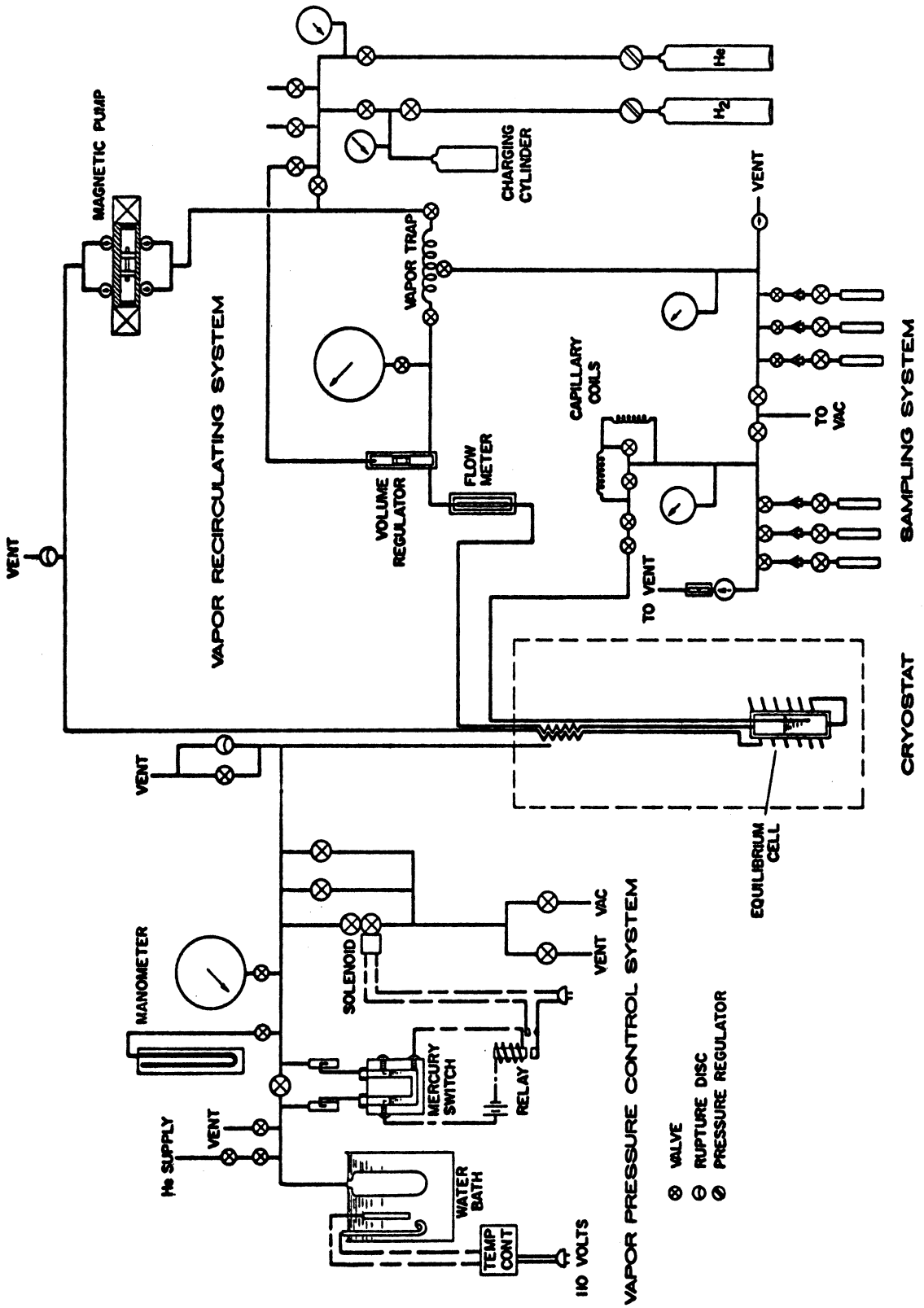
Fig. 1. Schematic diagram of experimental equipment.

TO VAPOR
CIRCULATION {
LOOP

LIQUID
SAMPLE LINE

LIQ.
N2

COUNTERFLOW HEAT
EXCHANGER

LINDE SUPERINSULATION

VAC

BELLOWS TYPE
VACUUM VALVE

STIRRING MECHANISM

LIQ.
H2
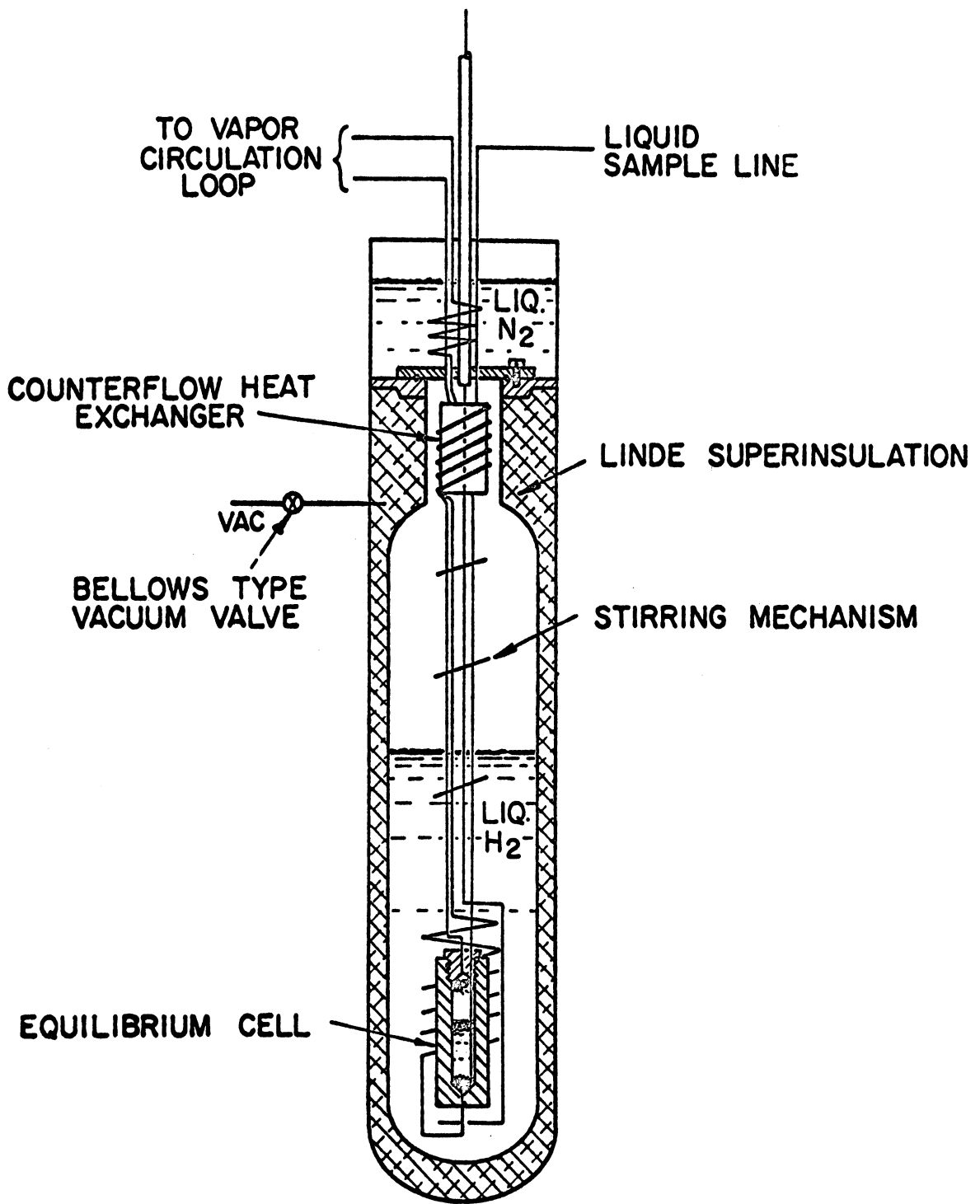
EQUILIBRIUM CELL

Fig. 2. Section through cryostat showing equilibrium cell.

Insulation of the cryostat is achieved by 0.8 inch of Linde SI-4 multi-layer insulation, and a liquid nitrogen reservoir, as shown in Figure 2. The cryostat was also covered with fiberglass and styrofoam insulation to further reduce the heat load.

The cryostat is provided with a vertical-acting solenoid operated stirring device actuated by a mechanical-electrical timing circuit. In the operation of the cryostat for investigation of the system normal hydrogen-helium, it was found that the bath liquid hydrogen was boiled away at the rate of about 1 liter in 6 hours. In the later experiments with equilibrium hydrogen, this rate was increased considerably when hydrogen was being converted in the loop, because of the large heat release associated with ortho-para conversion.

C. VAPOR RECIRCULATION SYSTEM

The vapor recirculation portion of the experimental apparatus is shown in detail in Figure 3, and includes the equilibrium cell, counterflow heat exchanger volume regulator, vapor sample trap, magnetic pump, pressure gage, flow meter and associated valves and tubing. The total volume of the loop including the equilibrium cell is approximately 180 cc, and was kept to a minimum so that the vapor can be recirculated in a small amount of time.

The equilibrium cell, shown in Figure 4, is constructed of free-machining copper, and has an internal volume of about 55 cc. A small piece of copper wool was placed at the top of the cell, to prevent liquid droplets from being carried out with the circulating vapor, and copper wool at the bottom was used to help break up vapor bubbles entering the cell. The 1/8 inch copper vapor line entering the bottom of the cell is loosely coiled several times around the cell to assure that vapor entering the bottom is cooled to the equilibrium
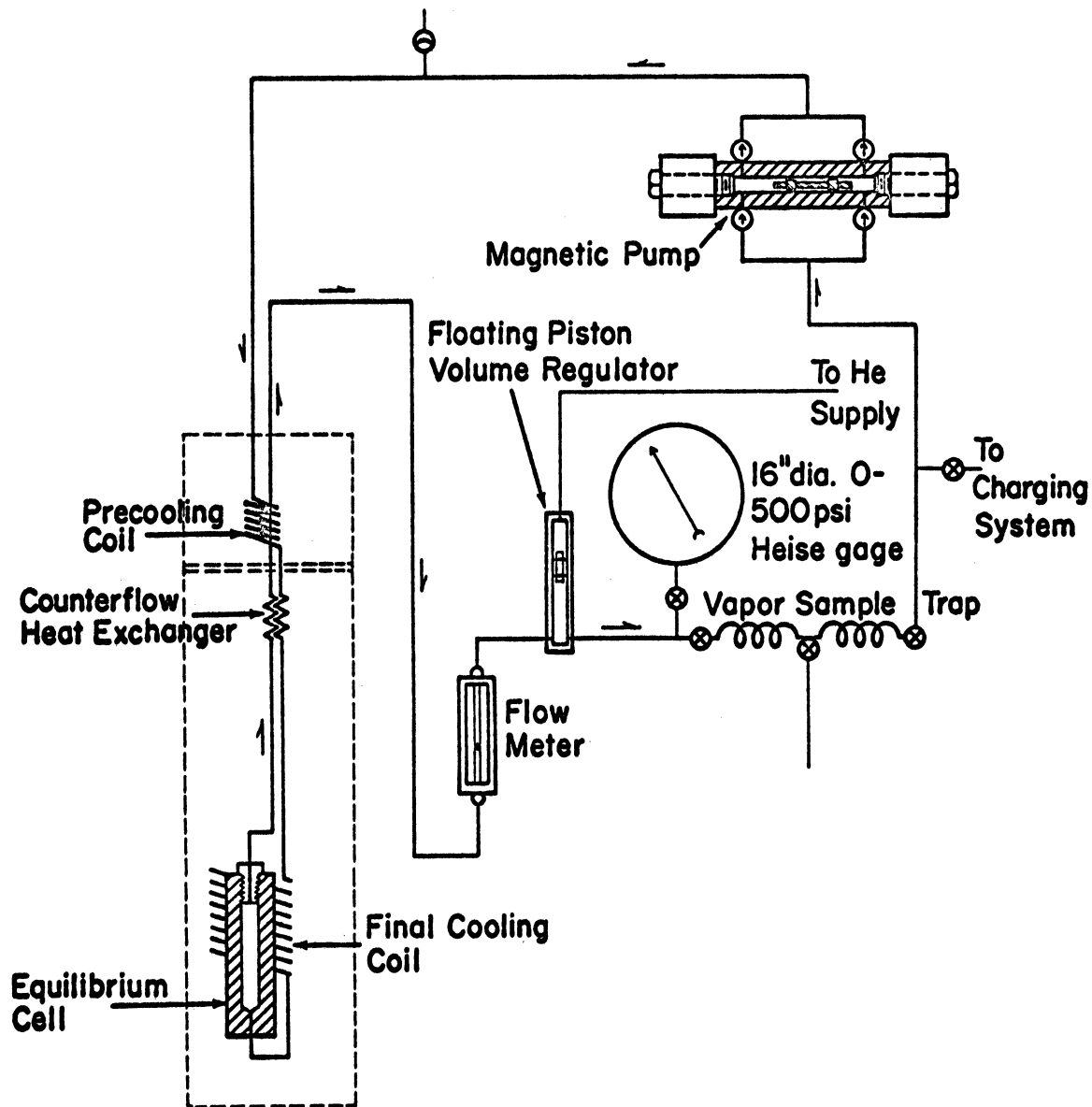
Fig. 3. Schematic diagram of vapor recirculating system.

**Liquid Sample Line
1/16"O.D. x 0.004" I.D.
Stainless Steel Capillary
Tubing**

**Vapor Outlet Line
1/8" O.D. Copper Tubing**

Silver Soldered Joints

3/16" O.D. Copper Sleeve

1/2"

1 1/4"

1/8"O.D. Stainless Sleeve

**Platinum Resistance
Thermometer**

Copper Wool

**Resistance Thermometer
Well 7/32" Dia.**

2 3/8"

1 3/8"

6 1/4"

6 3/4"

1"

Copper Wool

2 1/2"

**3/16"O.D. Copper
Sleeve**

Silver Solder

**Vapor Inlet Line
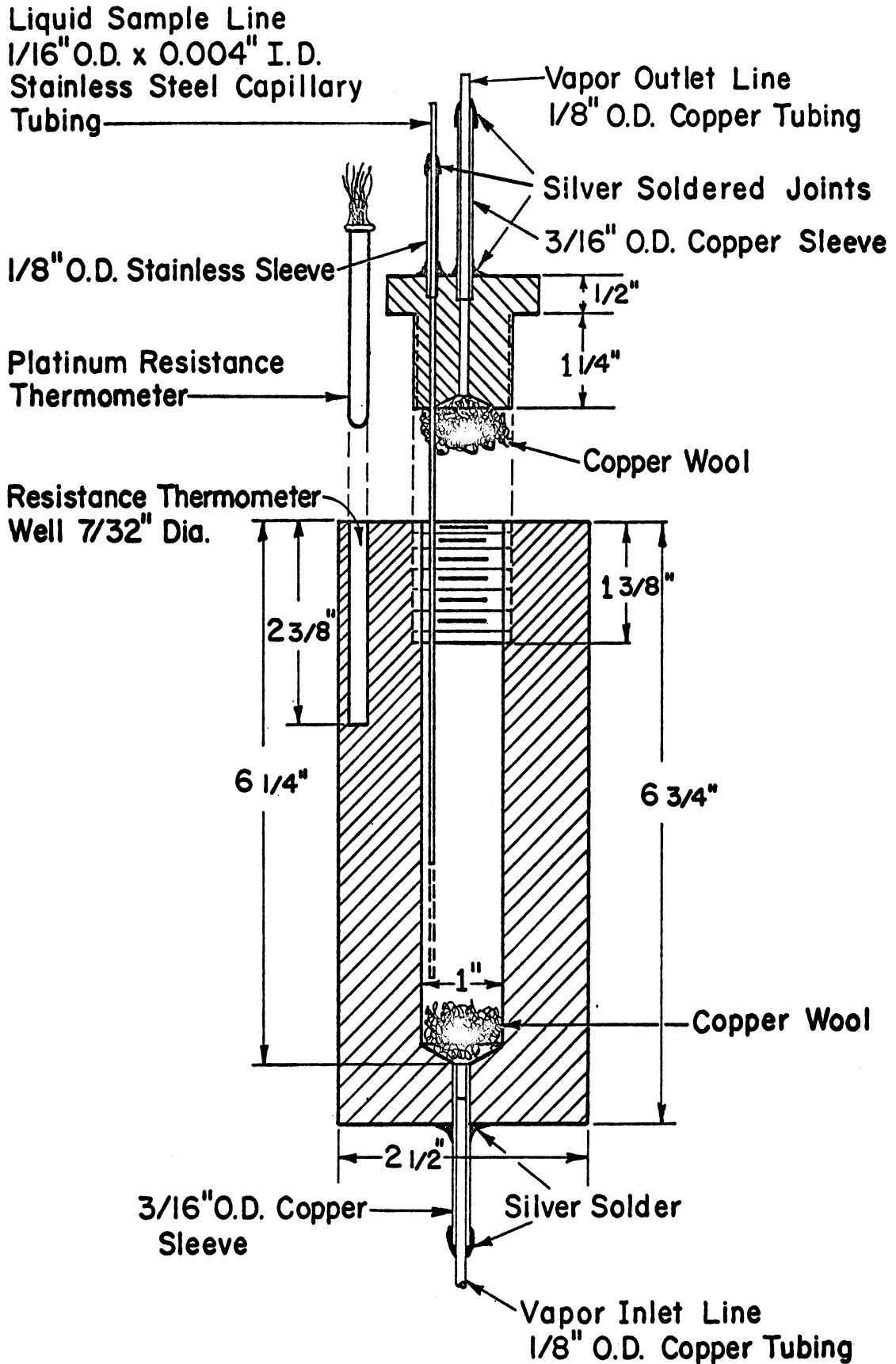1/8" O.D. Copper Tubing**

Fig. 4. Equilibrium cell.

temperature. The inlet and outlet vapor lines are wound together to form a helical counterflow heat exchanger in the cyrostat neck, as indicated in Figure 2 in order to precool the inlet vapor and reduce the cryostat heat load.

The floating-piston volume regulator was placed in the recirculation loop to permit the adjustments in loop volume and consequently in equilibrium pressure. The vapor sample trap consists of two coils of 1/4 inch copper tubing, in the center of which is a sampling valve. The valves at the ends of the coils serve to isolate a portion of equilibrium vapor in the trap before the sampling is performed.

The double-acting magnetic recirculating pump and its associated mechanical-electrical pulsing circuit were constructed for this investigation. It is necessary to have a non-contaminating source of pressure to circulate the vapor at a variable, low rate of flow.

D. VAPOR-PRESSURE TEMPERATURE CONTROL SYSTEM

Bath temperature control is achieved by an automatic vapor-pressure control system, shown in Figure 5. The mercury U-tube switch S is constructed from a 1 inch thick Plexiglas block, and has platinum wire contacts.

Operation of the control system is based upon comparison of the bath pressure with that in a reference volume V. Bypass valve C is manually adjusted to give rough control of the bath pressure at the desired value, after which valve A is closed. Fine control is then achieved automatically by the solenoid valve K, actuated by the mercury U-tube switch. The large bypass D is used in conjunction with the vacuum pump when operating the system at less than ambient pressure. Any tendency for long-term drift of the system can be compensated by making fine adjustments of the quantity of gas in the reference volume through valves G and
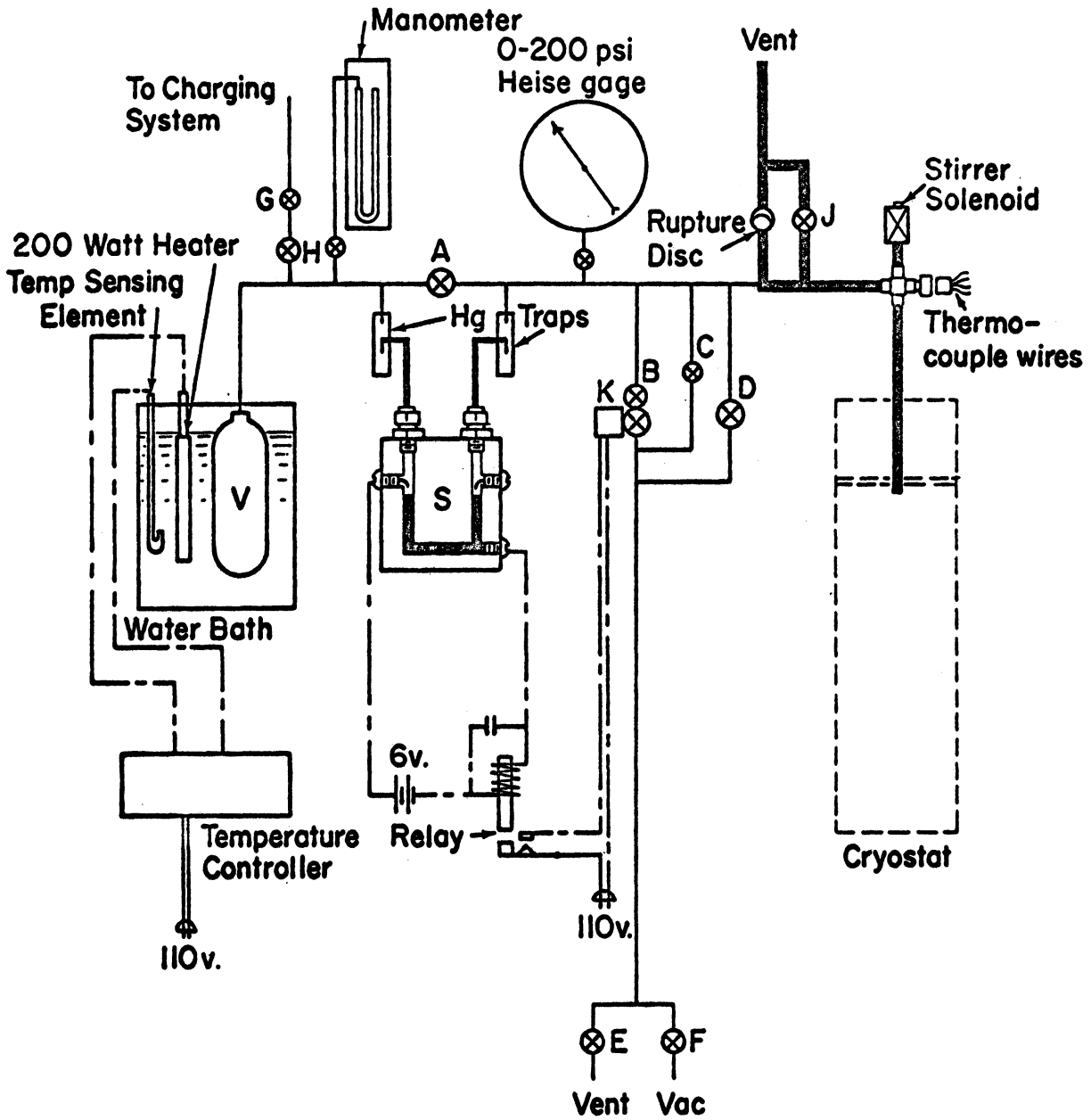
Fig. 5. Schematic diagram of vapor pressure control system.

H. Using this system, it is possible to control the cryostat pressure to within 1 mm mercury for long periods of time, which corresponds to a control in temperature of about 0.005°K over most of the temperature range of the investigation.

E. LIQUID AND VAPOR SAMPLING SYSTEMS

A schematic representation of the liquid and vapor portions of the apparatus, an extremely important part of the experimental equipment, is given in Figure 6. The vapor sample trap has been described previously. A length of stainless capillary tubing connects valve A with the sample bank, in order to control sample flow rate during high pressure runs. Check valve C opens to the vent line at 1.5 psi gage, thereby preventing pressure build-up in the glass sample bottles.

Liquid phase sampling is achieved through a 0.004 inch ID stainless capillary located in the equilibrium cell as shown in Figure 4. Extreme care must be exercised in sampling the liquid, inasmuch as the sample vaporizes in the tube as it warms to ambient temperature, and fractionation with subsequent change in composition must be avoided in withdrawing the sample. The first length of liquid sampling line is about 72 inches long, at which point two flow-regulating needle valves J and K are installed. Two bypass loops, each 72 inch lengths of capillary, are installed beyond the control valves, and provide a close control over the sample flow rates. Thus, the liquid can be withdrawn very slowly from the cell over a wide range of cell pressure. The flow meter is used in conjunction with the liquid sampling system so that the line can be purged by discarding a controlled initial quantity of sample at the time of taking the data. A check valve is also used in this system to prevent excessive pressure in the glass sample bottles.

Swagelok Bulkhead Adapter

Hex Nut

Tygon Plastic Tubing

Bushing

1/8"O.D. Copper Tubing

Solder

12-30 Taper Female Glass Joint

Front Panel

Detail of Metal To Glass Seal

Vapor Sample Trap (Coiled 1/4" O.D. Copper Tubing)

D   A   E

1/16" O.D. x 0.004" I.D. Stainless Steel Capillary Tubing

J K L M

Cryostat

Equilibrium Cell

Vent

Q Flow Meter

P Check Valve

30"-0-15 PSI Compound Gage

F

G

1/8"O.D. Copper Tubing

Vent

C

Metal To Glass Seal (See Detail Above)

Standard Taper Glass Joint

Sample Bottle With Vacuum Stopcock
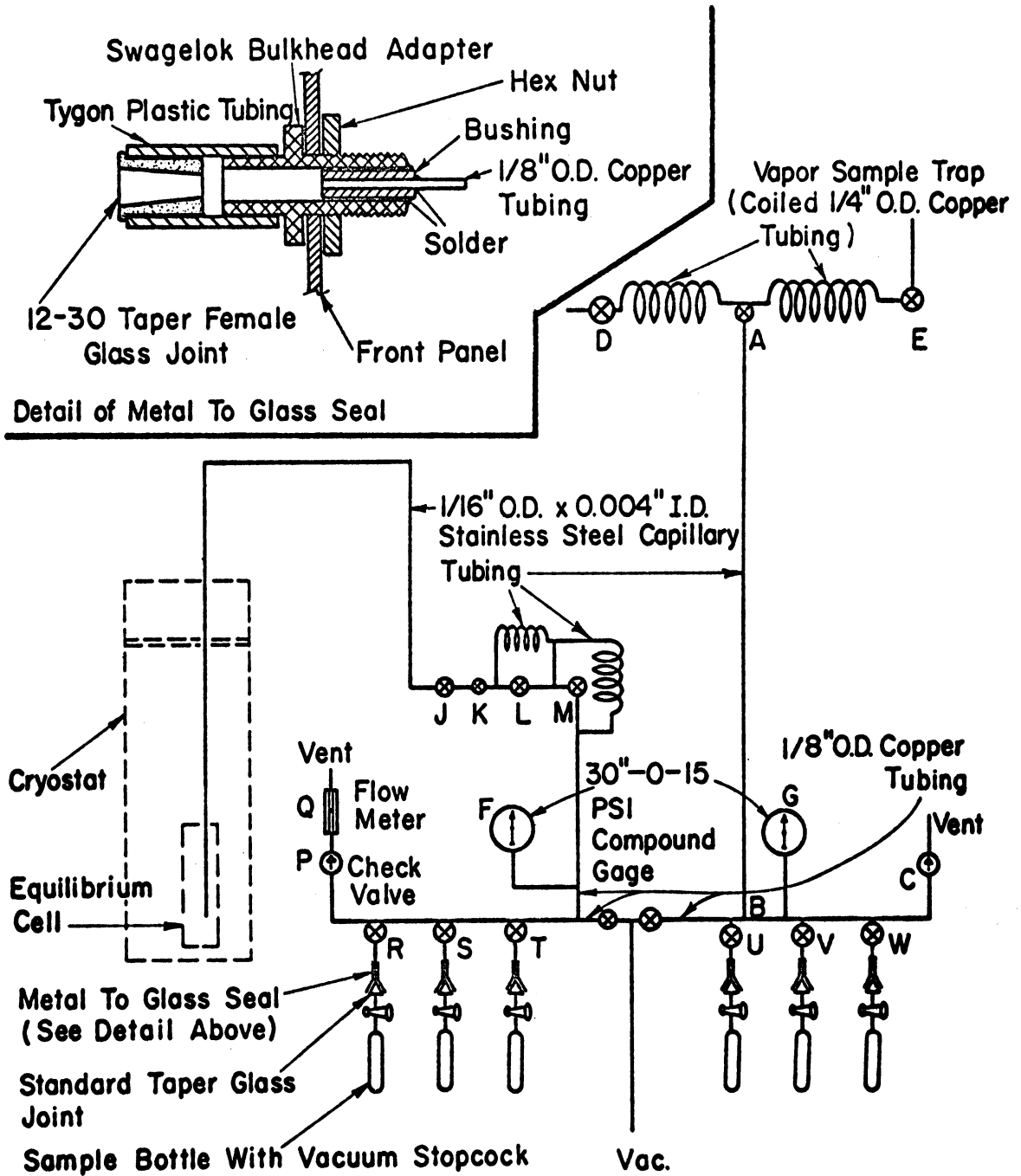
R   S   T

B   U   V   W

Vac.

Fig.   6.   Schematic diagram of sampling system.

F. INSTRUMENTATION AND ACCURACY

The equilibrium temperature is measured using a Leeds and Northrup type 8164 platinum resistance thermometer mounted in a hole in the equilibrium cell block, as shown in Figure 4. Measurements are made by a Leeds and Northrup #8069 type G-2 Mueller bridge, with a null-detecting type 2284-d reflecting galvanometer hung in a Julius suspension. Temperature changes of $0.002^{o}K$ can be detected with this equipment in the range of the present study, although the temperature scale is accurate to only $0.01^{o}K$.

Gold-cobalt vs. copper differential thermocouples are used to determine the temperature distribution throughout the cryostat. Five thermocouples were used in the study of the normal hydrogen-helium system; an additional thermo-couple was added in the subsequent study using equilibrium hydrogen in order to be able to check the catalytic reactor temperature. The thermocouples are constructed of 30 gage wire, and are all referenced to the platinum resistance thermometer location. Thermocouple EMF's are measured by a Leeds and Northrup type K-3 potentiometer with a type 9834 electronic D-C null detector. Accuracy of these differential measurements is of the order of $0.02^{o}K$ at the highest temperature and $0.04^{o}K$ at the lowest temperature of this study.

Equilibrium pressure is measured in the vapor recirculation loop on a 0-500 psi, 16 inch, calibrated Heise gage, shown in Figures 1 and 3. The gage is accurate to 0.1% full scale, or 0.5 psi for this work. Vapor pressure of the hydrogen cryostat is measured, for the purpose of rough initial settings, using a 0-200 psi, 16 inch Heise gage for pressures above atmospheric, and by a 0-30 inch mercury manometer for pressures below atmospheric. All auxilliary pressure measurements are made with standard bourdon tube gages.

Samples taken of the liquid and vapor phases were analyzed in the Instru-
mental Analysis Laboratory of the Department of Chemical and Metallurgical
Engineering of the University of Michigan. Analyses were performed using a
Consolidated model 21-103 mass spectrometer. The limits of accuracy of this
instrument are as follows:

Mole % of component	Max. mole % deviation	Max. % deviation
100.0	± 1.0	± 1.0
10.0	± 0.10	± 1.0
1.0	± 0.05	± 5.0
0.1	± 0.01	± 10.0

G. MODIFICATIONS FOR EQUILIBRIUM HYDROGEN STUDIES

Only minor modifications and additions to the equipment have been made
for studying the system equilibrium hydrogen-helium. A small catalytic reactor,
shown in Figure 7, was designed, and is constructed of copper. Since ortho-para
conversion is a highly exothermic reaction, the bar was milled to the cross-
section shown to provide maximum surface for heat transfer to the bath hydrogen.
The four-parallel-tube construction was used in order to minimize pressure drop
in the loop. The catalyst used for conversion in this work is hydrous ferric
oxide, ground to about 30 mesh size.

The reactor is installed inside the cryostat in the vapor recirculation
line immediately above the equilibrium cell. The recirculation line is loosely
coiled several times at both the reactor inlet and outlet, to assure temperature
equilibrium of the circulating vapor with the bath liquid hydrogen.
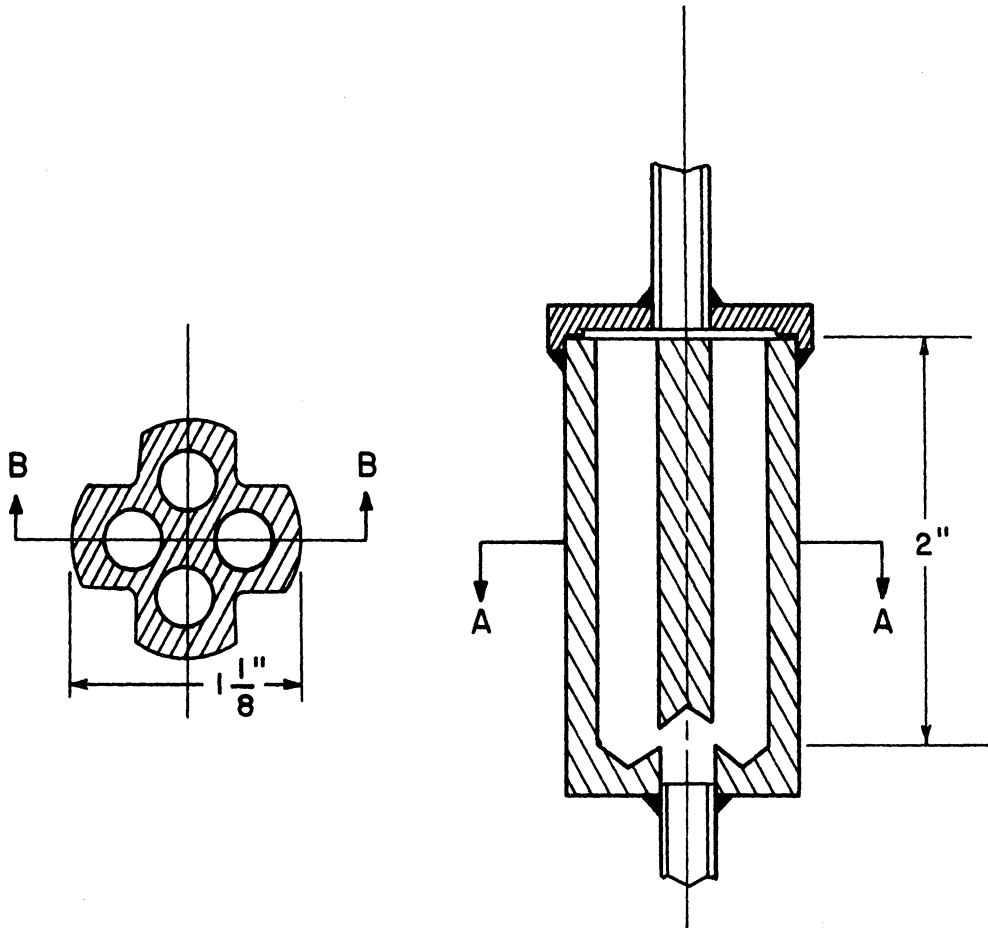
Fig. 7

Catalytic reactor

Before the experimental studies were begun, the catalyst was activated by immersing the reactor in a bath of boiling turpentine (159°C) for a period of four hours while purging with helium gas. It was necessary thereafter to prevent contact of the catalyst with air, so the recirculation system was always filled with helium when not in use.

Hydrogen analyses for ortho-para content are performed using a Gow-Mac model 9285 thermal conductivity cell with a power supply-control unit model 405Cl. The schematic diagram of the analyzing system is shown in Figure 8.

Provision was made to enable drawing a sample from either the vapor recirculating system or from the liquid sampling capillary. The pressure is closely regulated using a Matheson Series 70 low pressure regulator set at 10 inches of water gage. The flow rate through the cell is held at 50 cc/min. STP. The thermal conductivity of the sample is compared to that of a reference stream. Provision was made to pass either room-temperature hydrogen (normal H_2) or samples of cryostat boil-off hydrogen (20.4° equilibrium H_2) through the reference cell. Output from the analyzer is read on a Beckman model 93500 potentiometric recorder.

Fig. 8

Schematic diagram of thermal conductivity analyzing system

III. OPERATIONAL PROCEDURES

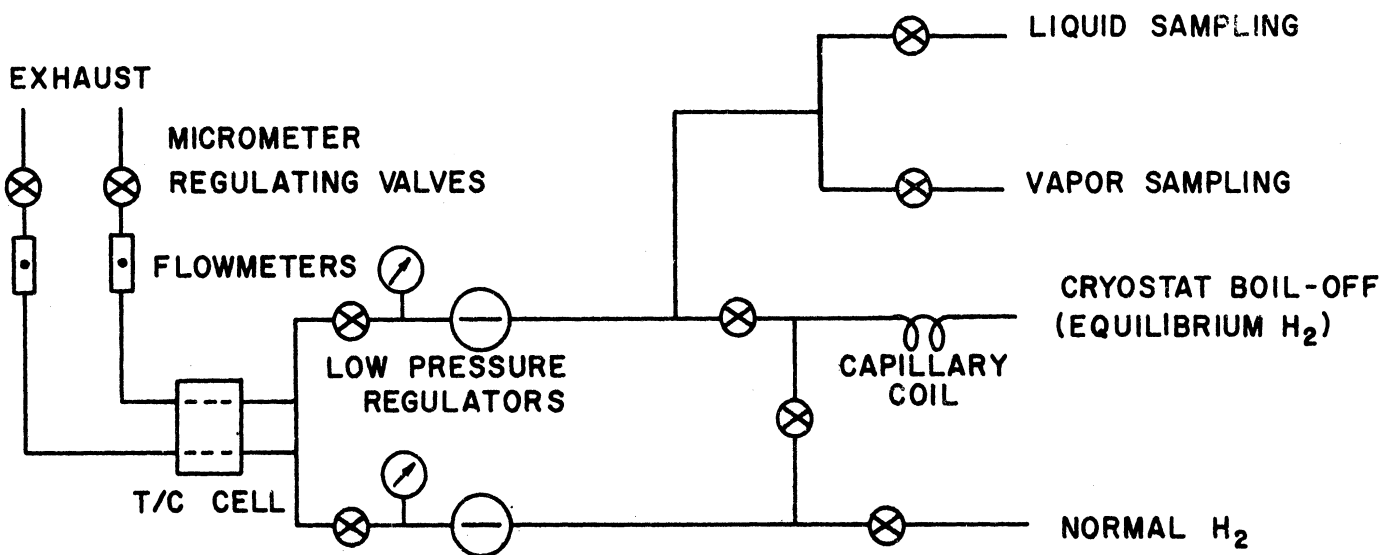### A. PREPARATION OF EQUIPMENT

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.

Because of the danger of explosion resulting from mixtures of air and hydrogen, extreme care must be taken to remove all traces of air from the system before hydrogen is introduced. Pure helium or nitrogen gas is allowed to flow continuously through the vent system for approximately 20 minutes before the hydrogen is introduced. The liquid hydrogen storage dewar is brought into the test cell and the transfer line connected to the dewar and cryostat. The cryostat, vapor pressure control system and transfer line are then alternately evacuated and purged with helium gas.

Liquid hydrogen transfer to the cryostat is achieved by the hydrogen dewar pressure (10 - 12 psig) at a rate of several liters per minute. The cryostat liquid level is checked with a small carbon resistor probe, and the temperatures indicated by the resistance thermometer and thermocouples are observed. The cryostat was normally filled to a depth of about 20 inches (about 10 liters) for runs involving normal hydrogen, and to about 24 inches for those for equilibrium hydrogen, since the latter boiled away more bath liquid.

B. RUN PROCEDURES

Operation of the vapor-pressure temperature control system has been des-
cribed previously. To obtain temperatures below the normal boiling point of
hydrogen (20.3°K) a vacuum is pumped over the bath as indicated before. For
temperatures above the normal boiling point, the vent lines are closed and the
cryostat pressure allowed to build up to the desired value. It has been found
that this procedure results in a stratification of the bath liquid, with persis-
tance of large temperature gradients. Thus, while a layer of liquid hydrogen near
the liquid surface reaches the saturation temperature corresponding to the set
pressure quite rapidly, the bulk of the liquid warms only very slowly. When the
system was first placed into operation, it was found that in several hours the
liquid bulk temperature would rise only a single degree. The cryostat stirring
mechanism did not provide sufficient liquid circulation to overcome these gradients,
and frequently jammed and did not function properly.

This problem of very slow bath temperature rise was eliminated in the normal
-H$_2$ study by inserting a length of tubing into the cryostat and pumping a small
quantity of warm hydrogen gas through the liquid, thereby achieving a rapid rise
to the desired value. It was unfortunately not possible to use this procedure for
those runs with equilibrium -H$_2$ when the hydrogen supply was drawn from cryostat
boil-off vapor, at least until a sufficient quantity of boil-off had first been
collected.

Once the desired bath pressure is reached, it is held automatically by the
vapor-pressure control system. It is frequently necessary to adjust very slightly
the quantity of gas in the reference volume, so as to obtain exactly the temper-
ature of the bath, once the temperature has stabilized the bath becomes uniform
in temperature throughout the liquid, with the gas space at the top of the
cryostat being somewhat warmer.

Charging the loop with hydrogen-helium mixtures is somewhat different for the
two systems studied. In the normal hydrogen-helium system, the supply of hydrogen
used in Matheson ultra-pure grade having total impurities of less than 10 ppm.

Since this is stored at ambient temperature, it exists as normal $-H_2$ (75% ortho, 25% para). The gas is first changed into a 1500 cc charging cylinder to a predetermined pressure. The mass of hydrogen necessary to fill the equilibrium cell approximately half full of liquid at the given temperature has first been calculated, as has the correlation between mass and pressure in the charging cylinder. The hydrogen is then slowly admitted to the loop until the desired amount has been charged, after which the loop is pressurized with helium gas until the desired system pressure is reached. The supply of helium used in this investigation is special analyzed helium donated by the U.S. Bureau of Mines Helium Research Center, Amarillo, Texas, and has total impurities less than 12 ppm.

In the investigation of the system equilibrium hydrogen-helium, the supply of equilibrium hydrogen was prepared by one of two alternate methods. In early runs, the hydrogen was charged in the same manner as for the previous work, in which case it was necessary to convert the hydrogen using the catalytic reactor. Using this procedure, the hydrogen charged into the loop is circulated by the magnetic pump, passing continuously through the reactor, which is located in the cryostat. Samples are periodically withdrawn and passed through the thermal conductivity analyzer system to be checked for ortho-para content. It was necessary to circulate the hydrogen for a period of several hours to achieve complete conversion to 20.4^o equilibrium composition, and this required time gradually increased because of the decrease in catalyst effectiveness. This resulted in the boil-off of large quantities of liquid hydrogen from the bath, as a result of the normal heat load and, in addition, the heat release of ortho-para conversion.

Part of the experimental data presented in this report were run using hydrogen converted in this manner. It ultimately proved to be more convenient, however, to use cryostat boil-off vapor as the source of equilibrium hydrogen. Samples of boil-off gas analyzed by mass spectrometry indicated a few hundredths of one per cent helium (perfectly acceptable in this study), and a trace amount of neon. The problem of using cryostat boil-off is that its pressure is not

sufficient to charge the 1500 cc charging cylinder to the desired amount.
Since a non-contaminating hydrogen compressor was not available, it was there-
fore necessary to charge this supply of equilibrium hydrogen into the loop in
small low-pressure increments. This process is very time-consuming, but was
ultimately felt to be more practical than converting room-temperature hydrogen.

Once the desired quantity of equilibrium hydrogen has been charged into
the system by either of the described procedures, helium is added until the
desired system pressure is reached, as in the earlier study. Repeated exper-
imental runs made using the alternate sources of equilibrium hydrogen showed
no differences in composition of the two phases, and it was concluded that
both methods are acceptable.

In each study, numerous runs were made to determine the approximate time
required for the hydrogen-helium mixture to reach equilibrium with continuous
vapor recirculation. This was tested by holding pressure and temperature
constant and taking samples of each phase at different time intervals. Analyses
of these samples indicated that composition remained constant after about 10-15
minutes. Thereafter, samples were taken after about 20 to 30 minutes, and in
some instances even longer, to insure that equilibrium was reached.

Sampling of the liquid and vapor phases was discussed in the previous
section. Extensive tests were run early in this study to determine the repro-
ducibility of liquid sample compositions over a range of sample flow rates and
capillary line length and purge time. It was found that by flowing the sample
for 15-20 seconds before admitting the sample to the bottle, the results were
very consistent and reproducible. It was also found that if the sample flow
rate was not too high, there was no pressure drop in the loop during sampling,
which indicates that equilibrium between the phases in the cell has not been
disturbed by the sampling process. There were in general no difficulties

encountered with vapor phase sampling during the course of this investigation.

C. OPERATIONAL DIFFICULTIES

In general the apparatus functioned satisfactorily, and no serious difficulties were encountered during the majority of this investigation. The principal problem in the first phase of the work was that of raising the bath temperature in a reasonable period of time to study those isotherms above 20.4°K. This was resolved by pumping hydrogen gas through the liquid as described previously.

There were difficulties with the bath stirring mechanism throughout the first phase of the study, as the stirrer rod frequently jammed on a guide ring in the cryostat, rendering the stirring device inoperable. This was not felt to be of importance, as temperature gradients were non-existant in the liquid once the temperature had stabilized. This was repaired, however, and the stirrer functioned properly during the second part of the research. The differential thermocouple located at the bottom of the equilibrium cell apparently shorted early in the investigation and was later replaced, although this difficulty recurred. This also presented no problems, since there was another thermocouple nearby in the liquid that consistently indicated no temperature gradient with respect to the resistance thermometer reference location.

One phenomenon, not associated with equipment failure, was encountered during the runs at 15.5 and 17.07°K in the system normal hydrogen-helium. At each of these temperatures, there is a pressure in the range studied at which the density of the vapor phase (principally helium) becomes equal to that of the liquid phase (principally hydrogen). At pressures above such a value, the vapor phase is more dense than the liquid, such that the mixture is apparently inverted in the equilibrium cell with the liquid floating on top of the vapor. Smith[1] observed this phenomenon in his studies of the system and concluded that it occurred at pressures slightly above 500 psia in the temperature range in which he was working (17.4 - 21.8°K).

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.[9] 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 included only a small portion of the total area of interest. These isotherms were not run for the system equilibrium hydrogen-helium, since comparisons with normal hydrogen-helium results at the higher temperatures indicated that differences between the two systems should be extremely small in this region.

Other difficulties, mostly of a minor nature, occurred when taking data on the equilibrium hydrogen-helium system. The brass fittings on the mercury U-tube vapor-pressure control failed as a result of corrosion by the mercury and were replaced by stainless steel fittings. The D-C motor operating the magnetic pump switching system also failed and had to be replaced. There were numerous problems with small vacuum leaks in the equipment, such that several fittings and valves had to be replaced as well. Several times these small leaks apparently developed in the recirculation loop as the loop was being evacuated prior to charging with hydrogen for an experimental run. Consequently, minute quantities of air entered the loop and partially poisoned the catalyst, thereby reducing its conversion effectiveness. More seriously, the air froze solid as it reached the portion of the loop inside the cryostat, so that operation of the equipment would have to be cancelled and the cryostat warmed to ambient temperature.

The difficulties described above can all be classed as minor operational nuisances. There was, however, one problem in running the equilibrium hydrogen-helium data that is of a more severe nature. In running the higher temperature

isotherms, 31.0 and 31.5°K in particular, it required long periods of time

to reach the equilibrium temperature and charge the cell with equilibrium

-H$_2$ by either of the methods discussed previously. These times were much

longer than for the investigation with normal hydrogen. Consequently, by

the time the system was prepared for the collection of data, the bath liquid

hydrogen level had frequently fallen to the point where it was possible to

take only one or two data points. Refilling the cryostat must be done at

atmospheric pressure (20.3K) with subsequent long waiting periods for the

bath to again rise to the desired to the desired temperature. When these

problems were compounded by those of the vacuum leaks and also the inherent

difficulty of obtaining a point inside the samll two-phase loop at the high

isotherms, the results were often unsatisfactory. From the results, it will

be seen that the data at 31.0°K turned out extremely well, in spite of these

problems. The results for the vapor phase at 31.5°K, on the other hand, are

quite disappointing, and cannot be considered of the same quality as the

results obtained in the rest of the present study.

IV. **RESULTS IN THE SYSTEM NORMAL HYDROGEN-HELIUM AND COMPARISONS WITH PREVIOUS WORK.**

A. **PRESENTATION OF RESULTS**

The experimental results for the system normal hydrogen - helium have been presented in the previous report, reference 7, by W.B. Streett, et. al. They are also included here for convenience and for the purpose of comparison with the system equilibrium hydrogen - helium.

The results of the experiment are summarized in Table I and Figs. 9-14. 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 30.60° were taken in an attempt to locate the critical point for that isotherm.

Figure 9 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. 10.

Figure 11 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, very little interpolation of the P-x isotherms was required to plot the curves in Fig. 11. Figure 12 shows the liquid region of the temperature-composition diagram on an expanded scale.

Figure 13 shows a cross-plot of the data from Figs. 9 and 11 on a pressure-temperature diagram. These curves are lines cut in the P-T-x surface by planes of constant composition.

Figure 14 is a plot of equilibrium constants K vs. pressure. The constant

TABLE I

NORMAL HYDROGEN-HELIUM

SUMMARY OF EXPERIMENTAL DATA

Temperature (°K)	Pressure (psia)	Liquid Mole % He	Liquid Mole % H$_2$	Vapor Mole % He	Vapor Mole % H$_2$
	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
15.50	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
	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
17.07	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
	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
20.40	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
	50.0	0.38	99.62	37.00	63.00
	75.0	0.75	99.25	53.44	46.56
23.00	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 % H₂	Mole % He	Mole % H₂
	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
	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
31.50	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
	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
31.90	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	---	---
	188.5	0.98	99.02	3.12	96.88
	200.0	1.68	98.32	4.80	95.20
32.50	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	---	---
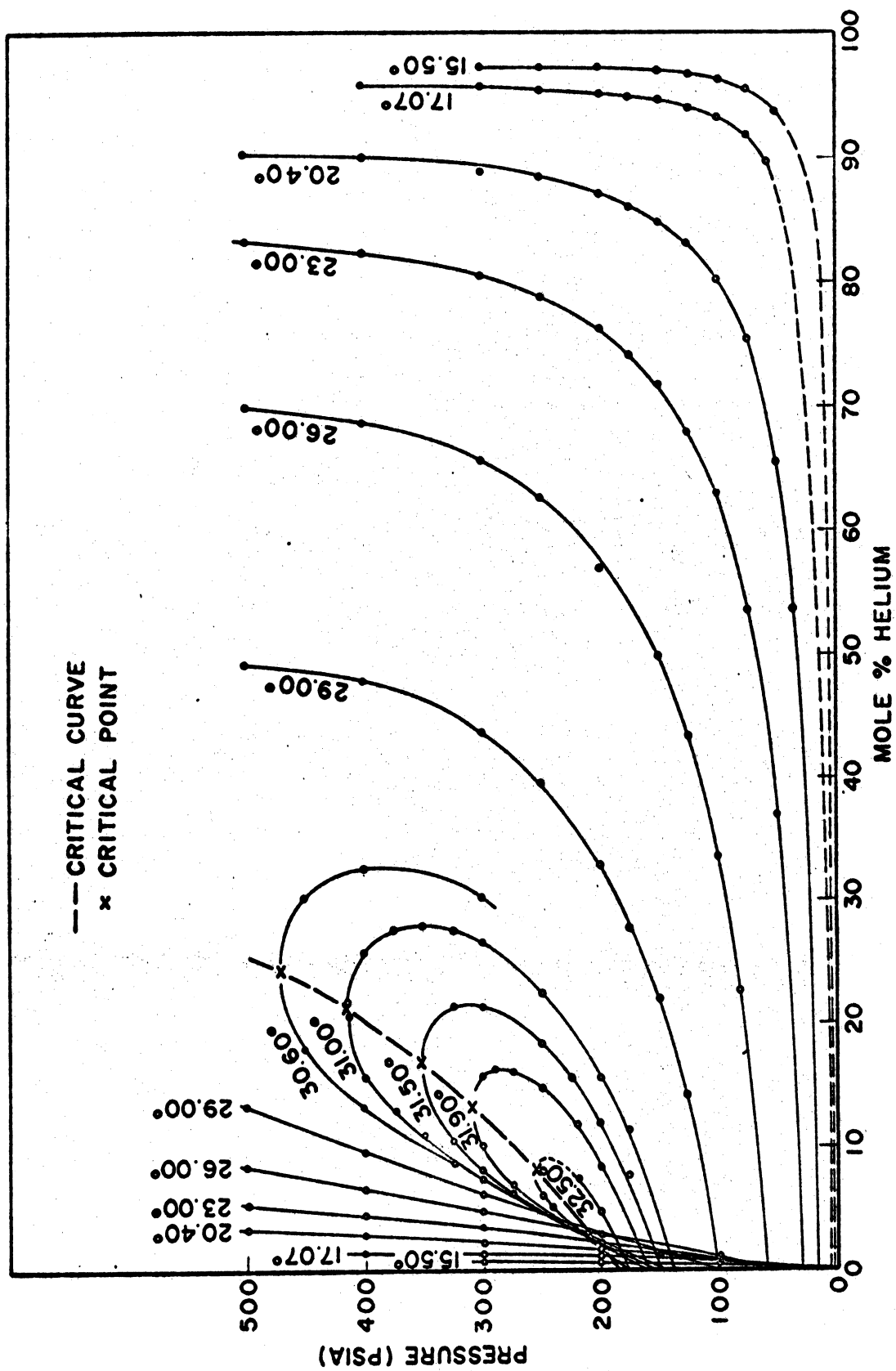
Fig. 9. Isothermal pressure-composition diagram.
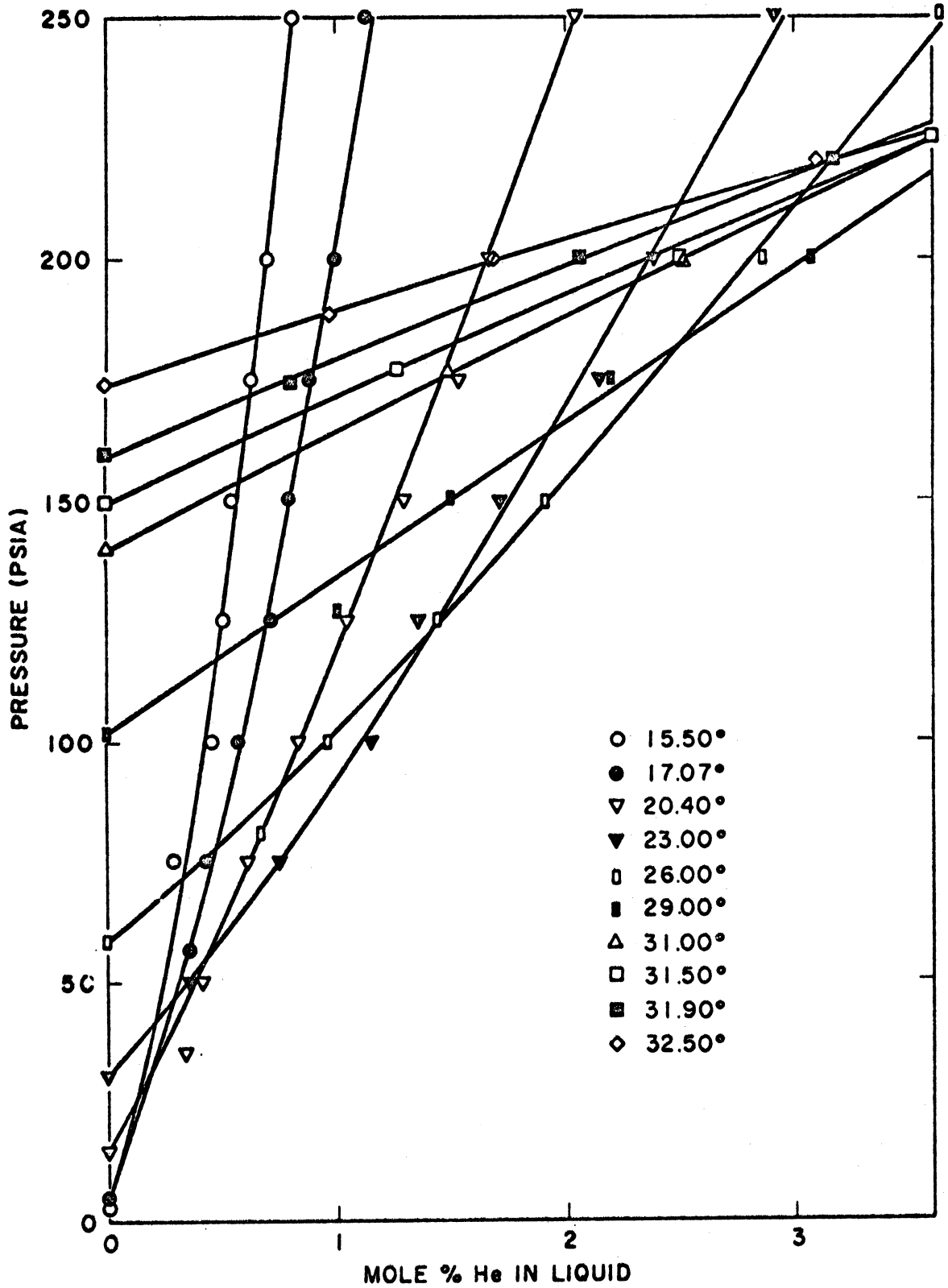
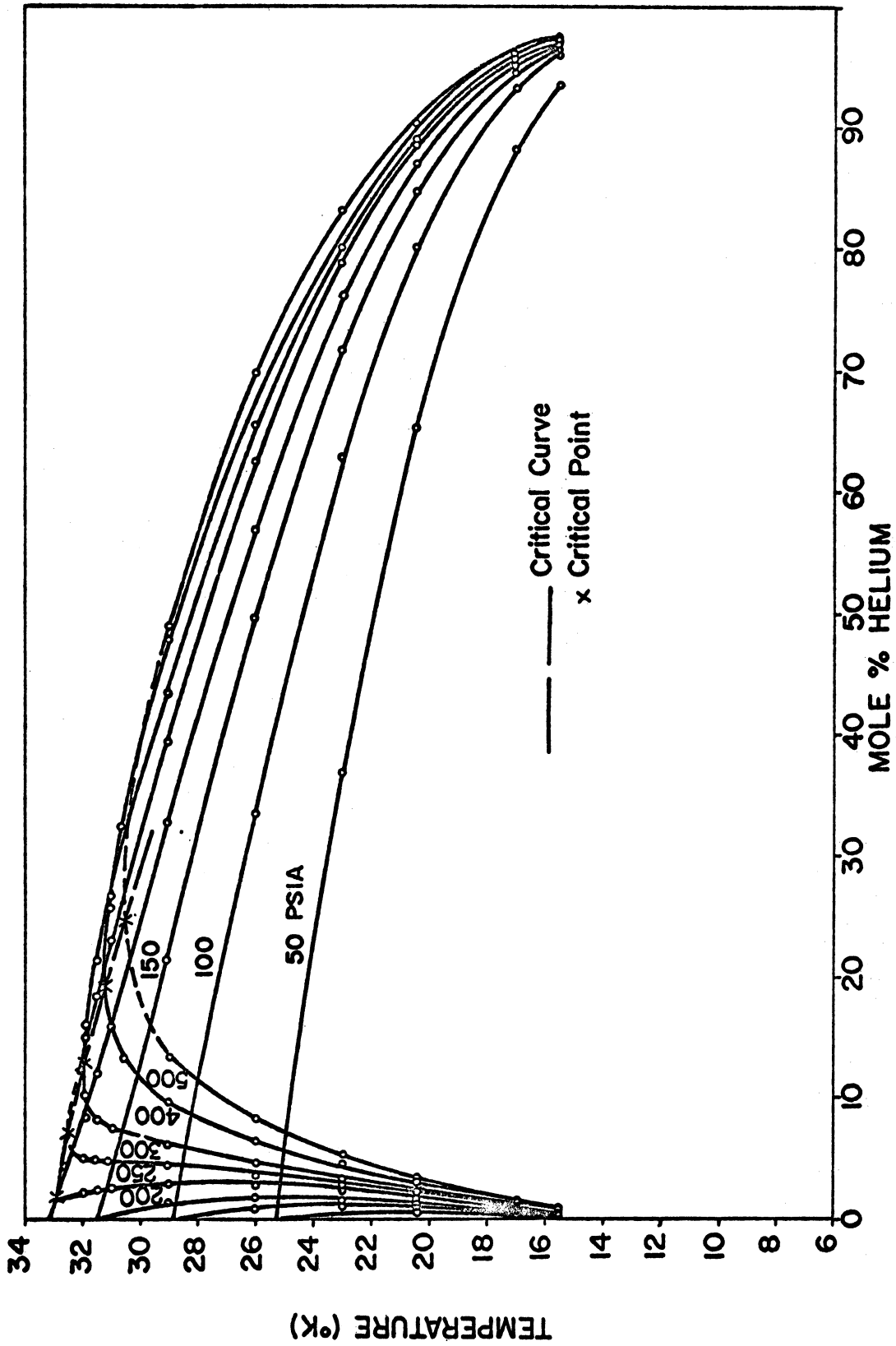Fig. 10. Isothermal pressure-composition diagram showing liquid region on expanded scale.

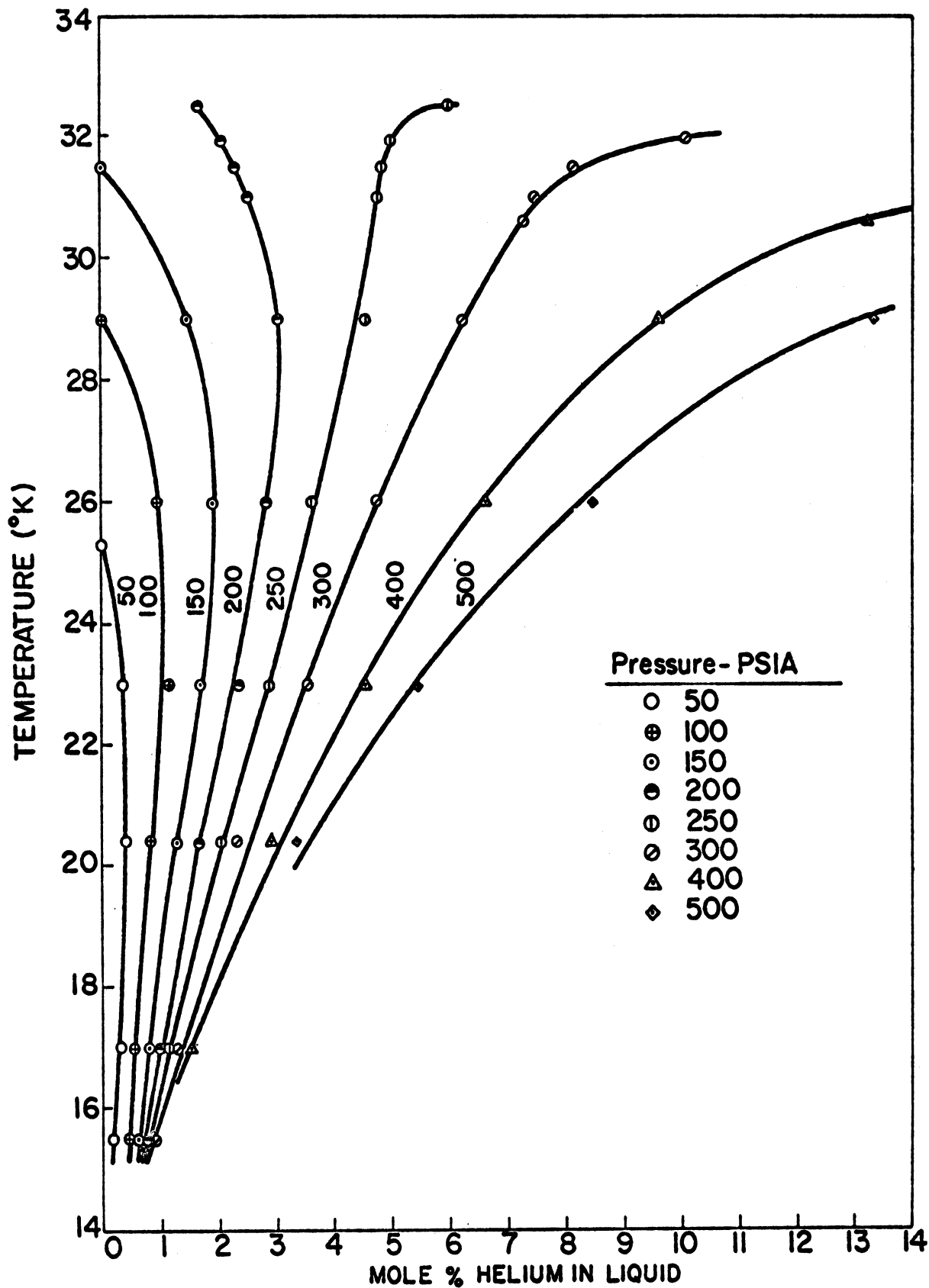Fig. 11. Isobaric temperature-composition diagram.

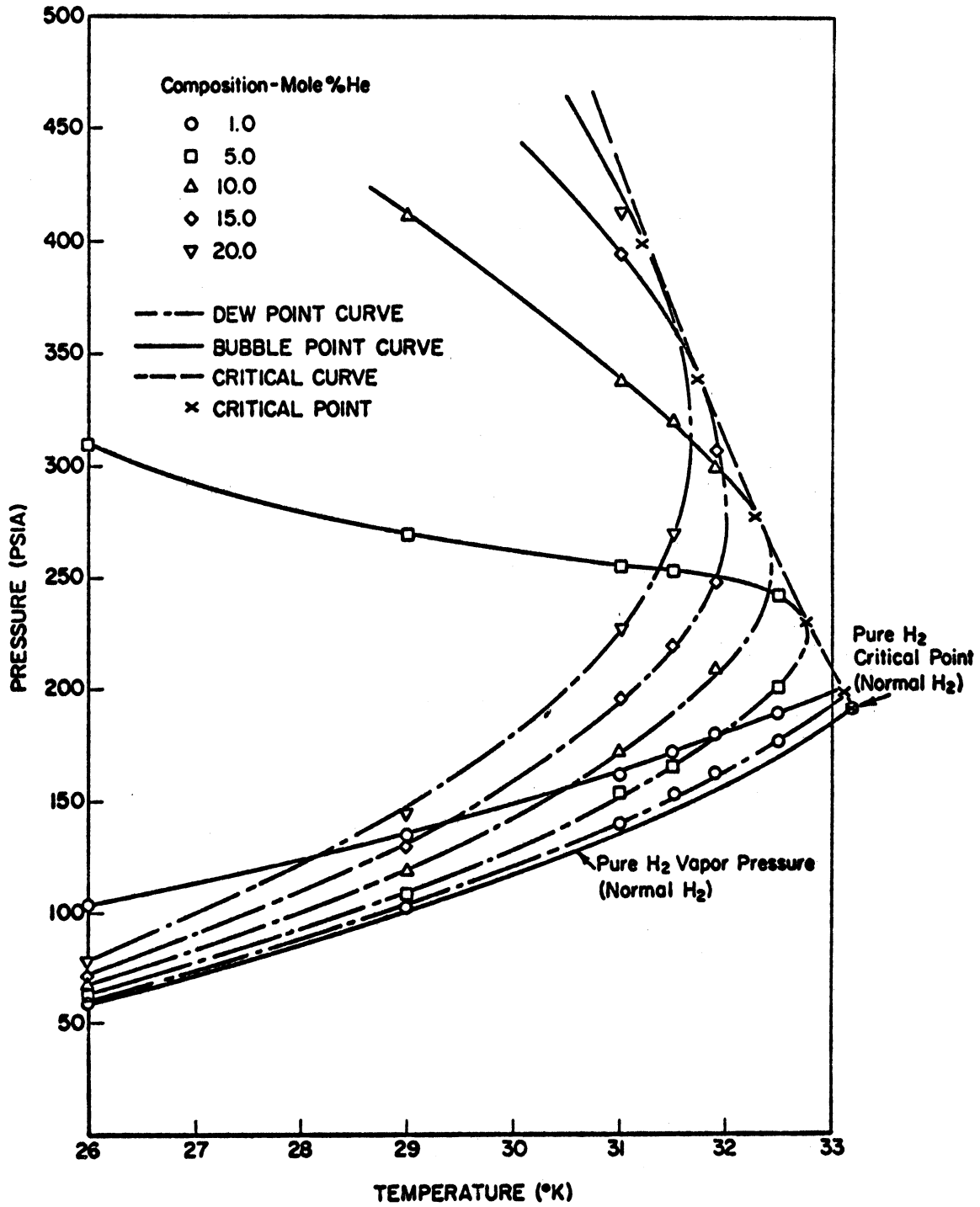Fig. 12. Isobaric temperature-composition diagram showing liquid region on expanded scale.
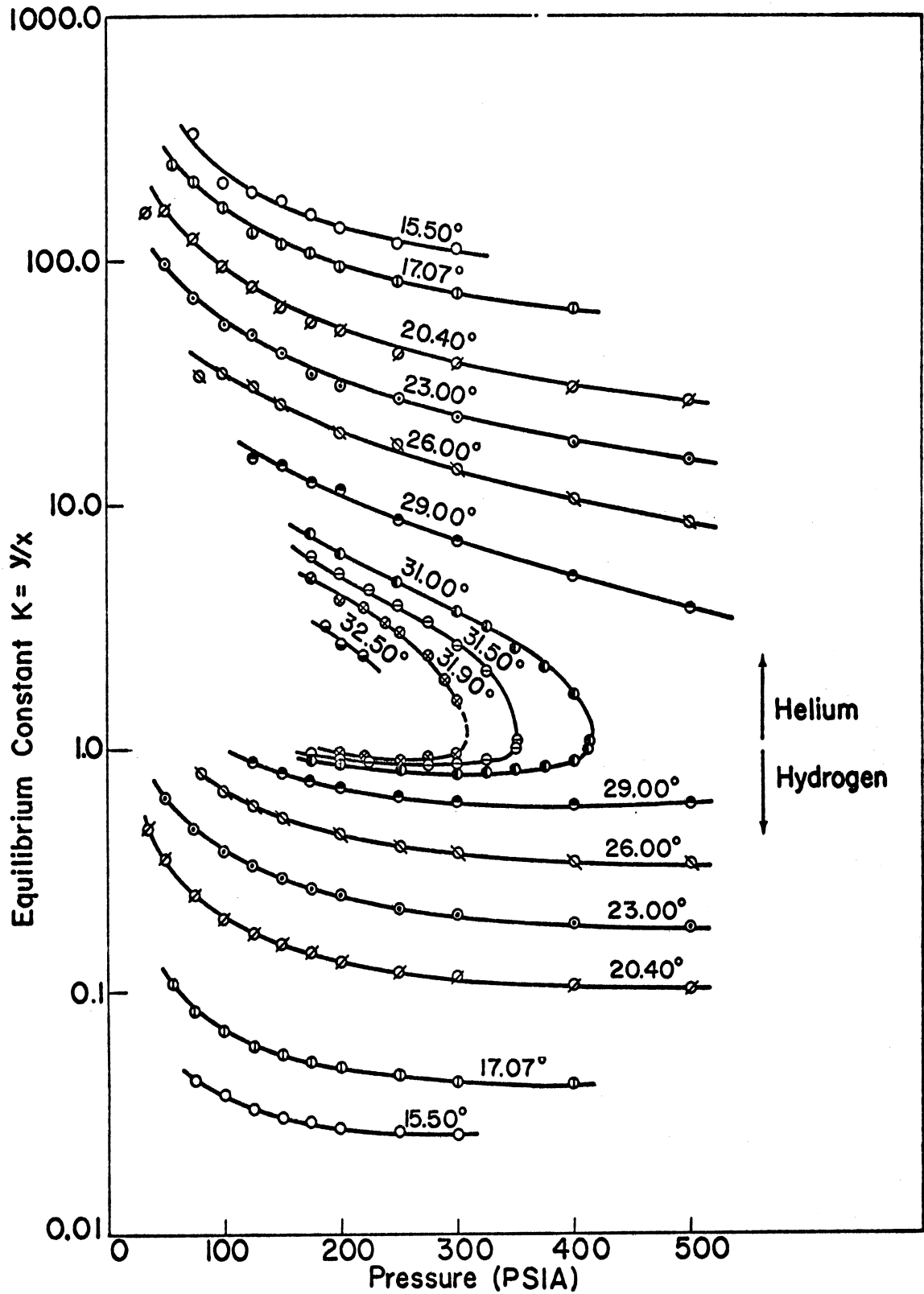
Fig. 13. Pressure-temperature diagram.

Fig. 14. Equilibrium K values.

K is defined as the ratio of the mole fraction of a component in the vapor
to its mole fraction in the liquid.

B. DISCUSSION

The behavior of this system, as shown by the curves in Figs. 9-13 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, 10, 11 and nitrogen-hydrogen.[12]

In the P-x diagram of Fig. 9 and the T-x diagram of Fig. 11, 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 com-
position; 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.[12]

Each of the closed loops in Fig. 9 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^{o}, 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. 10 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. 11 and 12, the data exhibit reverse-order solubility in the
liquid region. This is defined as an increase in the solubility of a cons-
tituent 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. 9 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. 13
is out of the range of the diagram to the left).

The critical curve shown in Figs. 9, 11 and 13 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 phe-
nomena in the critical region was possible in this experiment, due to the
nature of the apparatus.

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. 9 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 $\pm$ 10 psi, $\pm$ 0.2°K, or $\pm$ 0.2 mole percent.

C. COMPARISON WITH PREVIOUS WORK

The work of Smith[1] and of Roellig and Giese[2] 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. 15-18.
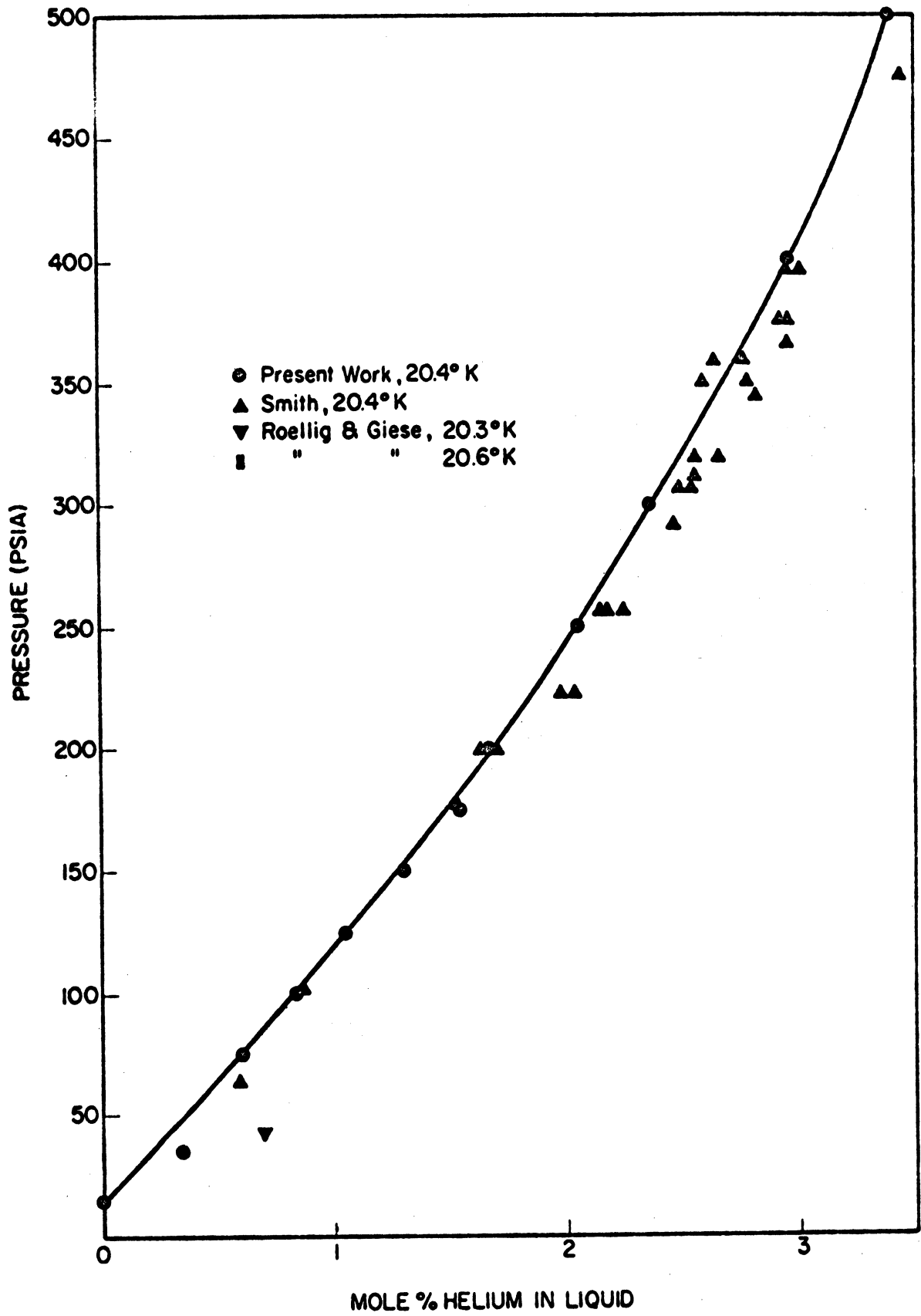
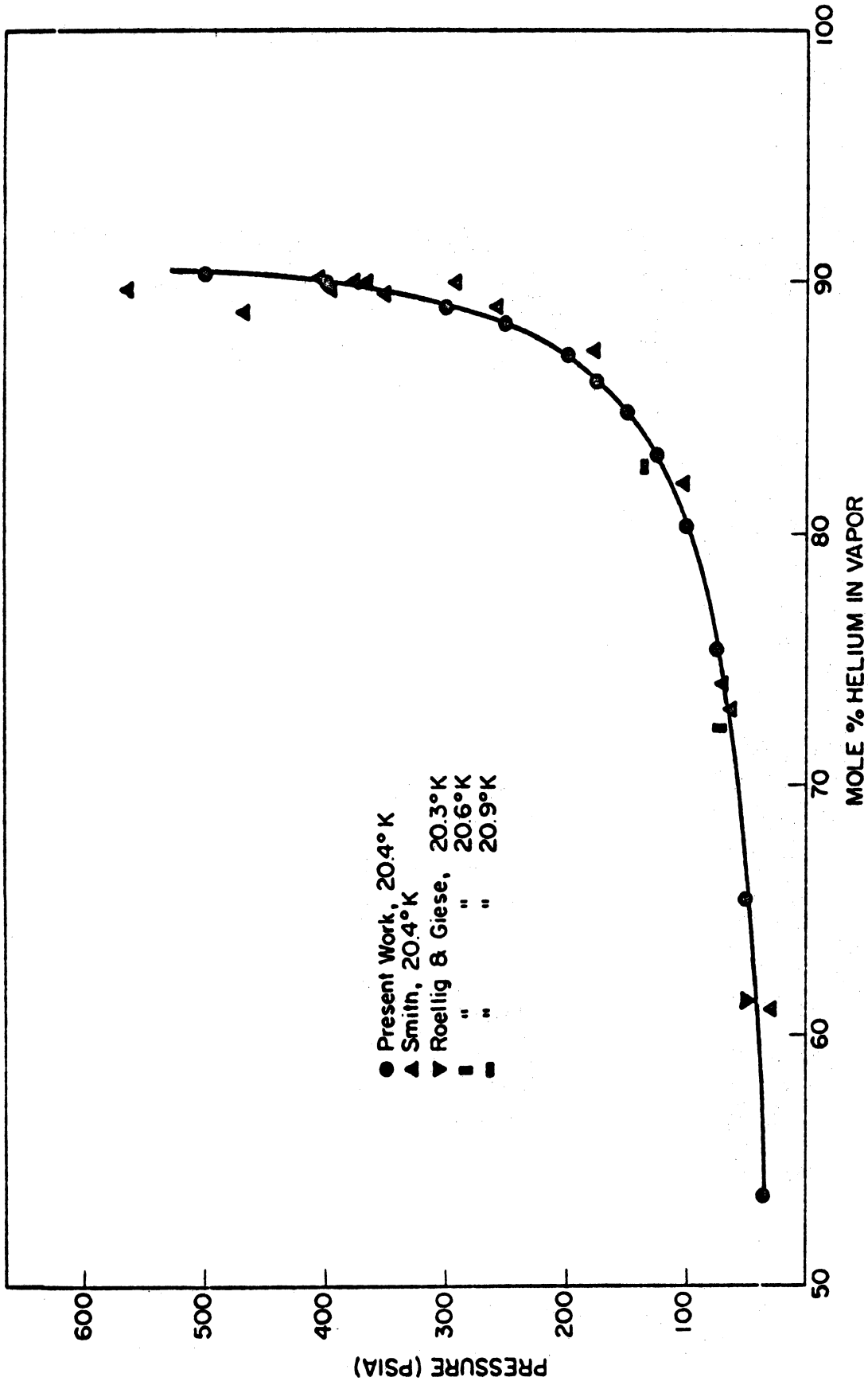Fig. 15.   Comparison with previous work, liquid data at 20.4°K.

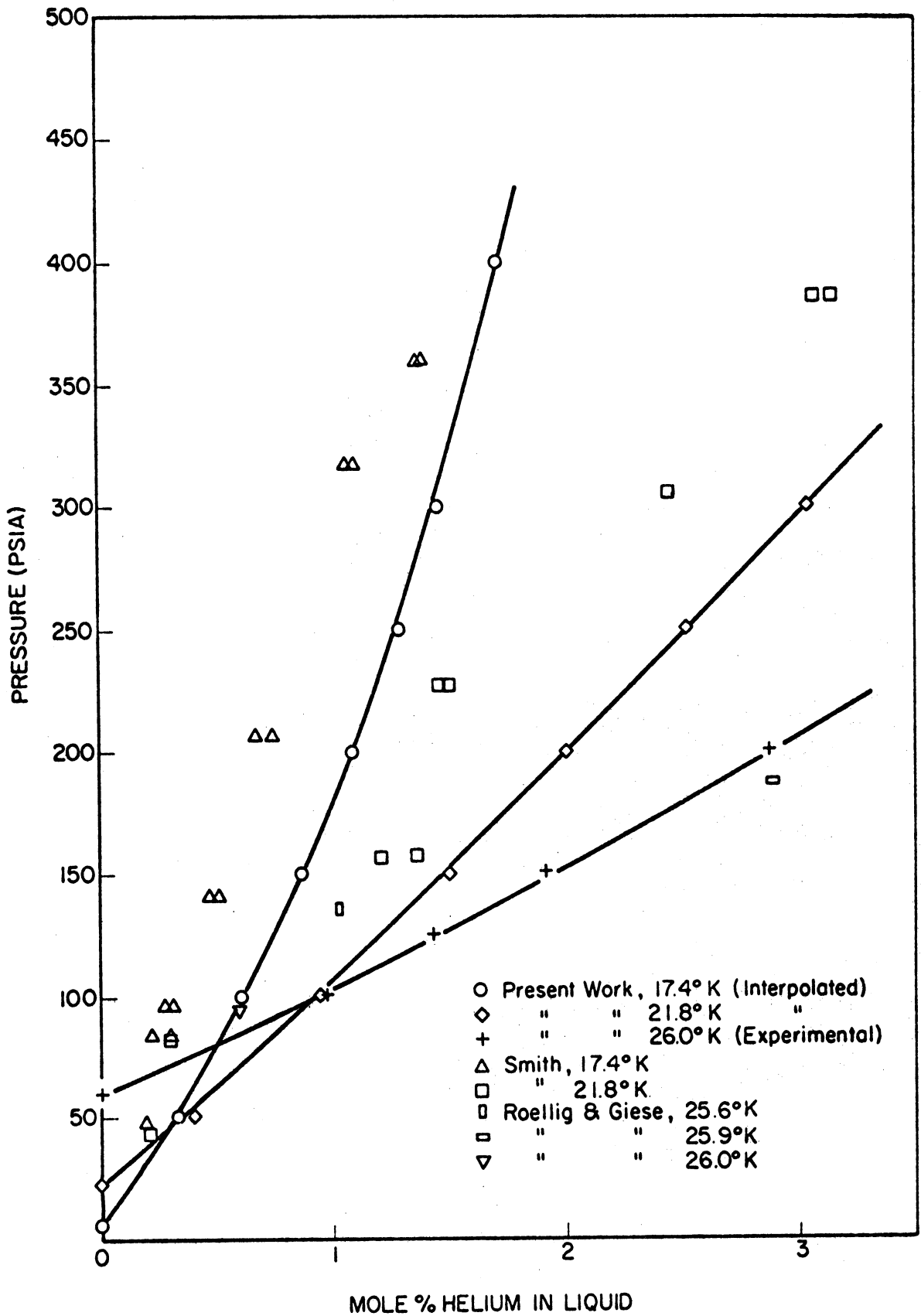Fig. 16. Comparison with previous work, vapor data at 20.4°K.

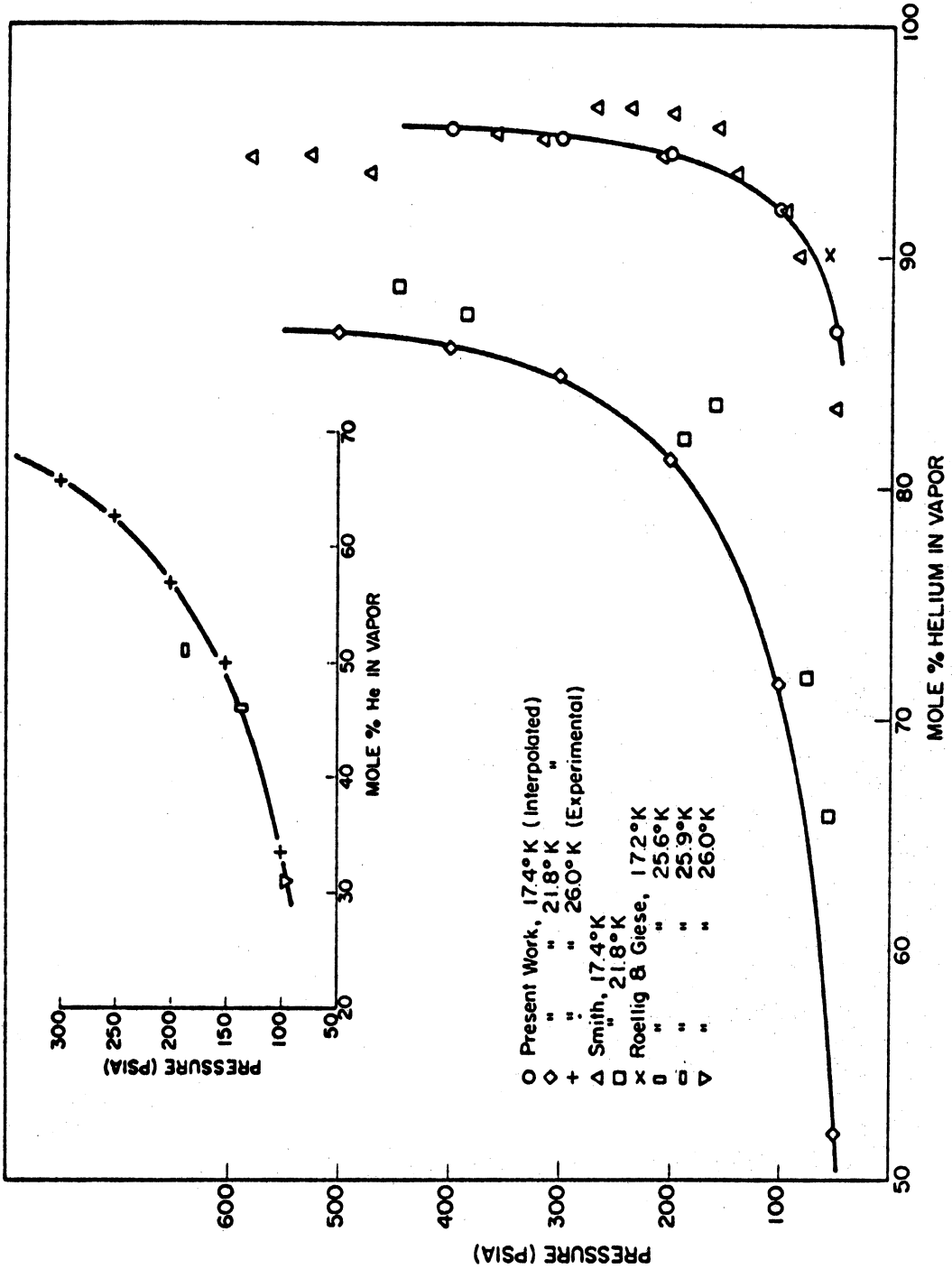Fig. 17. Comparison with previous work, liquid data at 17.4, 21.8, and 26.0°K.

Fig. 18. Comparison with previous work, vapor data at 17.4, 21.8, and 26.0°K.

Of the three isotherm studied by Smith, only that at 20.4^o was dup-
licated in the present work. A comparison with Smith's results at this
temperature is shown in Figs. 15 and 16. 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^o and 21.8^o, data at
these temperatures were obtained for the present work by graphical inter-
polation of the temperature-composition diagrams of Figs. 11 and 12. A
plot of this data on a large scale was used for this interpolation. The
comparison is shown in Figs. 17 and 18. The agreement is not as good as
that at 20.4^o. 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^{o}K lower than the temperatures reported by Smith. This
discrepancy may be due to the method of 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^{o}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
$\pm$ 0.01^o, as reported by Smith, the EMF would have to be measured to within
$\pm$ 0.05^o μv, or $\pm$ 0.008% of the total. Even then, the results would be
questionable. Scott[13] 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.

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[3] 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 incompressible 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 liquid phase compositions for the two temperatures 20.6 and 20.9° (calculated by Eckert and Prausnitz) are plotted in Fig. 15. The lack of agreement is apparent. The three liquid points at 26.0, 25.6, and 25.9° are plotted in Fig. 17, and agree reasonably well with the 26.0° isotherm of this work.

The vapor phase compositions for the above five points, along with that of the 17.2° points are shown in Figs. 16 and 18. They 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.

D. THERMODYNAMIC TREATMENT

The original work of Smith[1] 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[5] 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[3] 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.

V. RESULTS IN THE SYSTEM EQUILIBRIUM HYDROGEN - HELIUM AND COMPARISONS WITH THE
SYSTEM NORMAL HYDROGEN - HELIUM.

A. PRESENTATION OF RESULTS

Experimental results of the investigation conducted on the system equi-
librium hydrogen-helium are presented in the same manner as for those of the
first system studied. Since these results were collected for the purpose of
comparison with those found using normal hydrogen, it was not considered
necessary to take as many data points as in that study. Six isotherms are
reported here, covering the range 20.40 to 31.50^{o}K at pressures from hydrogen
saturation to 500 psia. Early results indicated that temperatures below 20.40^{o}
would not be of interest, in that differences between the two systems would be
negligibly small.

The data are summarized in Table II and in Figures 19-24. The points
were in general taken at the same values of pressure and temperature as run
for the previous system, for convenience in comparing the results.

Figure 19 is an isothermal pressure - composition diagram representing the
entire range of data for this system, while Figure 20 is the expanded - scale
liquid portion of this diagram. Figure 20 shows the solubility of helium
in liquid equilibrium hydrogen, the data of particular interest to the transfer
of hydrogen by helium pressurization.

Figure 21 shows the data on temperature - composition coordinates, the
expanded - scale liquid region of which is given in Figure 22. Figure 23
represents a cross- plot of the data of 19 and 21 on pressure - temperature
coordinates, showing lines of constant composition. Finally, Figure 24 is
a plot of the equilibrium constant K versus pressure, K being defined as the
ratio of vapor phase mole fraction of a component to its liquid phase mole
fraction.

TABLE II

EQUILIBRIUM HYDROGEN-HELIUM

SUMMARY OF EXPERIMENTAL DATA

Temperature ($^{\circ}$K)	Pressure (psia)	Liquid		Vapor	
		Mole % He	Mole % H_2	Mole % He	Mole % H_2
	34.7	0.23	99.77	49.40	50.60
	50.5	0.58	99.42	62.79	37.21
	75.0	0.60	99.40	72.80	27.20
	100.0	0.87	99.13	78.21	21.79
	125.0	1.02	98.98	80.83	19.17
	150.0	1.17	98.83	83.00	17.00
	175.0	1.55	98.45	84.71	15.29
20.40	200.0	1.77	98.23	85.79	14.21
	250.0	1.92	98.08	---	---
		2.04	97.96	86.64	13.36
	300.0	2.25	97.75	86.80	12.20
	400.0	2.66	97.34	88.72	11.28
		2.94	97.06	88.56	11.44
	500.0	3.08	96.92	---	---
		3.16	96.84	85.99	14.01
	64.5	0.54	99.46	45.60	54.40
	75.0	0.65	99.35	52.20	47.80
	101.0	1.05	98.95	61.70	38.30
	125.0	1.38	98.62	67.00	33.00
	150.5	1.75	98.25	70.90	29.10
23.00	175.0	2.27	97.73	73.50	26.50
	200.0	2.40	97.60	75.35	24.65
	250.0	3.00	97.00	77.90	22.10
	300.0	3.65	96.35	79.50	20.50
	400.0	4.73	95.27	79.10	20.90
	500.0	5.62	94.38	82.50	17.50
	100.0	0.79	99.21	29.66	70.34
	150.0	2.00	98.00	45.57	54.43
	200.0	3.03	96.97	53.55	46.45
	250.0	3.67	96.33	58.77	41.23
26.00		3.90	96.10	59.52	40.48
	300.0	5.08	94.92	63.00	37.00
	400.0	5.95	94.05	66.51	33.49
		6.37	93.63	65.05	34.95
	500.0	7.82	92.18	67.15	32.85
		8.10	91.90	68.04	31.96

TABLE II (Continued)

| Temperature ($^{\circ}$K)	Pressure (psia)	Liquid		Vapor	
		Mole % He	Mole % H_2	Mole % He	Mole % H_2
	142.0	1.19	98.81	17.60	82.40
	174.5	2.22	97.78	26.15	73.85
	200.0	3.05	96.95	31.15	68.85
29.00	251.5	4.78	95.22	37.90	62.10
	300.5	6.33	93.67	41.90	58.10
	400.5	10.06	89.94	46.00	54.00
	501.0	---	---	47.00	53.00
	200.0	2.17	97.83	13.17	86.83
	248.5	4.40	95.60	20.10	79.90
	250.0	4.55	95.45	---	---
	300.0	7.52	92.48	23.14	76.86
31.00	324.0	9.08	90.92	---	---
	332.0	---	---	23.68	76.32
	350.0	---	---	23.94	76.06
	366.5	12.55	87.45	23.53	76.47
	390.5	18.12	81.88	18.44	81.56
	176.5	1.07	98.93	6.34	93.66
	203.0	2.39	97.61	10.99	89.01
	225.0	---	---	14.02	85.98
31.50	250.0	4.55	95.45	15.68	84.32
	275.0	---	---	16.97	83.03
	300.0	8.08	91.92	17.13	82.87
	315.0	9.28	90.72	18.70	81.30
	332.0	14.90	85.10	16.57	83.43
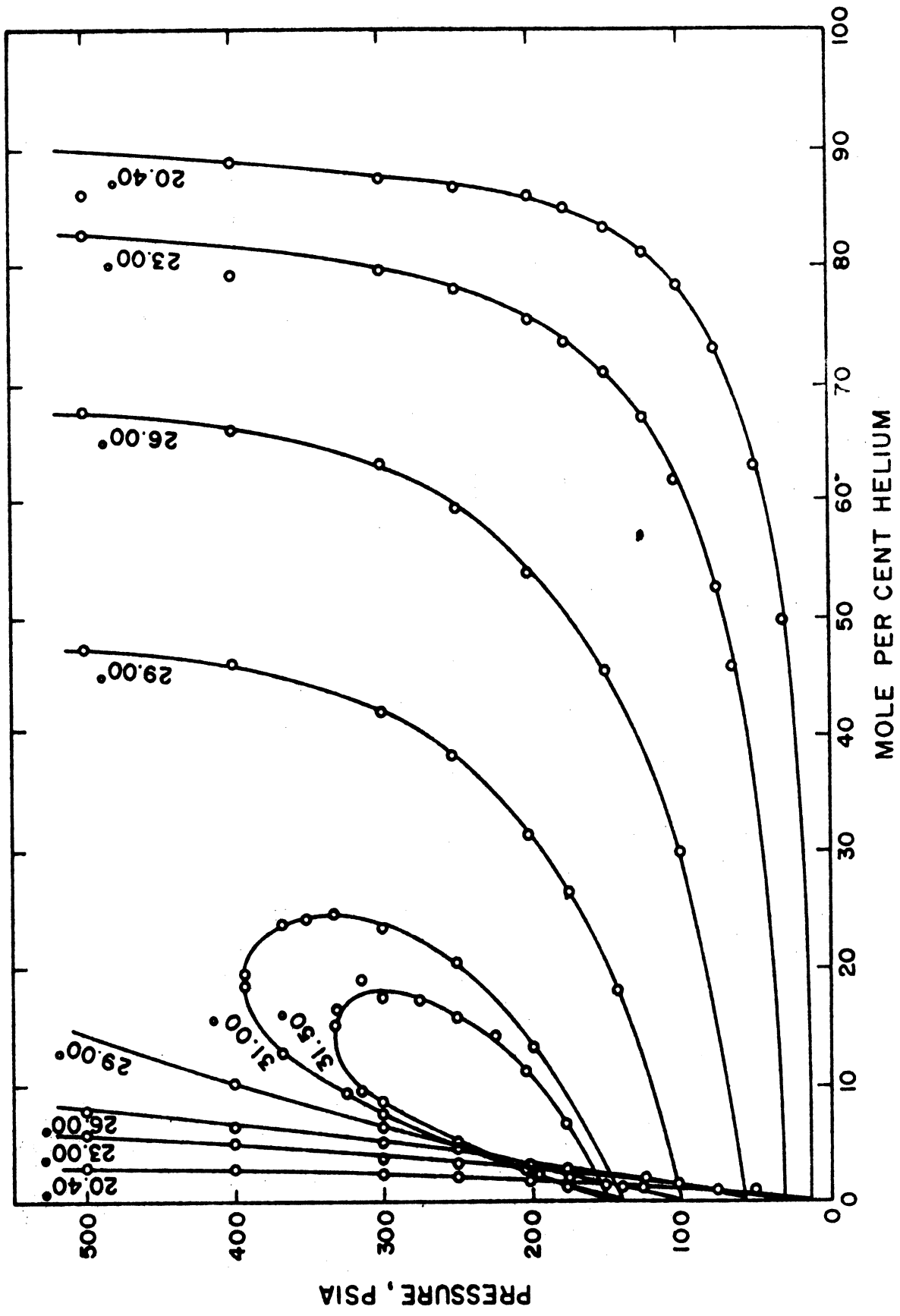
Fig. 19
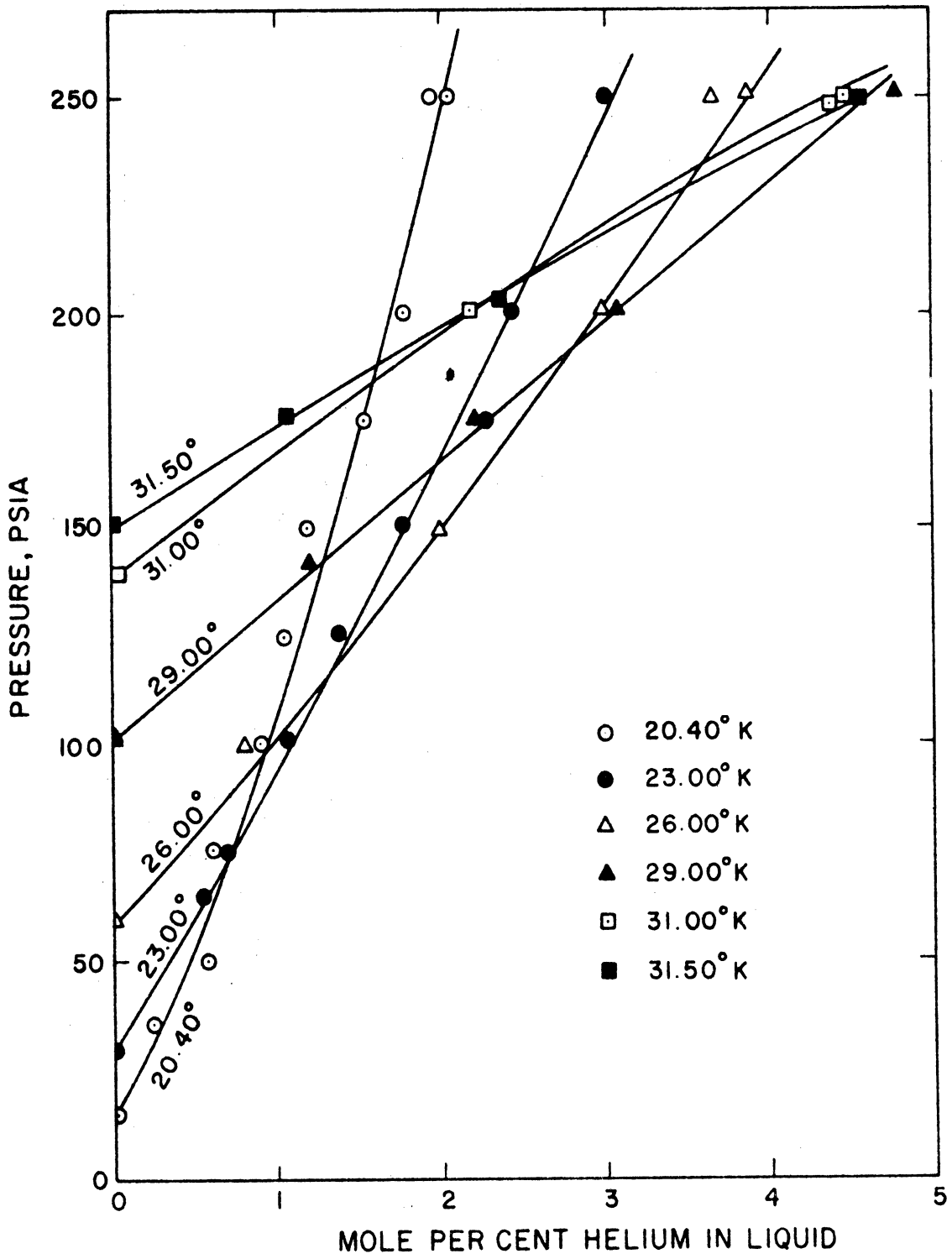Isothermal pressure-composition diagram

Fig. 20

Isothermal pressure-composition diagram showing liquid region on expanded scale
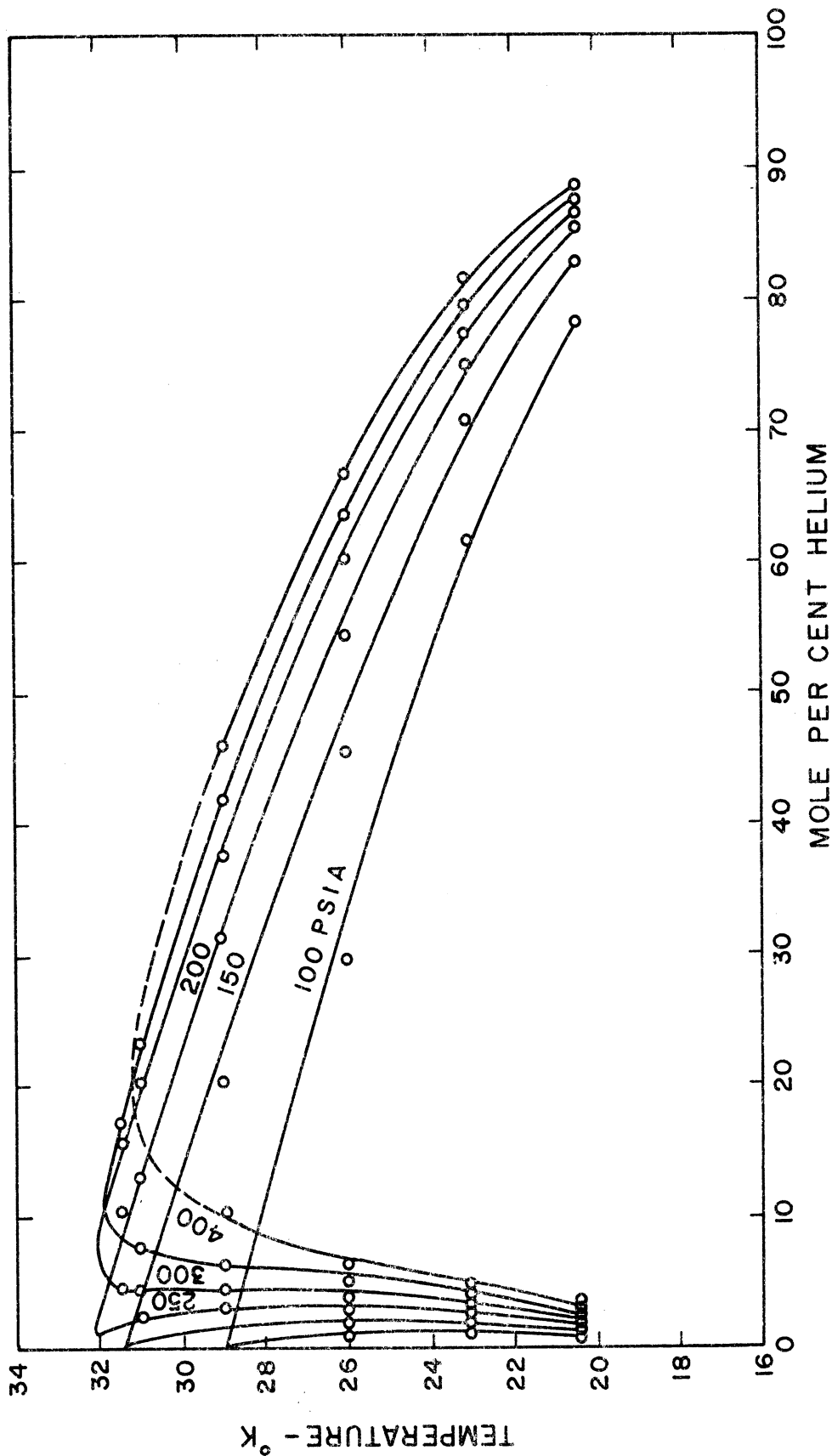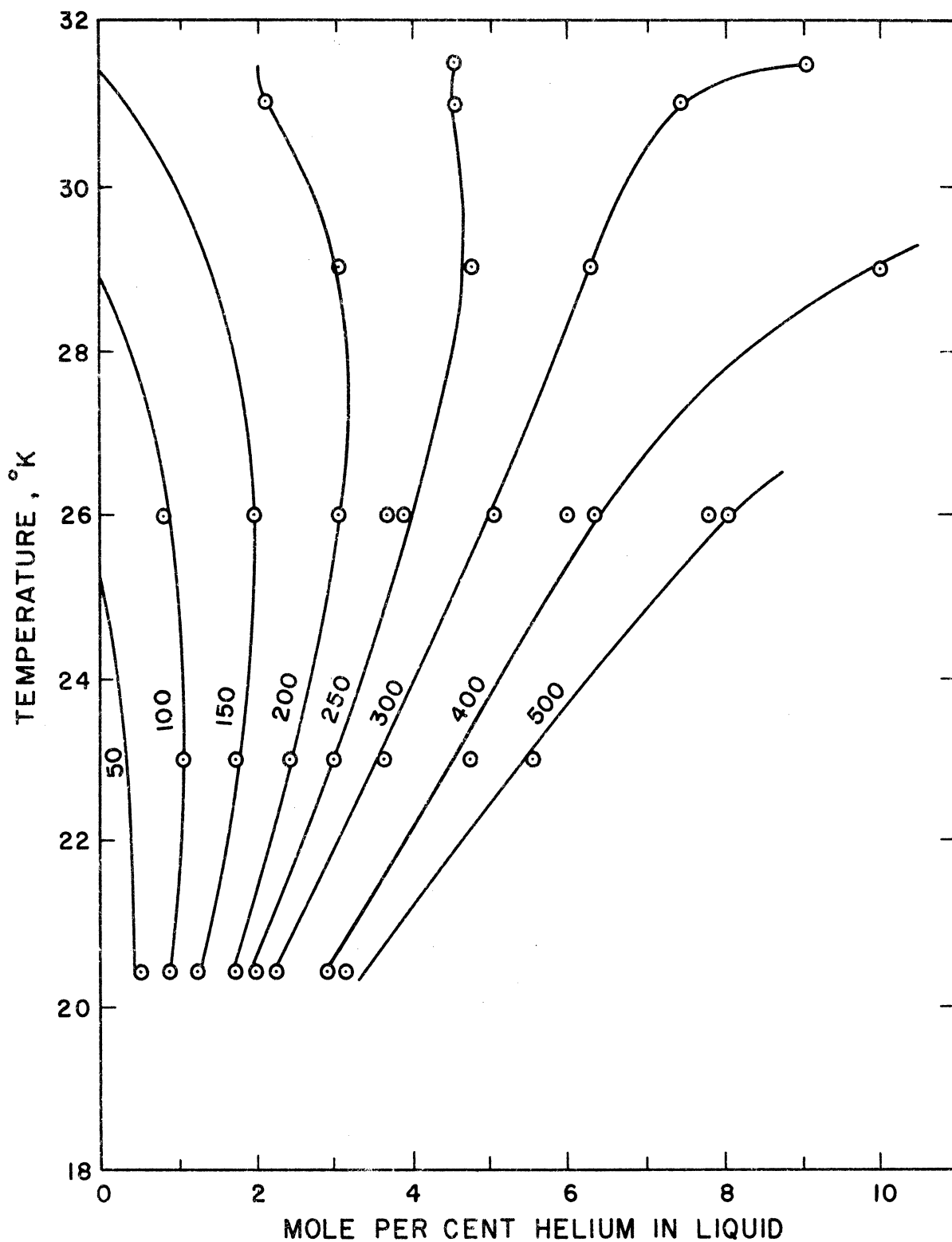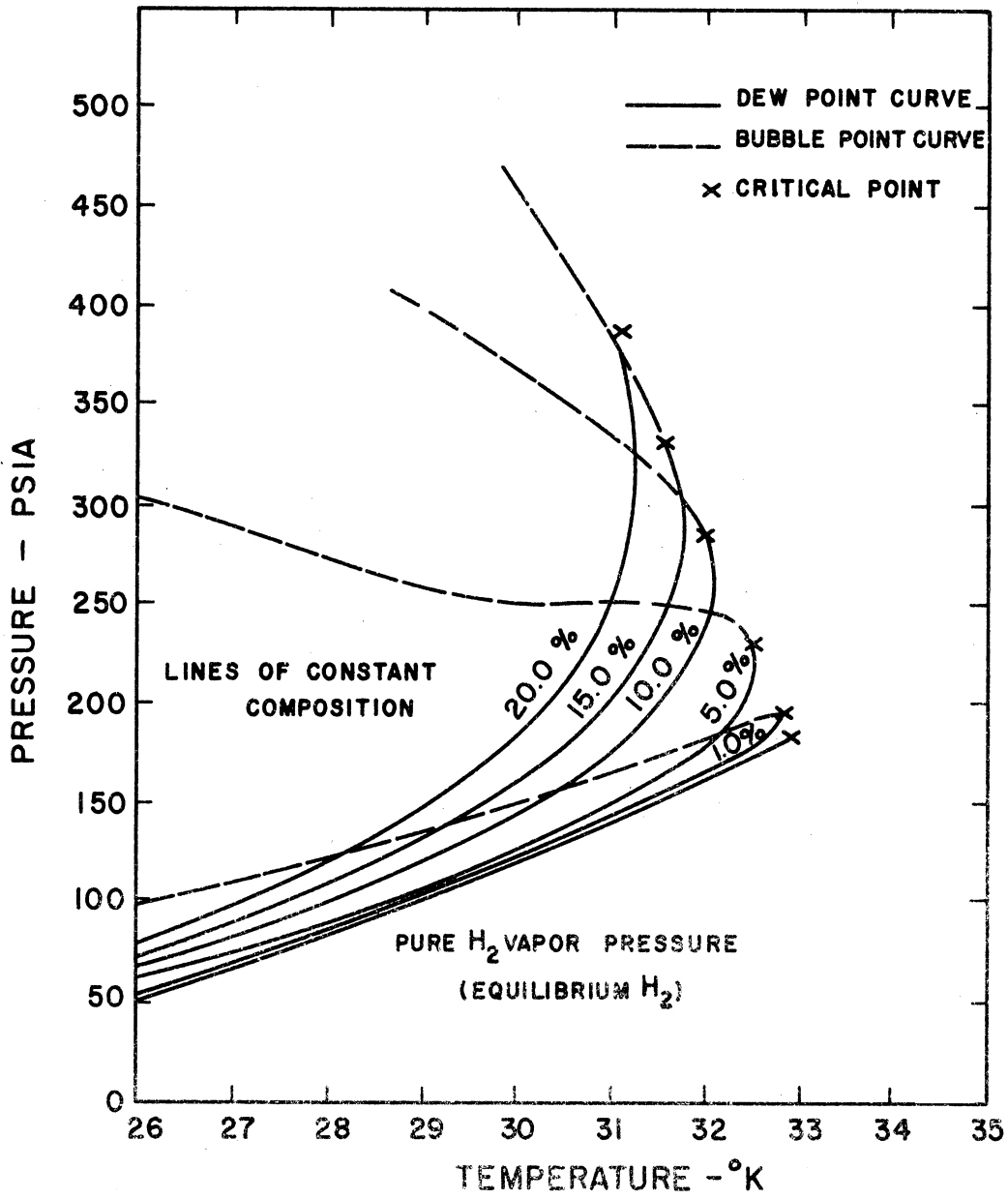
ISOBARIC TEMPERATURE—COMPOSITION DIAGRAM

Fig. 21

Isobaric temperature-composition diagram showing liquid region on expanded scale
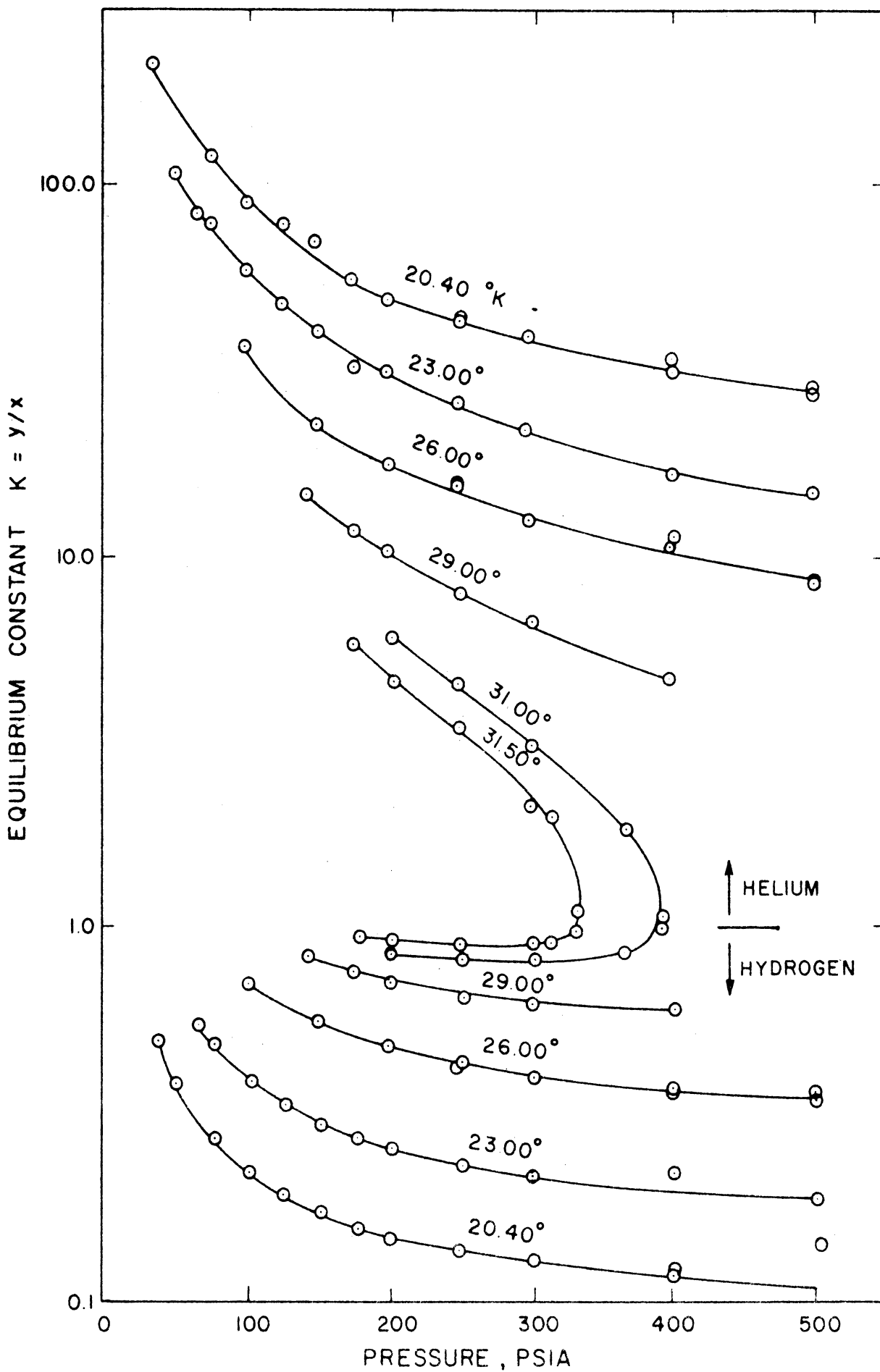
Fig. 22

Pressure-temperature diagram   Fig. 23

Fig. 24
Equilibrium K values

B. DISCUSSION

The results are, as expected, very similar to those for normal hydrogen-helium, there being only minor differences in the behavior of the two systems. The data are in general self-consistent, and show little scatter. Individual points that are not consistent with the results in general are mostly vapor phase samples. The vapor samples at 20.40°K, 500 psia and at 23.00°K, 400 psia are apparently low by approximately 3 and 2 per cent, respectively. The vapor phase curve at 26.00°K seems to be self-consistent on a P-x diagram, as shown in Figure 19. However, the T-x plot of Figure 21 and also a comparison with normal hydrogen-helium results at this temperature indicate that the values are somewhat low at pressures below 250 psia.

The liquid-phase sample at 29.00°K, 500 psia, had to be discarded. The liquid level in the cell had apparently fallen below the level of the sample probe when this point was taken, such that a sample of vapor instead of liquid composition was withdrawn. The vapor phase sample at that point is consistent with the remainder of the data at 29.00°K.

The vapor phase compositions for the 31.50°K isotherm at pressures above 250 psia are questionable, with appreciable scatter being evident, although the liquid phase results in this region seem acceptable. There was considerable difficulty in obtaining points for this isotherm, as was discussed in detail in Section III of this report.

From the expanded-scale liquid phase composition plots, Figures 20 and 22, it is seen that throughout the experimental range of this investigation the liquid compositions are very consistent and show almost no scatter. This is also evident from the plot of equilibrium constants in Figure 24, especially for the helium, where the values are large, because of the small concentration of helium in the liquid. Any scatter in liquid composition values would be greatly magnified on

this plot.

Difficulties encountered in experimental phase equilibrium investigations are commonly associated with the liquid phase, particularly in sampling. No such problems are evident from the results of this study. Instead, what scatter is apparent is concerned primarily with vapor phase results at the points mentioned above. The cause of these minor inconsistencies is not known, and these problems were not evident in the study of the system normal hydrogen - helium. It is felt that since these inconsistent values occurred at only isolated points, and for only one phase, the cause must be associated with a poor sampling technique at those points.

C. COMPARISONS WITH THE SYSTEM NORMAL HYDROGEN - HELIUM

Comparison of the experimental results in the system equilibrium hydrogen - helium with those for normal hydrogen - helium is best made in graphical form. The two systems are shown in Figures 25-30, isothermal P-x diagrams for the six isotherms studied using equilibrium hydrogen.

It is seen that with the exception of those few experimental points discussed in the previous section, the differences between the systems are consistent and increase with increasing temperature. If the systems behaved ideally, then Raoult's Law would describe the liquid phase and the ideal gas law the vapor phase. Differences between the two systems could then be explained and calculated entirely in terms of the difference in vapor pressure between normal hydrogen and equilibrium hydrogen. At any temperature, equilibrium hydrogen has a somewhat higher vapor pressure. Therefore, it would be expected that the isotherms for the equilibrium hydrogen - helium system should be shifted slightly from those for normal hydrogen - helium in the direction of increasing temperature. The two systems do not behave ideally, so that differences in P-V-T behavior for the two varieties
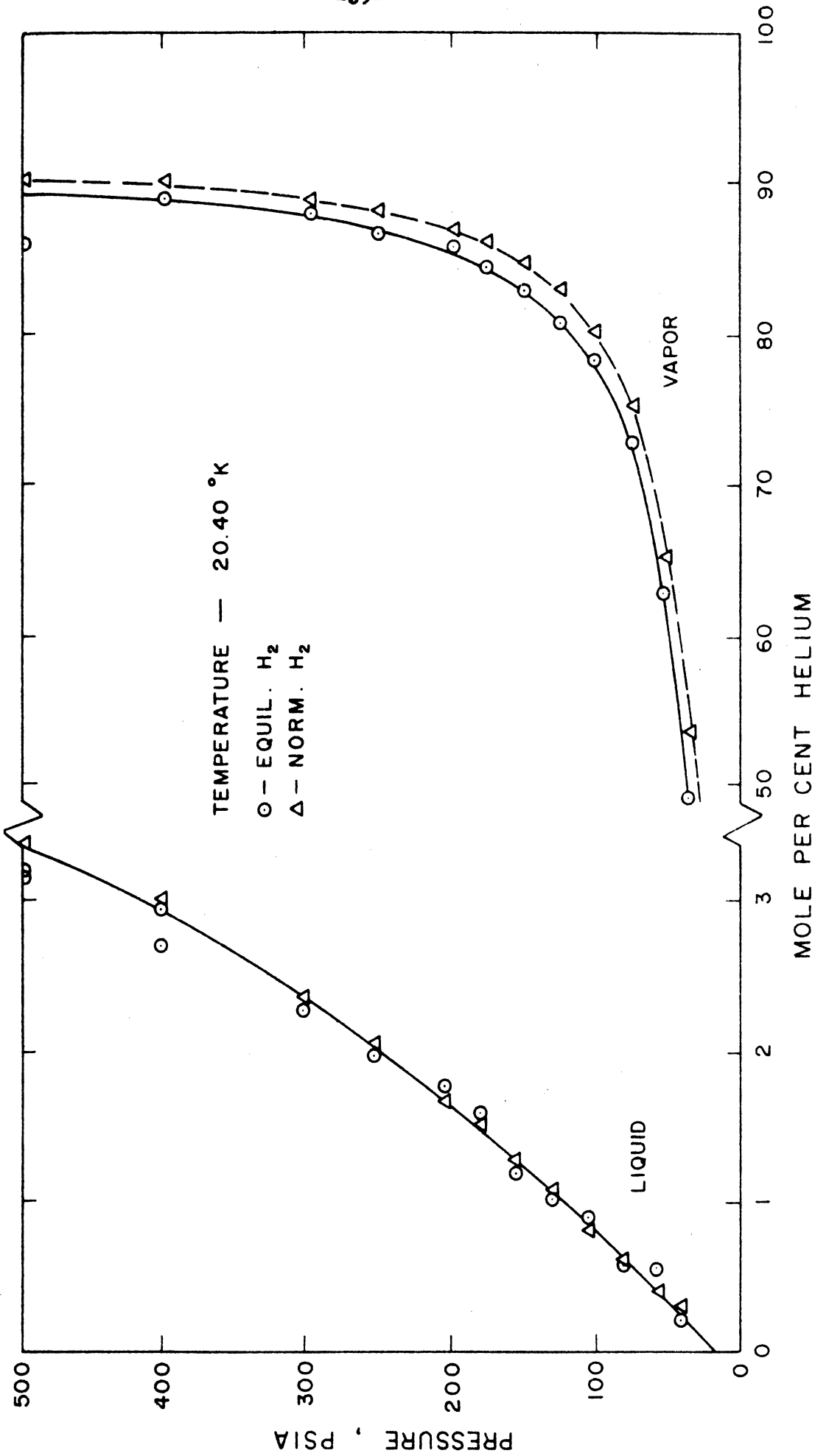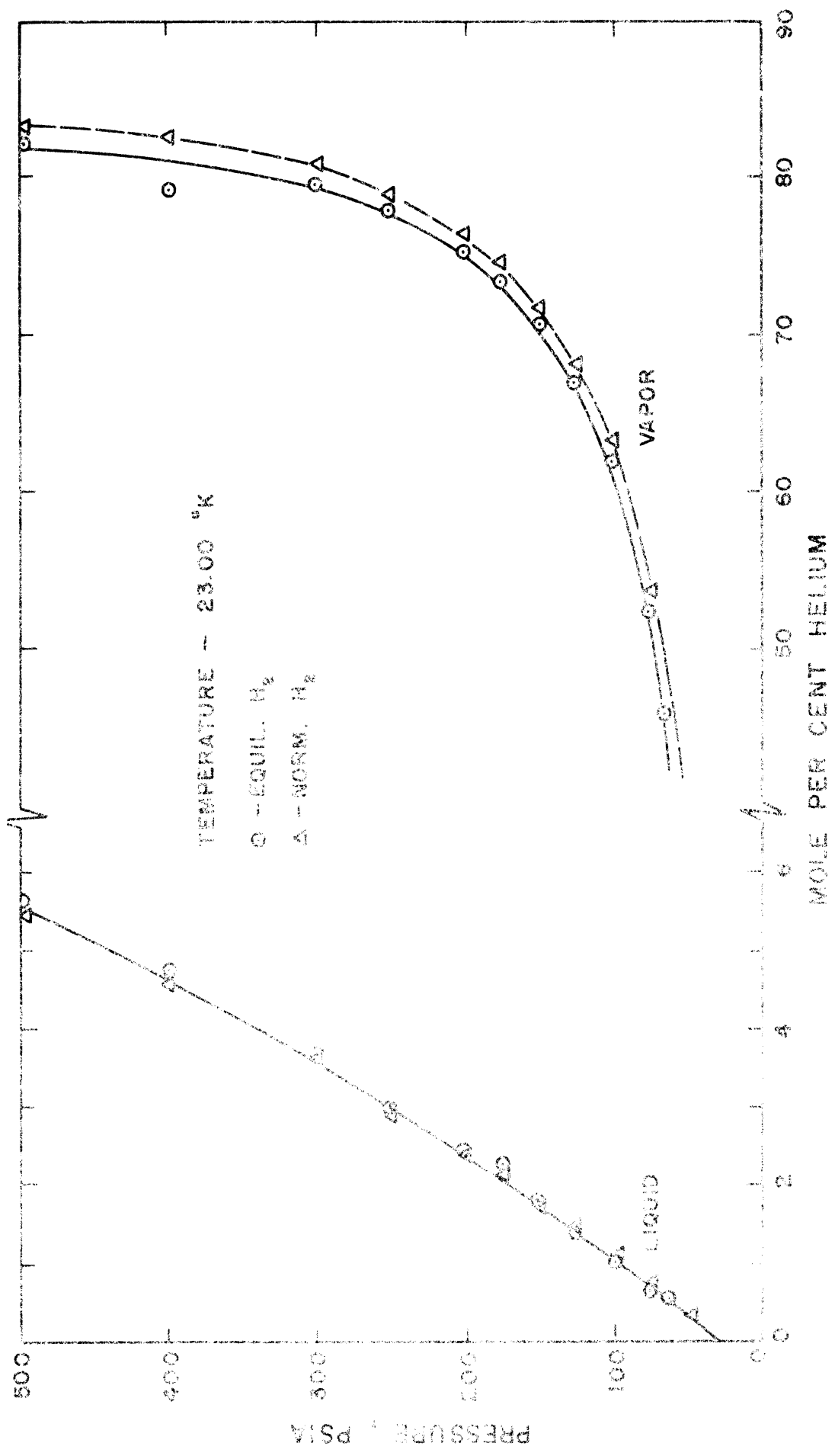
Fig. 25

Comparison of the two systems at 20.4°K
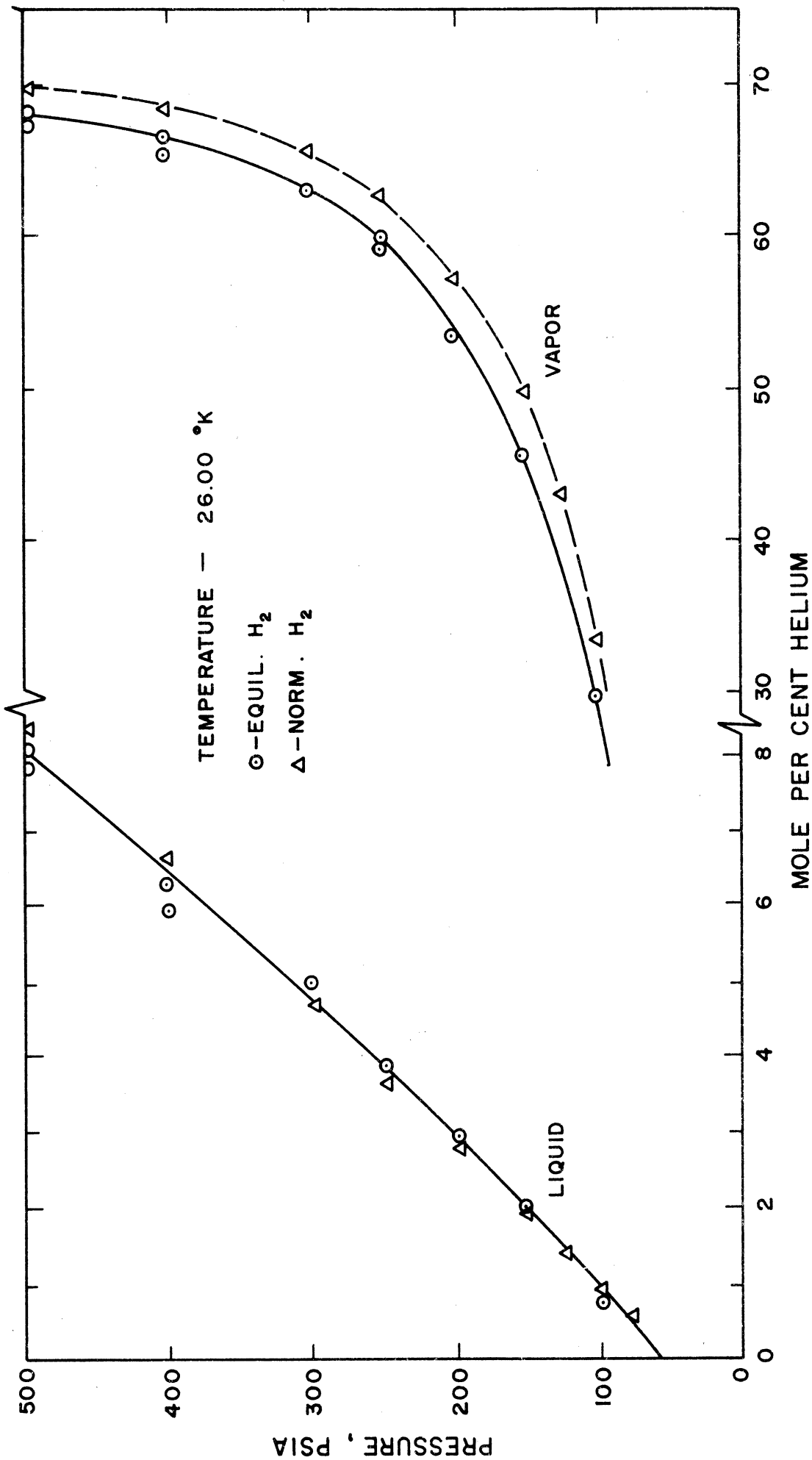
Fig. 26

Comparison of the two systems at 23.0 °K

TEMPERATURE — 23.00 °K

⊙ — EQUIL. H₂
△ — NORM. H₂

VAPOR

LIQUID

MOLE PER CENT HELIUM

PRESSURE , PSIA

Fig. 27
Comparison of the two systems at 26.0°K

TEMPERATURE — 26.00 °K

⊙—EQUIL. H₂
△—NORM. H₂

VAPOR

LIQUID
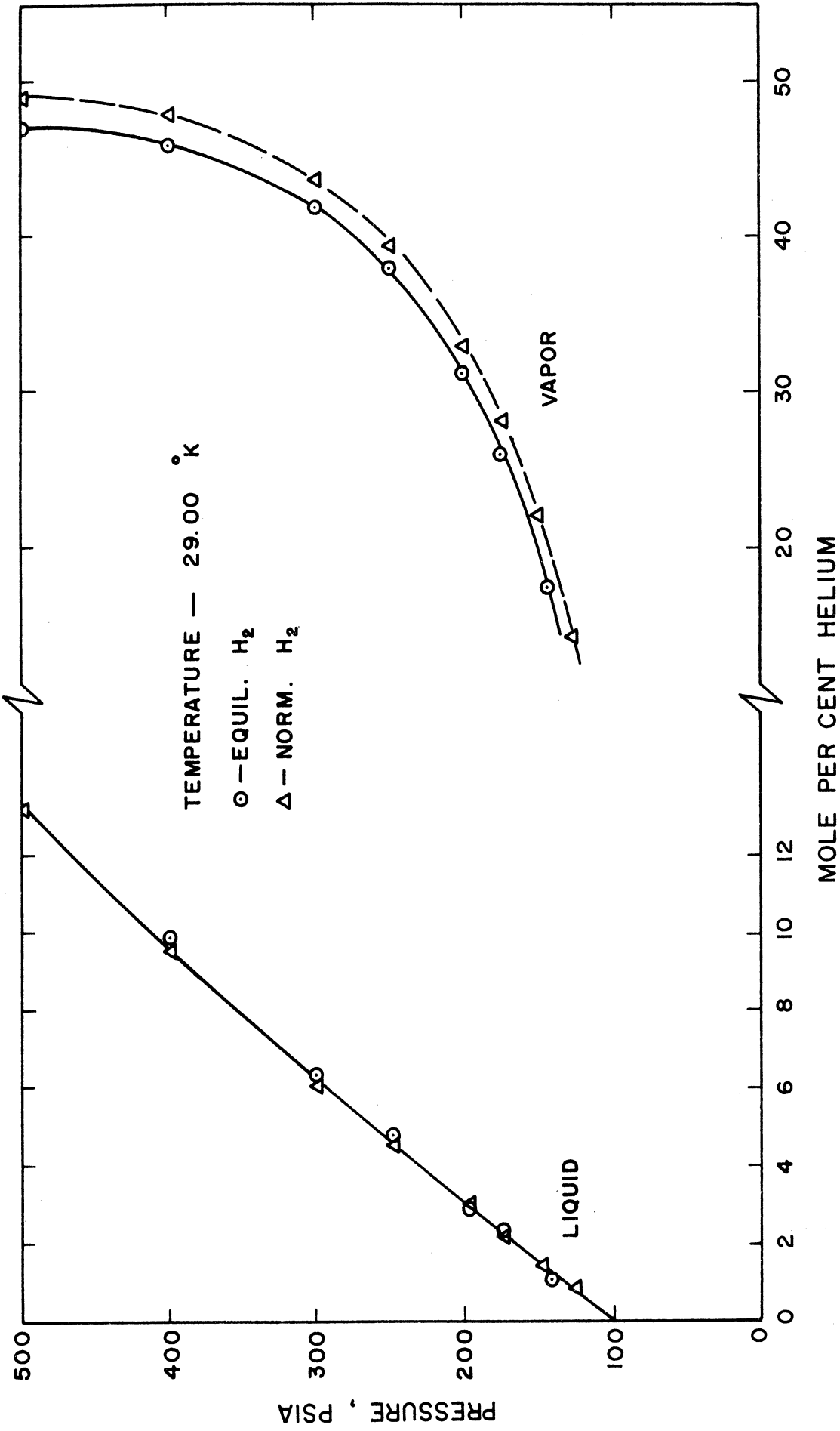
PRESSURE, PSIA

MOLE PER CENT HELIUM

Fig. 28

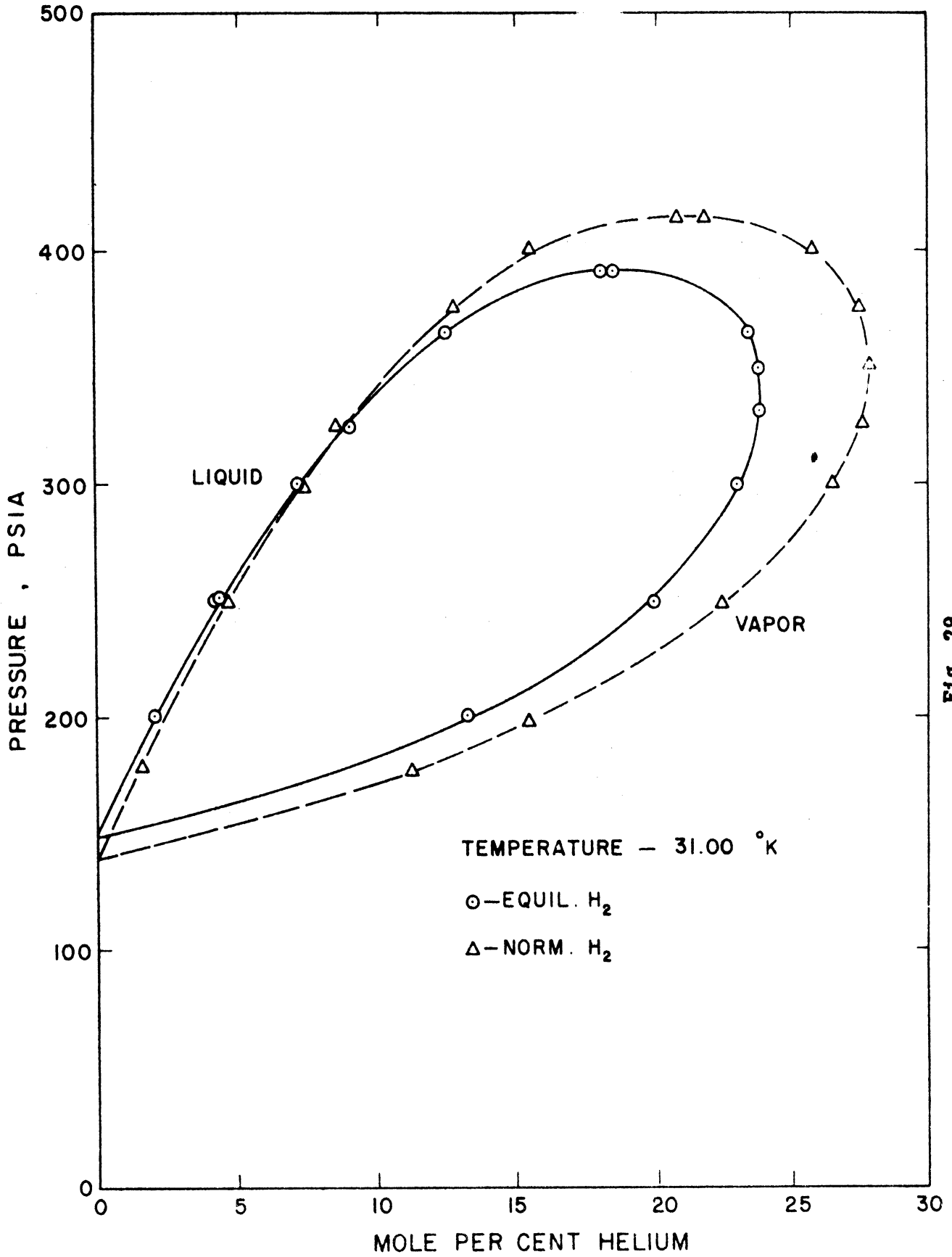Comparison of the two systems at 29.0°K

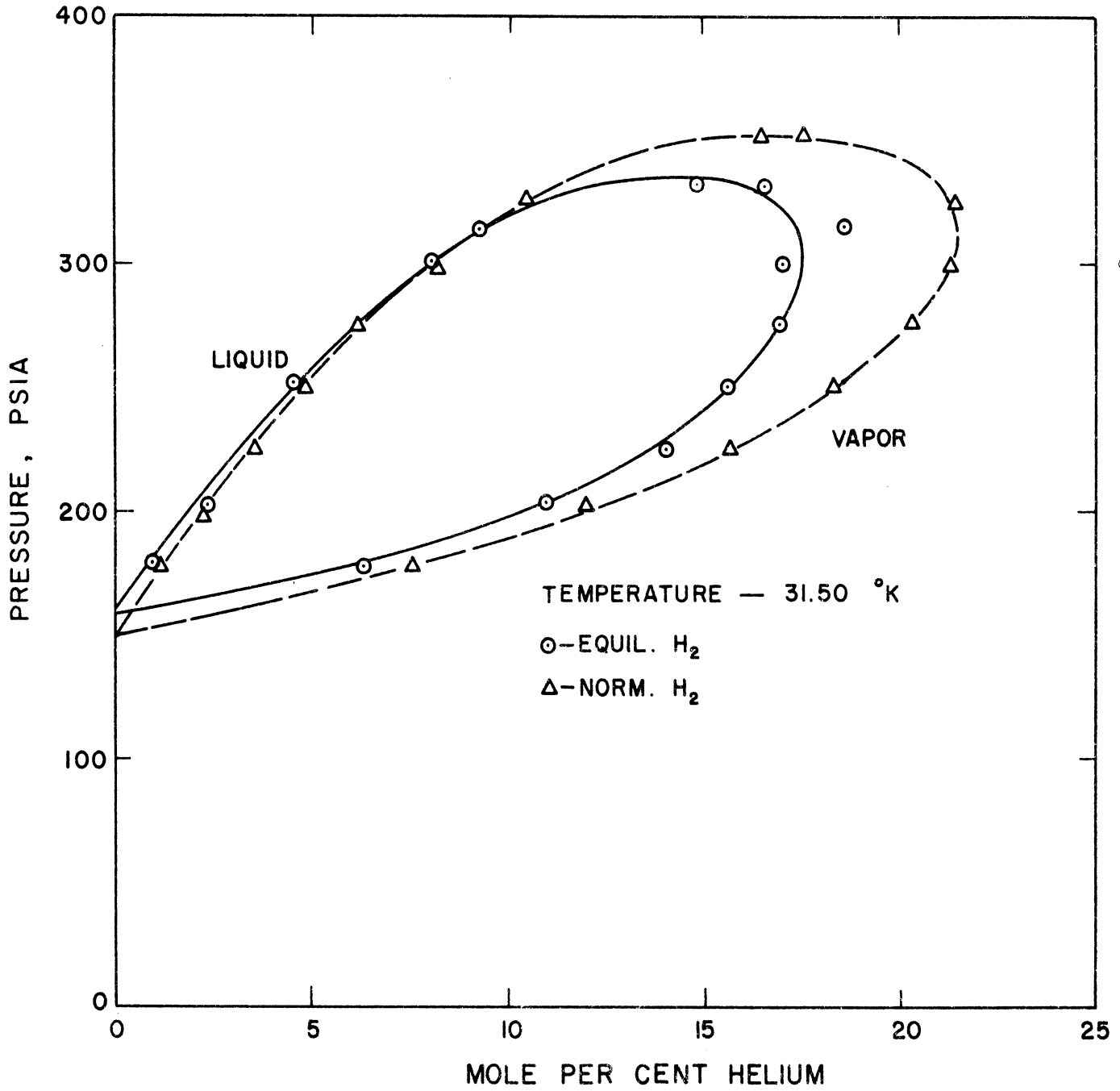Fig. 29
Comparison of the two systems at 31.5°K

Fig. 30 - Comparison of the two systems at 31.5°K

of hydrogen in both the liquid and vapor phases will also contribute to differences
in the behavior of the two systems. Differences in P-V-T behavior between normal
and equilibrium hydrogen are not large, however. Consequently, the vapor pressure
difference must be the principal factor accounting for differences between the two
systems.

The qualitative difference between the two systems discussed above is, in
fact, the result observed for the vapor phase at the various temperatures. The diffe-
rences between isotherms on P-x coordinates become larger as temperature increases,
and do so in a regular manner, with the exception of the $26.00^{\circ}K$ isotherm, for which
the vapor phase results are apparently low. This isotherm shown in Figure 27,
consequently indicates a wider separation than does the 29.00° isotherm plotted in
Figure 28. It was previously concluded from the T-x diagram of Figure 21 that the
26.00° values were somewhat too small. At 31.00°, Figure 29, separation between
the two vapor-phase curves becomes significant, and is even larger at 31.50°, as
shown by Figure 30. At temperatures below 20.40°, it would be expected that vapor
phase differences between the two systems would become negligibly small.

From the qualitative analysis given above, it is to be expected that the
liquid phase compositions are also slightly different for the two systems investi-
gated, with isotherms for equilibrium hydrogen - helium on a P-x plot being shifted
somewhat in the direction of higher temperature. This presumption is believed to
be correct, although the results in the range $20.40 - 29.00^{\circ}K$, Figures 25 - 28, do
not indicate any differences between the two systems. It must be concluded that in
this temperature range any differences in liquid compositions for the two systems
are smaller than the scatter in the experimental data. Thus, only a single curve
representing the liquid data has been drawn in Figure 25 -28. At the 31.00° iso-
therm, however, the data indicate a measurable difference in liquid phase helium

concentration. This result, shown in Figure 29, is as expected, with the curve

for equilibrium hydrogen - helium being shifted slightly in the direction of

higher temperature, crossing the curve for normal hydrogen - helium at about

300 psia. The same trend is also indicated at 31.50°, as shown in Figure 30.

At the higher isotherms the magnitude of the difference in vapor pressure between

equilibrium hydrogen and normal hydrogen becomes significant, which must be the

primary factor contributing to the measurable liquid - phase differences between

the two systems.

From the results obtained, it can be concluded that liquid phase compositions

in the system equilibrium hydrogen - helium at temperatures below $20.40^{\circ}K$ are, at

least within the limits of experimental accuracy, the same as for the system normal

hydrogen - helium. The phase inversion phenomenon observed in this low temperature

region for normal hydrogen - helium would be expected to occur for equilibrium

hydrogen - helium at approximately the same pressure at each temperature, because

of only small density differences between the two varieties of liquid hydrogen.

While no liquid composition differences were observed in the temperature

range below $29^{\circ}K$, it may be possible that such differences would be found at

higher pressures than those studied in the present investigation. It is not

possible at the present time to make quantitative predictions of such values, or

for that matter quantitative analytical comparisons of the two systems in the

range studied. Such calculations require P-V-T data for the liquid-phase solution,

which are not presently available.

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