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CRITICAL PHENOMENA IN BINARY AQUEOUS SOLUTIONS

THE SYSTEM SO_3 - H_2O

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JOHN EDMUND STUCKEY

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CRITICAL PHENOMENA IN BINARY AQUEOUS SOLUTIONS

THE SYSTEM $SO_3 - H_2O$

APPROVED BY

H H Rowley

C. H. Secoy

Max H. Bredig

S. H. Wender

Bernard C. Heaton

J. J. Zinnes

DISSERTATION COMMITTEE

TO

MARTHA

MOTHER AND DAD

whose love and encouragement

made this possible

ACKNOWLEDGMENT

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF ILLUSTRATIONS

CRITICAL PHENOMENA IN BINARY AQUEOUS SOLUTIONS

THE SYSTEM $SO_3 - H_2O$

CHAPTER I

INTRODUCTION

The phenomenon at the critical point has been known since 1822, when Baron Caignard de la Tour[1] first made his crude observations. Not until the early twentieth century, however, were experimental techniques refined and accurate critical temperature measurements obtained. This early experimental work has been reviewed and critically evaluated by Kobe and Lynn.[2]

Early measurements of the critical temperature of solutions were made by Hannay and Hogarth[3] in 1879. Their solutions consisted of various inorganic salts in alcohol or carbon disulfide solution. Aqueous solutions were not used because "the use of water as a solvent was quite out of the question, both on account of its high critical point and the corrosion of the glass tubes," so that workers "were debarred from the use of the liquid whose examination promised most".

Although the importance of aqueous solutions can not be denied, less is known about the critical phenomena of pure water and aqueous solutions than of most other substances. Table I summarizes values for the critical temperature and pressure of pure water. Data concerning these and other phenomena of aqueous solutions in the critical region are not

1

TABLE I

CRITICAL CONSTANTS OF WATER

Year	T_c	P_c	D_c	Investigator	Reference	Method
1822	362. °C.	atms.	g/cc	de la Tour	1	1
1885	358.1		0.429	Naejdine	4	1
1888	365.0	200.5		Cailletet and Colardeau	5	2
1890	364.3	194.6	0.2078	Battelli	6	1
1900	359.	205.		Knipp	7	2
1904	374.			Traube and Teichner	8	1
1910	374.07	218.		Holborn and Baumann	9	2
1927	374.2			Schröer	10	1
1931	374.11	218.53	0.3242	Keyes and Smith	11	2
1934	374.11	218.167		Keyes, Smith and Gerey	7	2
1935	374.2		0.329	Reichenfield and Chang	12	1
1936	374.			Chitaron and Iwonow	13	1
1937	374.2	218.26	0.3265	Eck	14	1
1937	374.15	218.39	0.32	Osborne, Stimson and Ginnings	15	2

Currently accepted values:

	T_c	P_c	D_c			
	374.2	218.3	0.32	Kobe and Lynn	2	

Method 1: Based on disappearance of the meniscus, usually an average of the disappearance and reappearance of the meniscus.

Method 2: Pressure-volume-temperature relations in which $\left(\dfrac{\partial P}{\partial V}\right)_T$ is equal to zero.

available except in limited quantity. [10, 16-25]

The purpose of this research was to study critical constants of the sulfur trioxide-water system and any related critical phenomena observed. It began with a thorough literature survey and an effort to correlate, condense, and present in summary the general field of critical phenomena. Many of the problems encountered in the experimental work were not foreseen but their solution and the development of the experimental technique were considered valuable contributions to the general research area.

Historical

Soon after the original work by Caignard de la Tour, two explanations of the critical phenomenon were advanced. One approach stated that the surface tension of a liquid decreased with increasing temperature to a point at which it became zero. At this point there would be no capillarity and no surface of demarcation between the gas and liquid phases. The phases would be indistinguishable and mutually miscible in all proportions. Physical identity of the two phases did not follow necessarily. The second approach noted that with a temperature increase the vapor density increased while the liquid density decreased and advanced the theory that the two phases finally would reach the same density. [26,27]

A review of critical phenomena and the methods used in experimental work is necessary to understand the problems involved and the non-uniformity of critical values cited in the literature.

For instance, the critical temperature may be defined in

various ways. In 1870, the work of Andrews[28] with carbon dioxide led to the liquefaction of the 'permanent gases' and advanced the concept that each gas has a temperature above which it can not be liquefied regardless of the applied pressure. This was called the 'critical temperature' and the pressure required to liquefy the gas at this temperature was the 'critical pressure'. The density of the substance under these conditions was the 'critical density'. Critical temperature may also be defined as the temperature at which the meniscus between the liquid and vapor phases disappears,[1] or the temperature at which the liquid and vapor phases become identical.[29] In terms of the kinetic theory it is the temperature at which the kinetic energy of translation of the molecules is equal to the maximum (negative) potential energy of attraction.[30] Critical temperature may be defined thermodynamically as the temperature at which the first and second partial derivatives of pressure with respect to volume, temperature constant, are equal to zero.[31] In terms of surface tension, it is the temperature at which the interfacial tension and energy become zero.[32] As pointed out by Hildebrand,[33] the different criteria for locating the critical temperature do not necessarily lead to exactly the same results.

Not all of these definitions provide practical experimental techniques for obtaining critical values. Many involve rather difficult methods and thereby limit the amount of available data in published literature. Problems of accurate temperature measurement and control of two phase areas, of accurate pressure and density measurements, of reaching states of true phase equilibrium, of containing systems often

at high temperatures and pressures and frequently of a corrosive nature,
and numerous problems related to each individual system harass the
investigator. The experimental difficulties encountered limit our
knowledge of the systems and make generalizations and hypotheses
concerning the work difficult to formulate.

There are various experimental approaches to the determination
of critical phenomena. They involve pressure-volume-temperature studies,
density measurements, and may involve visual observation of the properties
of the meniscus. In general these techniques have been applied to
one-component systems while studies of two-component systems have been
neglected.

One pressure-volume-temperature method for critical determi-
nations involves pressure-volume-temperature measurements and a plot of
the isotherms.[34-36] With sufficiently sensitive measurements the
critical temperature may be determined to within a few hundredths of a
degree by an analysis of the geometry of the isotherms. Figure I shows
a hypothetical diagram with the critical point indicated.

A similar method involves pressure-volume-temperature measure-
ments but a plot of isochores.[37] Figure II shows a hypothetical case
with the critical temperature indicated. Theoretically, the problem is
to find the correct initial amount of liquid for the tube or bomb so
that the pressure vs. temperature curve will not exhibit a discontinuity.
If the density is less than the critical density, the tube will fill
with vapor before the critical phenomena is observed and curve 1 will
result. If the density is greater than the critical density the tube
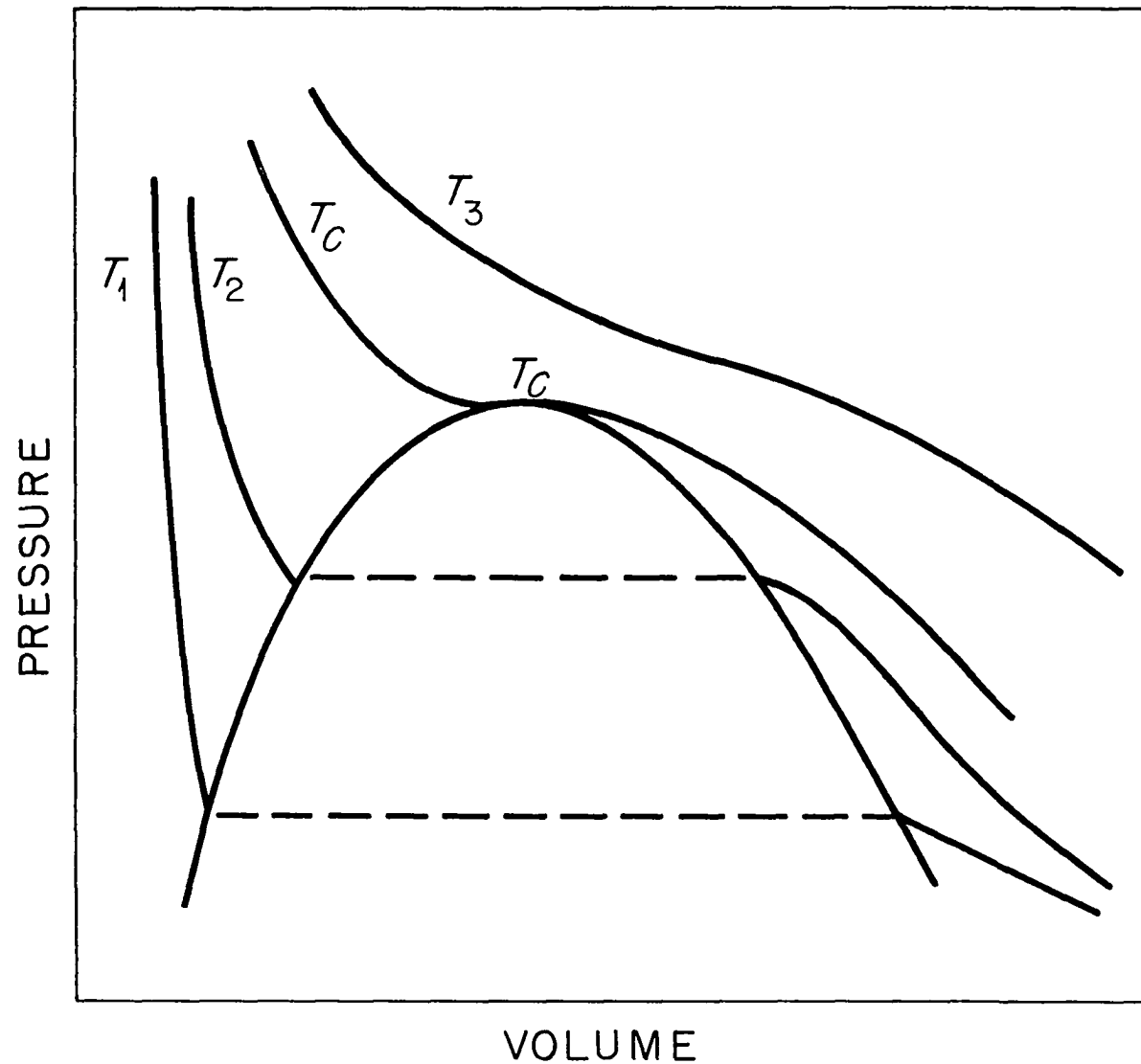
Figure 1
PRESSURE-VOLUME ISOTHERMS
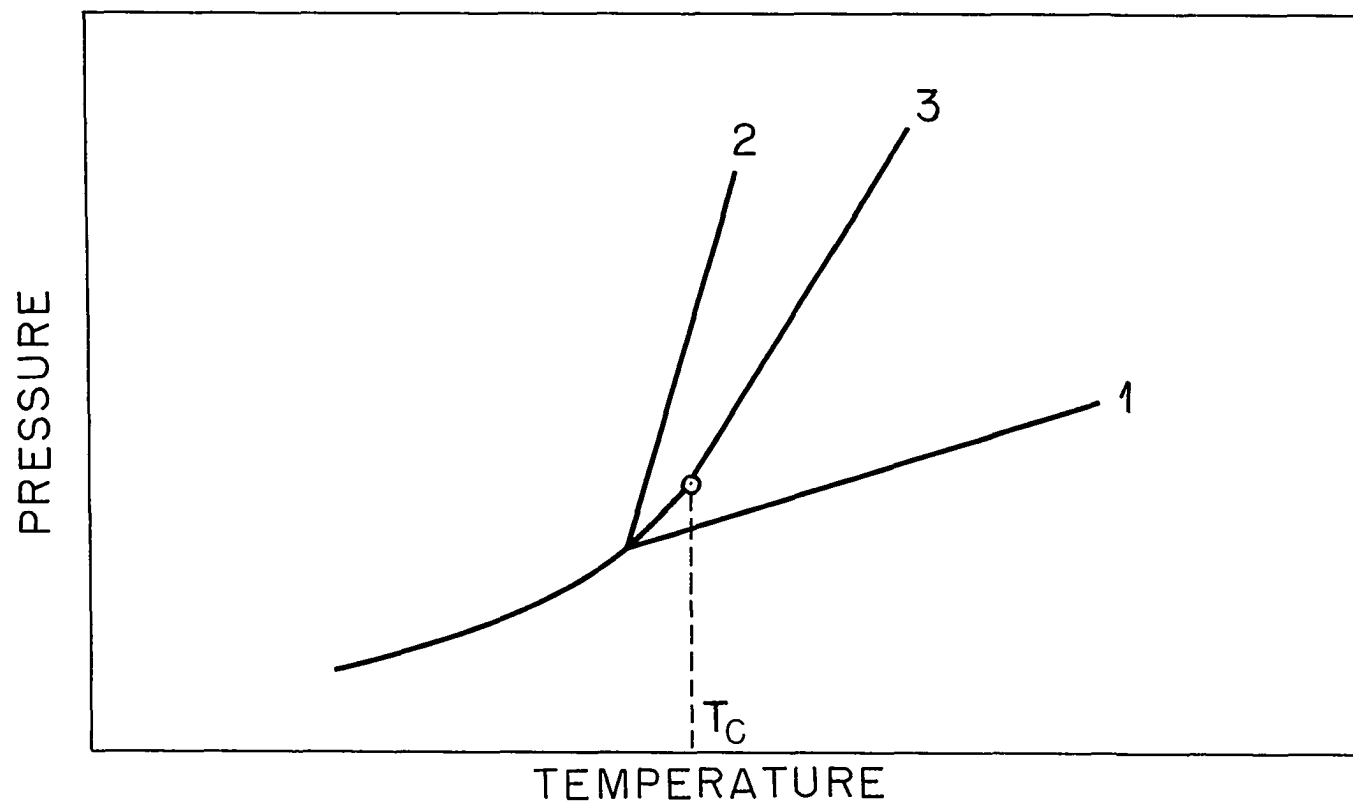
Figure II
PRESSURE TEMPERATURE ISOCHORES

will fill with liquid and curve 2 will result. Only when the density

has the critical value will the continuous curve 3 result. Curves 1 and

2 show first order discontinuity.

This method has been used on various one- and two-component

hydrocarbon systems.[38] It was found that the isochore curves had two

sections. The lower section was curved up to the critical point but was

essentially a straight line beyond that point. The initial amount of

liquid in the bomb was considered unimportant, varying between 20% and

50% of the initial bomb volume without a significant change in the

critical temperature.

The method of Cailletet and Mathias[39] for the determination of

the critical density may be used to determine the critical point. This

experimental law states that the mean of the densities of any substance

in a state of liquid and of saturated vapor at the same temperature is a

linear function of the temperature. The densities of the liquid and of

saturated vapor in equilibrium with it, known as the orthobaric

densities, are experimentally measured at a number of temperatures near

the critical point. The mean values are then either plotted against

temperature or a linear equation is deduced and from a knowledge of the

critical temperature the mean density can be obtained by extrapolation

or calculation. A plot of the liquid and vapor densities may be used to

determine the critical temperature.

It is apparent that the density definition permits use of the

rectilinear diameter law of Cailletet and Mathias and provides a ready

means for critical volume measurements but a less satisfactory way to

determine critical temperature. The thermodynamic definition offers a basis for theoretical treatment of the results but not a convenient experimental criterion. Interfacial tension and energy values in this region can not be fixed easily by direct measurement nor by extrapolation, because the linear relation between molecular surface energy and temperature formulated by the old rule of Ramsay and Shields[40] breaks down in the critical region.

Several attempts have been made to correlate data and arrive at a method of predicting the critical temperatures of various groups of substances. In general, this has been limited to one-component systems, to dilute solutions of non-volatile solutes,[41,42] and to hydrocarbons.[43] Prud'homme[44] pointed out what he called a "rule of three temperatures" which stated that the ratio of the sum of the normal boiling point and the melting point to the critical temperature, when all were expressed on an absolute scale, varied between 1.0 and 1.1. Later Watson[45] and Corner[46] presented a method developed for critical temperature calculations of non-polar liquids. This involved use of the boiling point, molecular weight, and liquid density and the error was considered about 2%. Such predictions have had only token success.

It therefore seems that the most convenient means of obtaining the critical point is to determine experimentally the temperature at which the meniscus between the liquid and vapor phases may be observed to disappear and reappear. In this work the critical temperature will be defined as that temperature at which the line of demarcation between the liquid and vapor phases becomes indistinguishable at the center of the sample tube when viewed through a telemicroscope.

Meniscus Method for Determining Critical Temperature

This method[47] depends on the visual observation of the action
of the meniscus as the critical temperature is approached from below and
from above the critical point. Theoretically, the meniscus disappears
with increasing temperature and reappears with decreasing temperature at
the same position and at the same temperature. Experimentally, the
process is not quite as simple.

Such a determination must be carried out in a closed system
which usually consists of a steel bomb provided with an observation
window or a sealed glass tube. The system may be enclosed by an inert
liquid if such is available, in which case the volume of the system may
be regulated. In the case of a sealed glass tube the volume of the
system can not be adjusted. Therefore, the initial amount of liquid
introduced into the system must be considered.

The critical temperature of some systems seems to be largely
independent of the initial fraction filling of liquid. The critical
temperature of other systems changes markedly with small variations in the
amount of liquid. The following shows theoretically the importance of
the proper fraction filling.

Let $\bar{p}$ be the average density in a closed system, p^v the
vapor density, and p^l the liquid density. The fraction of the closed
tube filled with liquid is: $f = (\bar{p} - p^v)/(p^l - p^v)$. At the initial loading
of the bomb, if $\bar{p}$ is greater than p_c , the density at the critical
temperature and pressure, the tube reaches a point at which $\bar{p}$ equals
p^l. Therefore, f becomes unity and the tube is full of liquid. If $\bar{p}$

is less than p_c the tube reaches a point at which $\bar{p}$ equals p^v and f becomes zero. Now the tube is full of vapor with no liquid remaining. When $\bar{p}$ equals p_c , f is equal to one-half and the meniscus disappears and reappears halfway up the tube.

A similar notation is given by Tapp, Steacie, and Maass[32] based on van der Waals'[48] theory of continuity of state.

W = weight of material V_l = volume of liquid
V_g = volume of vapor d_l = density of liquid
V = volume of tube d_g = density of gas

Under all conditions

$$(V - V_g)\, d_l + V_g\, d_g = W$$

$$V_g = \frac{W - V\, d_l}{d_g - d_l}$$

As $T \longrightarrow T_c$ then $d_c \longrightarrow \dfrac{d_g + d_l}{2}$

And $W = d_c\, V$

Substituting these special conditions into the general equation:

$$V = \frac{d_c\, V - d_l\, V}{d_g - d_l}$$

$$= \frac{\left(\dfrac{d_g + d_l}{2}\right) V - V\, d_l}{d_g - d_l}$$

$$= \frac{V}{2}\left(\frac{d_g - d_l}{d_g - d_l}\right)$$

$$V_g = \frac{V}{2}$$

This indicates that the critical phenomena would be observed only when the tube was filled with material to an extent which would conform to a single definite critical density value.

In a constant volume closed system where it is difficult to accurately control the quantity of liquid inserted, the resulting fraction fillings may vary over a considerable range. If the fraction fillings are too low the meniscus may vanish out the bottom of the tube as the tube becomes filled with vapor. If the fillings are too large the meniscus may disappear out the top of the tube as it becomes filled with liquid. If the fraction fillings are such that $\bar{p}$ is near p_c, the meniscus may seem to disappear and reappear either above or below the center of the tube. Whether the meniscus actually disappears here or moves up or down too rapidly to observe is difficult to ascertain. It has been observed in some systems that the fraction fillings may vary over a considerable range with no noticeable error in the critical temperature determination. This is true for some hydrocarbons.[38] In other systems, such as the two-component system sulfur trioxide-water, variations in the fraction filling have a noticeable effect on the critical temperature.

Mason, Naldrett, and Maass[49] noted the effect of varying the fraction filling while working with ethane in stationary bombs. They noted three categories for this substance, depending upon the mean density of the filling. Class I included those below a density of 0.19 g./cc. in which the meniscus gradually fell as the temperature increased and disappeared at the bottom of the bomb before the critical

temperature was reached. Class II included those between a density of
0.19 and 0.23 g./cc. in which the meniscus disappeared at the critical
temperature within the confines of the bomb. The phenomena occurring in
this class may be further subdivided as follows: (a) the meniscus fell
before it disappeared and reappeared at the bottom of the bomb, (b) the
meniscus remained stationary while it disappeared and reappeared at the
middle portion of the bomb, and (c) the meniscus rose on heating before
it disappeared and reappeared at the top of the bomb. Class III with
densities greater than 0.23 g./cc. exhibited a rising meniscus.

The same experiments were repeated with the bomb agitated and
the effect of shaking resulted in a reclassification. Class I now
included samples with densities below 0.201 g./cc. whose meniscus
disappeared at the bottom of the bomb below the critical temperature.
Class II samples had densities between 0.205 g./cc. and 0.207 g./cc. and
the meniscus disappeared at the critical temperature within the confines
of the bomb. Class III had densities above 0.211 g./cc. and the meniscus
disappeared at the top of the tube below the critical temperature. It
is apparent that shaking had considerable influence upon the phenomena
occurring in the critical region.

Shaking appears vital to insure conditions of equilibrium by
preventing metastable states of supersaturation and overexpansion.
Supersaturation is prevented by the presence of nuclei upon which
condensation can occur. These nuclei may form spontaneously, they may
form on ions, or on dust or other small particles of solid impurities.[50]
To prevent overexpansion it is necessary for the liquid to vaporize into

small bubbles or cavities, which may form spontaneously, by dissolved gases in the liquid, or by cavities on the surface of solid impurities which may be present.[51] Sufficient agitation is necessary for equilibrium to occur spontaneously in the absence of impurities.

Edwards and Maass[52] also reported limited work which indicated that the temperature and position of the reappearance of the meniscus was dependent upon the previous history of the material contained in the region formerly occupied by liquid. It appeared that the meniscus reappeared at a higher position and at a temperature nearer the true critical value when the contents of the bomb were not heated appreciably above the critical temperature. This led to the hypothesis that the ease of formation of liquid was proportional to the residual orientation of molecules.

Opalescence Near the Critical Temperature

The exact position at which the meniscus forms and fades away is often difficult to determine due to critical opalescence.

Various hypotheses have been advanced to explain this phenomenon. Altschul[53] ascribed the effect to mutual dispersion of the two phases in the critical region. Konowalow[54] concluded that it was caused by transitory condensations upon dust nuclei present. A more satisfactory qualitative explanation of critical opalescence was advanced by Küster,[55] and was subsequently developed quantitatively by Einstein,[56] Smoluchowski,[57] and others. It was based on light scattering arising from statistical fluctuations in density.

In 1935, Booth and Swinehart[58] described the critical

opalescence observed in studies of various halogen derivatives of methane and ethane and of silicon halides. They concluded that under closely controlled equilibrium conditions the critical temperature could be reached and exceeded without observing any opalescence, that the separation of two phases was possible within 0.05 $^{\circ}$C. of the critical temperature, and that very slight opalescence could be induced above the critical temperature by rapid stirring but was of short duration when the temperature and pressure were held constant.

These observations confirmed the earlier opinion of Cardoso[59] who attributed critical opalescence to the emulsifing of the two phases and its stability below the critical temperature to the low surface tension and near equality of densities.

In a symposium on the critical state in 1938, A. L. Clark[60] indicated that the amount of critical opalescence depended upon the manner of heating. If the liquid were brought slowly just past the critical temperature and then cooled, opalescence was slight and the band of 'fog' was narrow. If the material were carried, say 20 $^{\circ}$C., above the critical temperature or held a little above the critical temperature and stirred, the opalescence and 'fog' band were much broader. Careful examination showed that above the meniscus were numerous droplets of liquid falling through vapor and that below the meniscus bubbles of vapor were rising through the liquid.

Considerable work on ethylene brought forth an interesting conception. Mason and Maass[61] noted that the opalescence of all critical fillings increased as the temperature was lowered, passed

through a maximum at a temperature T_s, and subsequently decreased. It was not reversible, within the considerable time allowed for the establishment of equilibrium, once condensation had occurred.

This T_s , known as the critical dispersion temperature, has been noted by others.[62] Mayer and Harrison[63,64] advanced the hypothesis that below the classical critical temperature, T_c , and above the critical dispersion temperature, T_s , there is a finite area on the pressure-volume plane corresponding to an anomalous homogeneous phase in which the first, second, and higher partial derivatives of pressure with respect to volume, temperature constant, are equal to zero. This development was from a statistical mechanical treatment of condensation and was backed by the experimental data on ethylene. Opalescence was most pronounced at the critical dispersion temperature.

Density Measurements in the Critical Region

The phenomenon of critical opalescence has frequently been attributed to the effects of light scattering caused by microscropic density fluctuations near the critical temperature. MacLellan[65] reported microscopic density gradients in random directions superimposed upon the macroscopic density gradients in the vertical direction due to gravity. Macroscopic density gradients in fluids near the critical point have been observed by numerous investigators.[66-72]

From very early studies there have been reports of density fluctuations and of discontinuity in the density curve at the critical point. As early as 1893, Galitzine[73] reported that the vapor density of ether was about 20% less than the density of liquid ether at the

critical temperature. He asserted that the density difference maintained

itself even six or seven degrees after complete homogeneity was apparent

to the eye. In 1904, Traube[74] and Teichner[75] indicated density

variations in their work.

These density differences between liquid and vapor at the

critical point were believed by Young[76] to be due to small percentages

of impurities present in the substances under observation. These

gaseous impurities were credited with retarding rather than assisting

the formation of opalescence and the rapidity with which opalescence

spread was hence a measure of the purity. The behavior and distribution

of opalescence were construed to prove certain facts about the distri-

bution of densities. He believed that with the disappearance of fog all

density differences also vanished simultaneously. Young considered

density equality to be established throughout the tube during a lapse of

a few minutes (about ten minutes) following a temperature alteration.

This lag he attributed to the slowness of thermal conduction. Young

used highly purified samples but his visual method of density determination

was questionable.

Three years later, in 1914, Hein[66] attributed density

differences to gaseous impurities but believed rapid stirring offset

the effect and removed the density differences. His conclusions were

based on doubtful work due to the uncertainty of the temperature

measurements and temperature control.

By 1915, Clark[77] supported the ideas of Kuenen[78] that nearly

all phenomena observed may be regarded as transition phenomena and that

if final states only are considered, the density abnormalities disappear
after sufficient stirring. But not all disappear due to the great
compressibility of some substances in the critical region and the
resulting effect of gravity.

This effect of gravity was calculated by Ruedy[79] for a gas at
the critical temperature. He assumed R. Planks' equation of state and
calculated that densities measured at two levels one centimeter apart in
a column of gas may differ by more than 5%. A large correction is
therefore required for density determinations at the critical point
unless the entire contents of the tube are vigorously stirred. Van der
Waals' equation shows that the difference in level corresponding to a
relative difference in density, $(p - p_c)/p_c$, is proportional to the
third power of the relative difference in density. According to Wohl's
equation it is proportional to the fourth, and according to Plank it is
proportional to the fifth power of the relative difference in density.[80]

In 1928, observations with water indicated that the densities of
liquid and vapor may not become equal at the critical point. Callendar[81]
used very pure water in stationary bombs and traced the visible differences
in density beyond the vanishing of the meniscus and up to nearly 380 °C.
Above 374 °C. the 'liquid' and 'vapor' were capable of mixing in all
proportions and appeared to be in a somewhat unstable state of
equilibrium. This was easily upset by small traces of impurities,
such as air or gas, which promoted ebullition and caused rapid stirring.

The question of the existence of density discontinuities
remained until the early 1930's when O. Maass and co-workers[32,82]

began a concentrated effort to answer questions concerning density and surface tension at the critical temperature. The early work was done with methyl ether and propylene. In 1933 their published work noted the following conclusions.

The densities above and below the position at which the meniscus disappeared were not the same for several degrees above the temperature at which the meniscus became invisible. This generalization applied to experimental tubes filled with liquid to such a degree that the meniscus either rose or fell when the temperature was raised slowly from room temperature to the critical temperature. The unique case where the meniscus neither rose nor fell seemed to influence this density difference to such an extent that it completely disappeared immediately at the critical temperature. A slight temperature gradient along the length of the bomb during the density measurements greatly changed the results. The first two conclusions held when the temperature was held constant to within 0.02 $^{\circ}$C. along the whole bomb.

By creating temperature gradients, such that the bottom of the bomb was 0.1 $^{\circ}$C. warmer than the top, the densities within equalized over a period of forty to fifty minutes; without temperature gradients the densities showed no indication of equalizing even when vigorously stirred for periods of four to five hours. By increasing the temperature at the bottom by 0.2 $^{\circ}$C. over that at the top, complete reversal of the densities was obtained. Then the medium at the top apparently had a greater density than the material at the bottom. This condition would maintain itself in spite of vigorous stirring for indefinite periods of

time. By heating the top of the bomb 0.2 °C. warmer than the bottom,
the first conclusion could be accentuated.

Once a condition of uniform density had been reached throughout
the bomb in a manner outlined above, then a return to uniform temperature
would not in any way alter the density conditions in the bomb. Upon
slowly cooling the entire bath when conditions of uniform density
prevailed, fog formation was exceptionally pronounced and no meniscus
appeared until the temperature had fallen about one-half degree
Centigrade below that at which the meniscus disappeared with rising
temperature. Vigorous stirring of the contents had no effect upon the
final density obtained and very little effect upon the rate with which
it was reached. The rate at which equilibrium density was approached
increased markedly with the extent to which the temperature was raised
above the critical temperature.

Additional work on dimethyl-ether in 1935[52] confirmed the
persistence of density differences above the critical temperature. In
addition, density differences in the liquid below the critical
temperature, depending on the experimental conditions other than
temperature, were recorded for the first time. There appeared a
hysteresis effect which showed the density of the liquid to be
dependent on its past history of heating rather than solely on the
temperature at which the density was measured.[83,84] This led to the
hypothesis that there is an essential difference other than concentration
between a liquid and a highly compressed gas. This difference may be
ascribed to a structure in the liquid, whereas in a gas a completely

chaotic distribution of molecules exists. This explained the reappearance of the meniscus at a higher position and at a temperature nearer the critical temperature when the contents of the bomb had not been previously heated appreciably above the critical temperature. It was thought that the ease of formation of the liquid depended upon the residual orientation of molecules which remained.

Additional work by Marsden and Maass[85] and by Pall and Maass[86] substantiated the original work.

Adsorption in the Critical Region

In 1933 Morris and Maass[87] studied the adsorption of propylene on alumina and found a marked discontinuity in the adsorption curve with a change from the liquid state to the gaseous state. This was believed to be due to changes in the forces of attraction between liquid molecules and the solid as compared with the attraction between gaseous molecules and the solid surface.

Further investigation by Edwards and Maass[52] on the adsorption of dimethyl ether on alumina also indicated that a discontinuity in adsorption accompanied the transition of the liquid to a gas. It was demonstrated that the apparent changes in adsorption could not be ascribed to changes in the density of the adsorption phase or to the persistence of liquid in the pores of the sorbent above the critical temperature.

Dielectric Constants in the Critical Region

In 1907 Kamerlingh Onnes[88] reported data that indicated the

dielectric constant of a system exhibited a discontinuity at the

critical point; however, it was many years later that Marsden and

Maass[89] gave substantial backing to this conception. They measured the

dielectric constants of propylene and methyl ether both in the liquid

and in the saturated vapor. It was shown that above the critical

temperature a difference in dielectric constant persists between the

mediums above and below the disappearing meniscus. The dielectric

constant of liquid methyl ether decreases with extraordinary rapidity

from one degree below the critical temperature to one degree above,

whereas the relatively non-polar propylene shows a far less marked

dielectric constant temperature gradient.

Polarizibility in the Critical Region

The polarizibility of propylene and of methyl ether was

determined and was believed to be identical above and below the point of

disappearance of the meniscus.[85] The polarizibility of both liquids was

found to be constant to a remarkable extent, that is, nearly constant

at all temperatures. This was interesting since the dielectric constant

and the densities were not constant nor equal in the two phases. The

relation $(e - 1)/(e + 2) \times M/D$ when plotted against $1/T$ remained

constant over a wide temperature range. In the liquid the decrease in

polarizibility with an increase in temperature appeared to be offset

by a decrease in the influence of the attraction of molecules upon one

another.

Heat Capacity in the Critical Region

Since the density and dielectric constant phenomena appeared
to be explicable only in terms of molecular interaction, Maass and
co-workers[90] sought to measure the heat capacity of ethylene to obtain
an indication of the extent of molecular interaction at the critical
temperature. Any such molecular interaction must show up as a large
effect in the heat capacity of the system, as every intermolecular bond
represents an additional mode of heat absorption.

The heat capacity measurements demonstrated a difference in
heat capacity between the two phase system and that of a homogeneous
system when measured over the same temperature range. A large amount
of molecular interaction existed in ethylene in the critical region.
It was concluded also that this was not confined to the condensed phase
but that the same was true of the vapor, but to a lesser degree.

The work was repeated[91] with a smaller limit of error and
added support to the conclusions. This refined work also supported
previous indications that the difference in heat capacity due to the
thermal history of the sample was definitely beyond the limit of
experimental error.

Viscosity in the Critical Region

Viscosity measurements in the critical region had been less
satisfactory than measurements of other physical properties. In 1915,
Clark[77] attempted to measure the viscosity of ethyl ether. He claimed a
marked change in the viscosity at the critical temperature. In 1940,
viscosity measurements were finally refined and improved by Mason and

Maass[92] while working with ethylene. They reported a continuous transition
in viscosity on the equilibrium isochore with a minimum viscosity just
0.1 $^{\circ}$C. above the critical temperature as defined thermodynamically.

This work was in direct contrast to that of Naldrett and
Maass[93] who claimed no minimum in the viscosity of carbon dioxide at
the critical temperature nor even up to 7 $^{\circ}$C. above this point. For
the region just above the critical temperature the viscosity was noted
to be more dependent on density than on temperature. The viscosity-
temperature isochores were quite flat along the temperature axis but the
individual isochores were well separated.

These investigations confirmed the conclusion that there is a
fundamental difference between the liquid and gaseous states of aggrega-
tion. The form of the isochores indicated that the natures of the
liquid and gas are different. Above the point of condensation the
different isochores are well differentiated and the viscosity appears
to be more dependent on density than on temperature. At the condensation
temperature, however, the isochores converge and for the liquid phase
the viscosity appears to be much less dependent on density and
considerably more dependent on temperature.

Solubility in the Critical Region

Hannay[94] and Hogarth[3] in the late nineteenth century concluded
that solubility was a property of all fluids and depended merely on the
molecular closeness and thermal activity. They did not ascribe to the
liquid state any particular virtue, in regard to solvent power, over the
gaseous state at an equal concentration. Solubility data were supplemented

by Bertrand and Lecarme[95] and Schröer[96] who gave limited data on the solubility of potassium dichromate in water, alizarin in alcohol, and cobalt and copper chlorides in water. Holder and Maass[97] in 1940 added some knowledge with their study of hexachloroethane in water and Copeland and Benson recently gave solubility data for sodium chloride in water.[19,21] However, very little general information can be acquired from these limited sources.

Friedricks[98] discussed the possible temperature vs. composition curves from a phase rule approach. The solubility curve may lie beneath the critical curve at all times throughout its course or the system may be such that the solubility curve intersects the critical curve. This intersection may take place as the solubility curve reaches zero at the critical temperature of the pure solvent or it may intersect the critical curve at one or more points other than at zero. Solubility data were too limited in quantity and quality to permit any generalizations or classifications of any types of solutes.

'Top Hat' Area in the Critical Region

Over a considerable number of years data accumulated which indicated that the phenomenon occurring near the critical point of a pure substance was more complicated than expected from the simple van der Waals' theory. This theory predicted a roughly parabolic shape for the coexistence curve in a pressure-volume diagram, which enclosed those sections of the isotherms over which a distinct meniscus could be observed. However, evidence appeared that this curve actually had a finite constant pressure portion at the top which was flat.[99]

Mayer and Harrison[63] used a general development of Gibb's
phase integral for a system of chemically saturated molecules to obtain
equations for the thermodynamic properties of the system. The equations
predicted an unusual condensation phenomenon and as a result of this
statistical mechanical theory, they predicted two critical temperatures,
T_m and T_c. Above T_c and below T_m the properties corresponded to those
predicted classically above and below the critical point, but between
T_m and T_c for a certain volume range they predicted properties which
were not given by any classical description of the critical phenomenon.
T_m was the temperature at which the meniscus disappeared but above which
the pressure-volume isotherms continue to have a horizontal portion.
T_c was the true critical temperature above which such a horizontal
region did not exist. This idea was also presented by Pinter[100] and
Jacyna.[101] According to the theory, the isotherms in the region close
to the critical temperature should differ from those below the
temperature at which the meniscus disappears, in that there should be
no break in the slope of the curve as the horizontal portions are
approached.

The best experimental data on these properties of the
isotherms are not entirely unequivocal. McIntosh, Dacey, and Maass[62,68]
obtained isotherms for ethylene and the curves which they fitted to
their experimental points showed horizontal sections. A sudden change
of slope was shown at the ends of the horizontal portions. The data,
however, did not necessarily demand a sudden change in slope nor even,
for that matter, a horizontal portion in the isotherms.

If a difference does exist between T_m and T_c , Brescia[102] pointed out that one would expect associated liquids to have larger intervals between the two temperatures than non-associated liquids. Data in Table II show that carbon dioxide and the saturated lower hydrocarbons, typical unassociated liquids, possess zero intervals or intervals too small for experimental detection. The more strongly associated lower ethers, alcohols, and water appear to have measurable intervals. However, present data are too scarce to deduce a quantitative relationship between the degree of association and the magnitude of the interval. Of course, the physical significance of the T_m measurements made in stationary bombs is seriously questioned by the effect which shaking has on the disappearance of the meniscus. Nevertheless, Brescia feels that the interval between T_m and T_c , although perhaps small, is real for non-associated liquids.

The theory of Mayer and Harrison is highly mathematical and the results depend upon the behavior of certain integrals which are difficult to evaluate near the critical point. Consequently, the magnitude of the temperature interval between T_m and T_c has not been theoretically calculated.

Mayer and Harrison also predicted that in a finite density and temperature range above the temperature of the disappearance of the meniscus, a range of microscopic densities is equally stable, and in a sealed bomb different densities may be observed at a given temperature and average density. The densities observed in various parts of the bomb will depend in a predictable way on its previous history. This

TABLE II

T_m AND T_c VALUES

System	T_m Stationary Bomb	T_m Shaken Bomb	Reference	T_c	Reference
Carbon dioxide	30.96 °C.		103	31.04°C	34
Ethane		32.23°C.	49	32.27	104
Propane	96.85		105	96.81	104
Butane	152.2		106	152.01	104
Pentane	197.2		107	197.	108
Ethylene		9.21	109	9.90	110
Propylene	91.4		111	91.4	111
	91.9		82	91.9	112
				96.4 °	89
Methyl ether	126.9		32	138. °°	
Ethyl ether	192.3		113	194.6	99
Methyl alcohol	240.6		113		
Ethyl alcohol	241.7		113		
	243.6		114	243.6	114
Water	374.2		96	380. °°°	81

Temperatures given as T_c have been determined, unless otherwise noted in the references, from isotherms carefully measured through the critical region at small temperature intervals, as the temperature at which the tangent to the inflection point for an isotherm is horizontal.

  ° Temperature at which the dielectric constant of vapor equals that of liquid.

  °° Approximate extrapolation from the seventeen measured differences in densities of liquid and saturated vapor plotted as a function of temperature to the temperature at which the density difference is zero.

  °°° This is the temperature at which the density of the liquid equals that of its saturated vapor, reference 81.

was in agreement with the published results of Maass.

However, Naldrett and Maass[109] observed that a system held slightly above the temperature at which the meniscus disappeared but still showing layers of different density, finally settled down to a completely homogeneous state. This indicated that the different layers, which presumably represented points along the horizontal portion of the isotherm, had different free energies and consequently, the isotherm could not be exactly horizontal.

Rice[115] felt it would be more advantageous if the phenomenon could be considered from a somewhat more pictorial point of view. He presented a method based on the association of molecules somewhat similar to a treatment by Frenkel,[116] although Frenkel did not attempt an application in this region. His procedure follows closely one supported by Rashevsky[117] in considering emulsion phenomena. The theory of Mayer and Harrison was based on a molecular cluster first introduced by Ursell[118] which considered the cluster merely as a mathematical abstraction.

Rice came to the following conclusions. Apparently the isotherm at the highest temperature at which a meniscus is distinguishable, T_m, has a horizontal portion. Above this temperature there is a critical region in which a transition from vapor to liquid takes place over a finite range of volumes but where the isotherms never have zero slope. Before final conclusions can be drawn, Rice points out the need for more experimental data with more attention to surface tension measurements and to controlled experimental procedures which will

insure vapor-liquid equilibrium.

Liquid Structure in the Critical Region

From the earliest investigations workers have sought to assign a structural model to the liquid state. Such models have achieved reasonable success for solids and gases but have given only partial help in the study of liquids. It is generally agreed that a liquid structure does exist and that it is intermediate between structures representing the restricted motion in a unit cell of molecules of a solid and the random motion of gaseous molecules.

The question of the behavior of the liquid state in the critical region was the natural result of the discovery of the critical phenomenon itself. In 1889, Cailletet[71] believed that the liquid and gaseous states persisted separately after the critical point had been exceeded. Qualitative proof of this was obtained from experiments with iodine and carbon dioxide[119] in a sealed tube. Above the critical temperature the portion of the tube previously filled with liquid retained its violet color while the upper part of the tube remained colorless.

In 1935, Edwards and Maass[52] prepared a simple liquid state theory to explain their findings on density and adsorption studies. They proposed a liquid state which possessed a certain amount of molecular orientation. The nature of this orientation was pictured by considering a sphere with a radius equal to the average distance between the centers of the molecules in any part of the liquid. The molecules in such a sphere have on the average a definite orientation relative to

one another. If a radius twice as great is chosen the molecules may still have a resultant mean orientation but of smaller magnitude; thus, with increased radius the average orientation rapidly diminishes. Therefore, a liquid has a tendency to form a structure into and out of which the molecules move. The number momentarily in the structure is decreased by an increase in temperature, and at the critical temperature this structure no longer corresponds to the minimum potential energy of the system due to heat energy (translational, rotational, and vibrational) of the molecules. This structure has a tendency to persist above the critical temperature and in a sense may be regarded as metastable.

This conception of the liquid state was not a new one.[120,121] However, previously it had been thought that the liquid structure should vanish at the critical temperature. When Maass and Geddes[122] reviewed the theories presented thus far, they concluded that the structure which had been alluded to in most papers was that of regional orientation of molecules and that the liquid state did persist above the temperature at which the meniscus disappeared.

Regional orientation had also found support in various studies of X-ray diffraction patterns of the liquid state.[123-126] The name of 'cybotactic' groups in liquids had been used to explain the patterns and the groups were based upon molecular orientation. However, other workers[127,128] claimed that X-ray diffraction patterns of a fluid at various densities could be accounted for by a distribution of atoms about any one atom chosen for the calculation. This did not prove the

absence of regional orientation but did weaken the hypothesis.

The liquid theory also needed to explain a discontinuity in properties other than those due to concentration which seemed to exist at the critical temperature. The total surface energy was reported not to be zero,[82] the velocity of a chemical reaction had been noted to undergo a discontinuous change,[129] and the adsorption of a liquid had been noted as different than that of the corresponding gaseous state.

In 1937, Holder and Maass[130] studied the reaction velocity of the system hydrogen chloride-propylene in the critical region. They believed the existence of a 'structure' promoted the velocity of the chemical reaction and that its disappearance above the critical temperature would bring about a decrease in the rate of the reaction. This might mean that a change to a perfectly chaotic distribution of molecules had taken place. Benz and Stewart[124] and other workers[125,131] indicated that, while this is probably the case when the two-phase system liquid-vapor is heated to the critical temperature, under pressure greater than the critical pressure the 'dynamic structure' would persist above the critical temperature.

This idea was substantiated and a decrease in density of the liquid in equilibrium with its vapor had the same results as a rise in temperature as far as tending to destroy the 'structure'. Eventually a critical density could be reached where the 'structure' was destroyed very rapidly. Conversely, a medium at a temperature above critical and compressed to a pressure greater than the critical value could produce a density greater than that of the liquid at its critical

temperature and it should develop a 'structure'.[122,132]

About a year later Barnes[133] reviewed the situation and stated

that it was now evident that liquids possess a 'structure' which

persists under certain conditions above the critical temperature. This

structure may consist simply of a preferential distribution of molecules

throughout the fluid or of regions of preferred distribution and

orientation. Some evidence is found for both cases.

Up to this time it had been considered impossible to take a

system above the critical temperature to a homogeneous phase and cool

to a heterogeneous system while still above the critical temperature.

However, this was done with ethylene by subjecting the bottom portion

of the system to pressure.[134] It thus became possible in a one

component system to produce a dense and a less dense medium apparently

in equilibrium with each other.

Two-Component Systems in the Critical Region

The critical point of a two-component system, as well as that

of a one-component system, may be defined as the limiting conditions

under which the two phases have the same properties. For the one-

component system this is the highest temperature and pressure at which

the two phases may coexist. However, for a two-component system the

critical point does not necessarily correspond to the highest tempera-

ture and pressure at which the two phases coexist. This was observed

early by Kuenen.[135]

Among the work with two-component systems was that of

Schneider and Maass[136] with the two-component system ethylene-propylene in a 1:1 ratio. They determined the critical temperature and critical density. It was evident from their experiments that the true critical phenomenon, which was characterized by the meniscus disappearing near the center of the tube, would occur only over a very limited density range near the critical density. It was also found that when heated for twelve hours at a temperature 4.9 °C. above critical and without stirring, the composition of the liquid and vapor phases differed by about 34 mole percent of ethylene and the phase densities were 0.13 and 0.36 g./cc. for the vapor and liquid phases, respectively. Admittedly, agreement in the results were poor. It was concluded that without stirring attainment of equilibrium was slow and uncertain. With stirring, results indicated that experimentally measured compositions as well as densities of vapor and liquid phases became uniform at the critical temperature.

Phase behavior in two-component systems[18,137] has been throughly investigated in the lower temperature regions but less has been done in the critical region. In this region true critical phenomenon was often confused with that of retrograde condensation.

Retrograde condensation was first observed by Cailletet[138] in 1880. He observed that by increasing the pressure on a closed system a liquid phase would appear and with continued increase of pressure this liquid phase would disappear. Later, a second type of retrograde phenomenon was observed. This involved passing from a one phase system to a two phase system and back to a single phase merely by

a temperature increase. A phase diagram approach shows these phenomena will occur when the path of a point moving in a straight line through a three dimensional representation enters and leaves the heterogeneous region through the same phase boundary. The path does not necessarily have to parallel the temperature or pressure axis but may combine changes in both.

Literature surveys of the early retrograde phenomena reveal the ambiguity of terms used to describe similar phase changes and the need for a uniform nomenclature. This standardization of terms was undertaken by Katz and Kurata[139] and the following rules were suggested.

Condensation was interpreted as the formation of a more dense or liquid phase and vaporization was interpreted as the formation of a less dense or vapor phase when the system was on or within the boundary curve for a two-phase fluid system. The term 'retrograde' was used to earmark phase changes in which the direction of the temperature or pressure travel causing the phase change was opposite that which causes the phase change for a normal case, such as pure substances or mixtures at low pressure. At one atmosphere of pressure a temperature drop or a pressure rise may cause condensation of a vapor to a liquid. Above the critical temperature or pressure a situation may arise within the limits of the two-phase region in which a rise in temperature at constant pressure or a decrease in pressure at constant temperature causes vapor to change into liquid. This process is condensation but because the condition of temperature or

pressure is changing in a direction opposite to that normally encountered, the condensation is said to be retrograde.

Although a combined temperature and pressure change may occur, only isothermal or isobaric changes are considered retrograde, since a combined change has no standard of comparison.

Figure III shows a general phase diagram for which both the bubble point and dew point curves reverse to the critical point. Therefore, both retrograde phenomena are possible. Points 'A' and 'B' are the maximum conditions for the existence of two phases but at these points the vapor and liquid phases do not become equal. This identity of phases occurs only at the critical point, 'C'. The maximum temperature for the existence of two phases, 'B', has been called the 'cricondentherm'.[140-142]

Katz and Kurata also suggest that when discussing systems in this region, the terms 'liquid' and 'gas' or 'vapor' be used only when the system is on or within the border curve. The practice of calling a state reached by isothermal compression of a liquid, such as 'D', a compressed liquid and a state reached by isobaric heating of a vapor, such as 'F', a superheated vapor, may convey some idea of the properties of the phase but the extension of this practice to the critical temperature and critical pressure may lead to confusion. The identity of a single phase should be made by the term 'fluid' with further qualifications as to temperature, pressure, density, or position on the phase diagram. Continued use of liquid and vapor to differentiate between two phases is satisfactory.
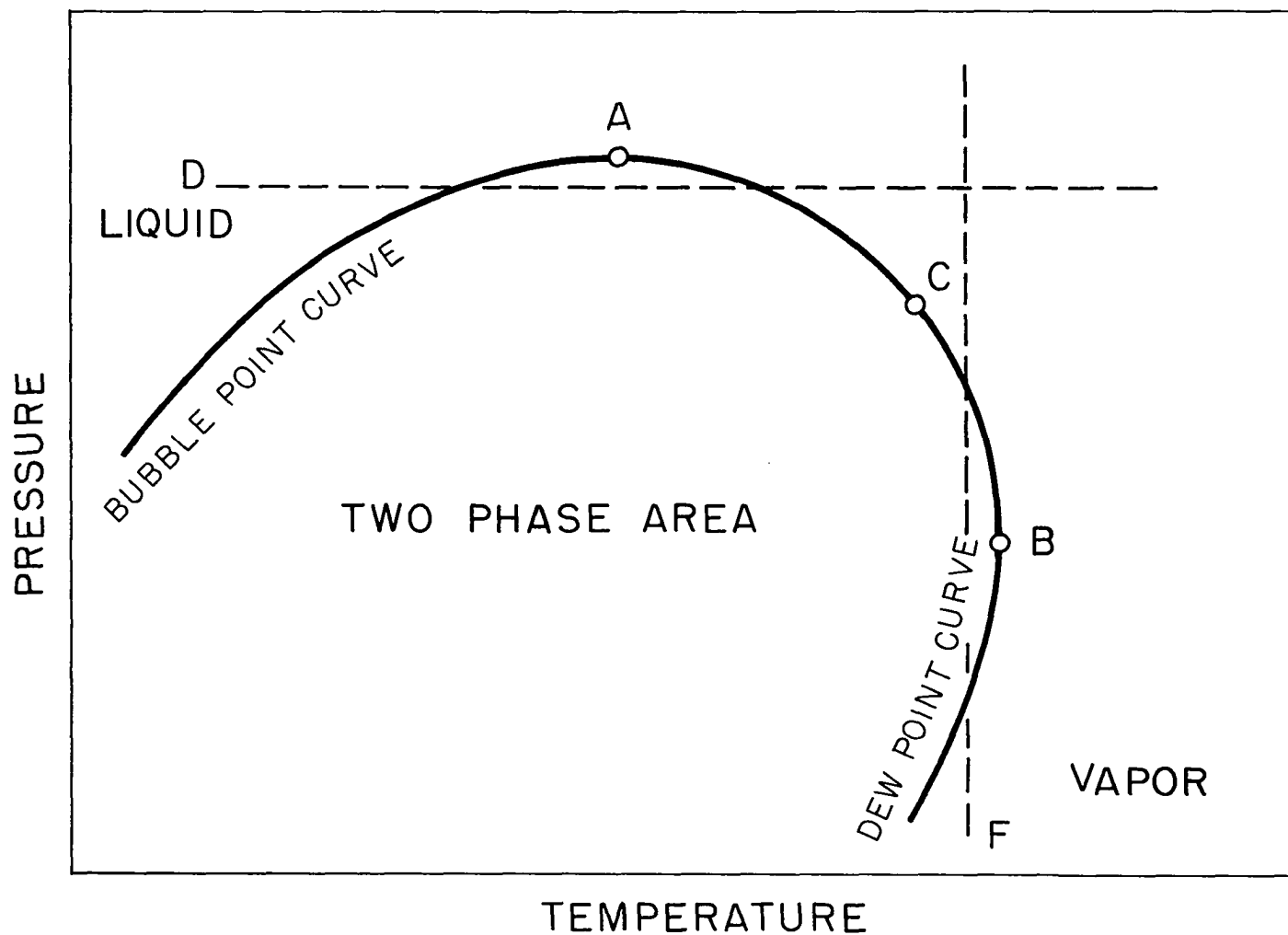
Figure III
PRESSURE-TEMPERATURE ISOCHORE
SHOWING POSSIBLE RETROGRADE PHENOMENA

The term 'double retrograde condensation' was suggested in the case of binary mixtures where a single uniform phase gave three phases, two of which were liquid, by isothermal pressure reduction or isobaric temperature increase.

There are several other properties of solutions of non-volatile solutes in the neighborhood of the critical region of the solvent which have been noted. Iodine molecules remain solvated by carbon tetrachloride molecules when such a solution passes through the critical point of the solvent.[143] This demonstrates the persistence of solvent action above the critical point, as does the case of sodium chloride in water.[24] The usual ionic condition in the liquid persists in alcohol above the critical point.[3,94] Third, the enormous effect of small amounts of solutes on the behavior of the solvent near its critical temperature is emphasized.[24] Fourth, for some dilute solutions the elevation of the critical point is proportional to the molar concentration of the solute. For liquid carbon dioxide the elevation is 8.8 $^\circ$C. per mole of solute and for liquid ammonia it is 13.0 $^\circ$C. per mole of solute.[41] Fifth, electrical conductivity shows a discontinuous temperature derivative in passing through the critical point.[144] In the neighborhood of the critical point the electrical conductivity of the vapor increases and the electrical conductivity of the liquid decreases. Above the critical point the conductivity gradually decreases.

Tables III - VI give critical temperatures for various aqueous solutions as reported by different investigators.

TABLE III

CRITICAL TEMPERATURES OF AQUEOUS SOLUTIONS[145]

Solute	Concentration	Elevation of T_c
K_2CO_3	0.25 M.	18.3 °C.
Na_2CO_3	0.25	24.4
Na_2SiO_3	0.25	18.0
K_2SiO_3	0.25	41.2
SiO_2 gel	0.25	41.2
Li_2SiO_3	0.05	8.1
$Al(OH)_3$	0.10	23.0
$Al(ONa)_3$	0.11	58.0
$NaOH$	0.22	68.3
H_3BO_3	0.65	12.3
$Na_2B_4O_7$	0.20	29.8
H_2MoO_4	0.06	30.5
Na_2MoO_4	0.06	36.2
H_2CrO_4	1.00	26.3
$Na_2Cr_2O_7$	0.50	39.0

TABLE IV

CRITICAL TEMPERATURES OF AQUEOUS SOLUTIONS[146]

Solute	Concentration	T_c
$Fe(OH)_3$	0.25 M.	397 °C.
SiO_2 gel	0.25	385
H_3BO_3	0.65	386
$Mg(OH)_2$	0.50	380
NaOH	0.22	442
H_2MoO_4	0.06	405
H_2CrO_4	1.00	400
$Al(OH)_3$	0.10	397

TABLE V

CRITICAL CONSTANTS OF SALT SOLUTIONS[20]

% NaCl	T_c	P_c
0.0	374.0 °C.	224 kg./cm^2
0.2	379.5	239
0.5	383.5	248
1.0	388.5	259
1.5	395.0	271
2.0	399.0	283
3.0	408.5	309
4.0	416.5	332
5.0	424.0	354
6.0	431.0	376
7.0	437.5	397

TABLE VI

CRITICAL TEMPERATURES OF AQUEOUS SOLUTIONS[10]

Salt	Molarity	T_c	Elevation of T_c
NaCl	0.0342	378.1 °C.	3.9 °C.
NaCl	0.0855	380.95	6.65
NaCl	0.171	385.55	11.35
NaCl	0.342	394.65	20.45
NaCl	0.684	406.55	32.35
NaCl	0.810	411–410.5	36–37
RbCl	0.04275	379.4	5.2
RbCl	0.0855	382.95	8.75

Concentration	T_c			Elevation of T_c		
	KBr	KCl	KI	KBr	KCl	KI
0.04275	379.6	378.85	379.50	5.3	4.55	5.25
0.0855	383.0	382.7	382.75	8.7	8.35	8.55
0.171	389.35	389.0	389.2	15.15	14.7	14.9
0.342	399.35	398.3	399.0	25.15	23.9	25.8

Proposed Experimental Work

In speaking of the liquid-vapor equilibrium of any system it is necessary to deal with at least four variables. These are pressure, volume, temperature, and concentration. In multicomponent systems more than one concentration term will be necessary but only one pressure, one volume, and one temperature. The number of independent variables to define any given state will vary from system to system and may be determined by Gibb's Phase Rule.

In a one-component system the concentration term is fixed and only three variables remain. Any state may then be defined in terms of pressure, volume, and temperature. Experimental apparatus can be assembled in which direct measurements of pressure, volume, and temperature can be made on a given system. Thus any one variable can be expressed as a function of the other two, such as:

$$P = f(T, V).$$

In binary aqueous systems the experimental technique is complicated in several ways. In addition to pressure, volume, and temperature variables, we must also measure the concentration of one of the components. A more serious difficulty in the sulfur trioxide-water system arises because of the chemical interaction between sulfuric acid and any acceptable confining fluid. It was therefore deemed necessary to plan all experiments at constant volume. Too, apparatus for work in the extreme temperature and pressure ranges has not been developed. Multicomponent systems which have been studied, in general, have not involved the combination of high temperatures and pressures to the

extremes required for the sulfur trioxide-water system.

Mathematically, we wish to express our system by an equation such as: $P = f(T, V, X_a)$. X_a is the mole fraction of either component and automatically fixes the concentration of the second component. Since we can not relate simultaneously all these quantities we must depend upon another experimental approach. Even though working with a constant volume, we can vary the quantity of liquid inserted so that the fraction filling of that constant volume is known. By first observing critical temperatures at measured fraction fillings and independently observing the dependence of pressure on fraction filling, the temperatures and pressures can be related for a given solution composition. Therefore, the proposed work for this dissertation consisted of two parts. First, for known solution compositions, temperatures in the critical region were to be measured as a function of the fraction filling. Second, apparatus was to be developed which would permit the measurement of pressure at a known temperature, concentration, and fraction filling. After collection of adequate data selected isobars, isotherms, or isopleths could be constructed.

CHAPTER II

CRITICAL TEMPERATURE MEASUREMENTS
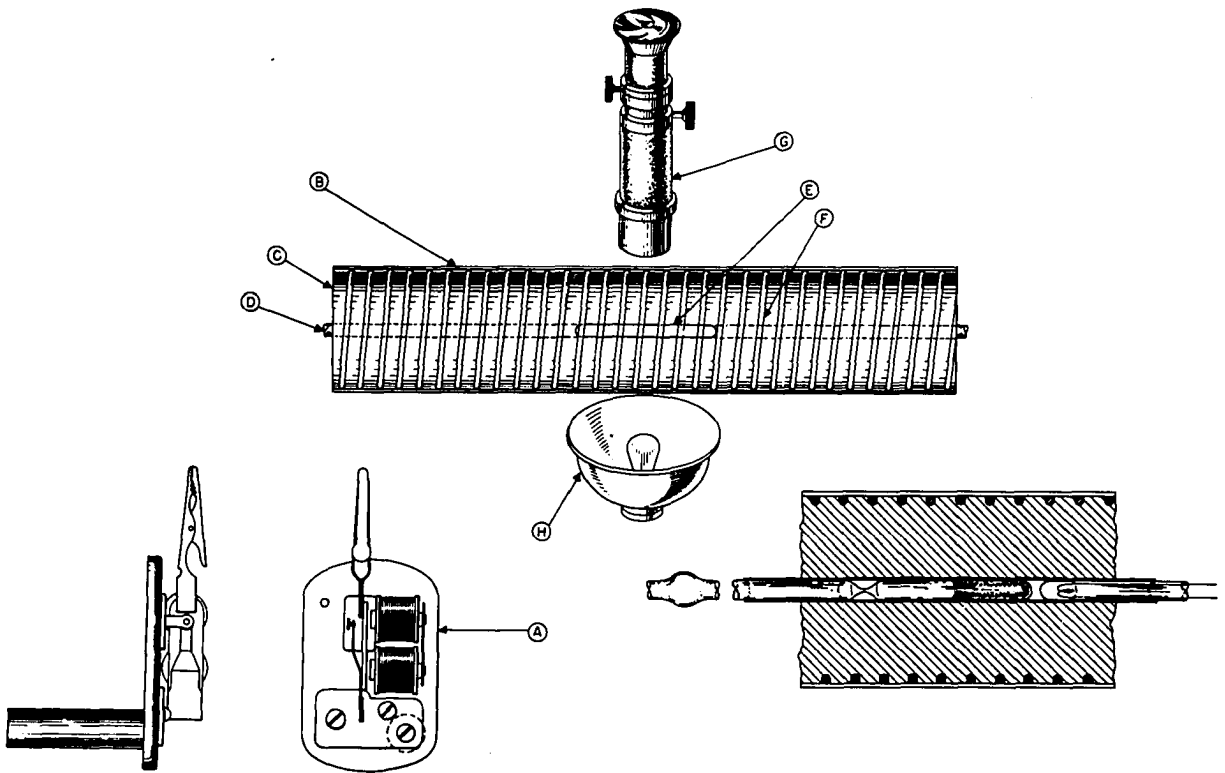
Apparatus

The apparatus used for critical temperature determinations was a modification of that developed by W. L. Marshall, H. W. Wright, and C. H. Secoy at the Oak Ridge National Laboratory.[147] Their method involved a semi-micro technique for phase studies above atmospheric pressure. Figure IV shows the original design of the apparatus.

Furnace

The heating element for this work was a small cylindrical aluminum furnace thirty centimeters in length and five centimeters in diameter. An eight millimeter diameter hole was drilled longitudinally through the cylinder and a window eight centimeters by eight millimeters was machined through the cylinder normal to the longitudinal hole. Four turns per inch of twenty gauge Nichrome heating wire were wound around the cylinder in evenly spaced grooves machined over the surface of the furnace block. Heating current through the wire was manually controlled by a twenty ampere variac on a constant one hundred ten volt power source.

Closely fitting pyrex glass sleeves were placed inside the eight millimeter hole and outside the cylindrical furnace. These acted

A. BELL BUZZER
B. OUTER PYREX SLEEVE
C. HEAT-CONDUCTING BLOCK
D. INNER PYREX SLEEVE
E. OBSERVATION WINDOW
F. HEATING WIRE GROOVES
G. TELESCOPE
H. LIGHT SOURCE

FIGURE IV
A PHASE STUDY APPARATUS FOR SEMI-MICRO EXPERIMENTATION
ABOVE ATMOSPHERIC PRESSURE

as insulators and reduced air currents inside the furnace. They also served as shields against flying glass in case of sample tube failures and permitted easy observation of sample tubes placed in front of the furnace window.

The furnace rested in an asbestos-wrapped cradle supported on a wooden base. The furnace and sample tube could be mounted in a horizontal or vertical position. All critical temperature determinations were made with the furnace in a vertical position to permit accurate measurement of the position along the tube at which the meniscus disappeared. The furnace base was also equipped with various rods and supports for auxillary equipment.

The furnace assembly was satisfactory to temperatures near 550 $^\circ$C. In this range the aluminum and pyrex glass began to soften. For temperatures held here for any length of time and for higher temperatures the aluminum furnace was replaced by one of the same design but machined from a block of electrode graphite. This furnace was assembled in the same manner with inner and outer pyrex sleeves. Pyrex was satisfactory as long as the glass was not required to support the weight of the furnace. Aluminum foil was wrapped around the outer glass sleeve to decrease heat losses through radiation. Small slits in the foil permitted observation through the window. This furnace arrangement would reach temperatures near 700 $^\circ$C. readily.

Continued use of the furnace in this temperature range caused gradual decay and crumbling of the graphite cylinder due to oxidation of materials in the block. It was thus necessary to replace the graphite

cylinder periodically. The Nichrome heating wire insulation was also short-lived at high temperatures.

A safety-glass shield was mounted between the furnace and a Gaertner telemicroscope. With light from a source behind the furnace coming through the window directly into the telemicroscope, it was possible to observe phase changes occurring inside the sample tubes. Cross hairs in the scope permitted measurement of the position of the meniscus in relation to the center of the sample tube.

Observations were also made using light from a source located at an angle of 120 ° from the telemicroscope. This permitted reflected light to be observed and was satisfactory for observing solids present in the liquid phase. It was not as desirable for observing the action of the meniscus as was directly transmitted illumination.

Thermocouples

Temperatures in the furnace were measured by inserting iron-constantan thermocouples. The hot junction was inside the inner sleeve next to the sample tube and the cold junction was in an oil bath immersed in an ice-water bath. A Leeds and Northrup K-2 potentiometer and model 2430-C galvanometer were used for voltage measurements. Voltage readings were converted by Leeds and Northrup thermocouple conversion tables to degrees Centigrade.

The iron-constantan thermocouples were first calibrated against a sensitive platinum resistance thermometer. These were then used to determine temperature gradients in the furnace. At 350 °C. a maximum gradient of 0.1 °C./inch in the sample tube area was observed after

sufficient time was allowed for establishing equilibrium. At maximum temperatures the heat gradient was slightly larger but still of negligible proportion. A check also revealed that a thermocouple placed inside a sample tube recorded the same temperature as a thermocouple outside the tube.

Iron-constantan thermocouples were used because of their high voltage output per degree and because they could be placed next to sample tubes without concern for expensive and permanent damage in case of a sample tube failure. However, in cases of tube failures it was necessary to cut off the damaged end of the thermocouple, thermally weld the ends, and recalibrate. At higher temperatures prolonged use caused insulation deterioration and necessitated the same repairs. After the initial calibration, thermocouples were frequently calibrated against a platinum-platinum (10% rhodium) thermocouple previously standardized by the National Bureau of Standards.

Sample Tubes

Sample tubes were constructed from four-inch lengths of quartz tubing approximately one millimeter in inside diameter. The tube wall thickness was equal to or slightly greater than the tube bore. One end of the tube was sealed with a natural gas-oxygen torch and the open end was placed in a solution of known composition while the sealed end was still hot. Solution was drawn into the tube as cooling occurred. The liquid was centrifuged to the closed end of the tube and the tube sealed.

Liquid samples having very low pressures were first frozen in a Dry-Ice-trichloroethylene bath, melted, refrozen, and remelted while

under partial vacuum to remove dissolved gases. More volatile samples and those with very low freezing points could not be degassed. However, degassing was considered superfluous as no differences in critical temperature readings were noted on samples degassed and those that were not. With such small samples and with the precision of the measurements the effect of dissolved gases was negligible. The samples were maintained as cold as possible while tubes were sealed at a selected distance from the solution meniscus.

Sample tubes were then placed under a Gaertner micrometer slide comparator and the tube length accurately measured. The liquid portion was measured in order to calculate the fraction filling of each tube. The center of the tube was marked as a reference point for locating the position at which the meniscus disappeared during subsequent heating to the critical temperature.

The sample tube was sealed to a six-inch quartz rod, placed inside the furnace, and a commercial Vibra-tool connected to the sample tube arm. This permitted shaking of the solution as it was heated. The Vibra-tool was held by an adjustable mount and was regulated for continuous shaking or for intermittent shaking by using a Flexopulse timer control.

Various sizes of tubing were tried as it was desirable to have a fairly large volume in each sample for ease of observation. Tubes with approximately three millimeter inside diameter and with six millimeter wall thickness were tested first. This heavy quartz tubing required an oxyhydrogen torch for sealing and the heat transfer to the

solution was sufficient to cause evaporation of part of the liquid. During sealing the vapor pressure was frequently sufficient to form a bubble at the seal and rupture the tube. Tubes that were successfully sealed were examined under polarized light and were observed to have regions of strain near the seals. These tubes exploded near 250 °C. when tested with water. It was felt that the strains materially weakened the tubes.

Tubing with two to three millimeter inside diameter and with two to three millimeter wall thickness was also used. It was somewhat easier to seal the tubes and the strains at the seals were not as evident. However, the tubes would not hold pressure much above that developed by water at 300 °C.

Tubing with two millimeter inside diameter and with two millimeter wall thickness was examined and withstood pressures almost equal to the critical pressure of pure water. The tubes generally ruptured near 360 °C.

It thus seemed evident that the larger the tube the more strain in the glass as a result of sealing and the less pressure the tube would contain. Therefore, it was necessary to use tubing of one millimeter inside diameter and an equal wall thickness which was readily sealed without heat transfer to the liquid and without strains developing during sealing. These dimensions resulted in practically no tube failures.

Previous workers[148] indicated that four millimeter silica tubing had been used for aqueous systems up to 300 °C. and 1200 psi.

For critical work two millimeter inside diameter and eight to ten millimeter outside diameter silica tubing was successfully employed by Secoy.[16] No doubt, the quality of the glass itself is an important factor.

The actual sealing of the tubes was not as easy as one might expect. Since heat was transferred down the tube it was desirable to seal as rapidly as possible and at the same time produce no areas of strain. To speed up the sealing process numerous tubes were sealed while under a partial vacuum. It was thought that this would collapse the tube wall as soon as it was soft enough to flow. However, even though seals could be successfully and rapidly completed, the tubes would not withstand pressures as great as the critical pressure of pure water. The same size tube could be sealed by using a very small but very hot flame by rotation and by slight stretching of the tube as it softened. These would hold under the desired pressures. The method of sealing required considerable practice and skill.

Quartz tubing was used because of its strength, chemical inactivity, and resistance to corrosion. Pyrex tubing of similar size would contain similar pressures but was frequently found to be highly etched even by distilled water. Vycor tubing was employed but only in the larger tube sizes which proved unsatisfactory. No difference in corrosion rates was noticeable. Different quartz tubes of the same dimensions sometimes showed different corrosion rates, depending on the quality of the quartz itself.

Evaluation

This particular apparatus and procedure had several advantages. A smaller sample was required on the semi-micro scale and the apparatus was inexpensive and readily assembled. Sample tubes could be prepared in a few minutes after the technique was mastered and the use of a telemicroscope gave increased visual perception of phase changes. The small tubes would withstand the high temperatures and pressures without the use of special apparatus and techniques. Explosions occurred occasionally due to improper sealing but because of the small tube size little damage resulted. Seldom was the outer pyrex sleeve broken although the inner sleeve usually had to be replaced. Too, it was possible to vary the temperature of the furnace very rapidly or very slowly although a given temperature could not be held longer than a few minutes. Temperature gradients inside the furnace were very small as compared to larger furnaces.

The chief limitation of the procedure was in the accuracy of the thermocouples which were used in place of more desirable resistance thermometers. Thermocouple readings gave temperatures to the nearest 0.1 $^{\circ}$C.; however, this reproducibility was greater than their accuracy.

In addition, there were undesirable characteristics. One was the delay caused by a tube failure as the furnace was cooled, cleared of broken glass, and one or both pyrex sleeves replaced. Too, frequent rewinding of the heating element was required as the insulation of the Nichrome wire was not permanent at higher temperatures. Frequent repair and calibration of thermocouples were required.

Special techniques and problems involved with certain solutions will be discussed in sections which follow.

Experimental Data

Water

The water employed here and in the preparation of all solutions was laboratory distilled water which was demineralized. A commercial Deeminizer manufactured by Crystalab was used. The Deeminite ion exchange resin decreased the mineral concentration below one-half part per million.

The critical temperature of pure water was determined first. After preparation of the sample tubes as previously described, including degassing, a sample was placed in the furnace at a temperature a few degrees below the critical temperature. The temperature was allowed to increase slowly until the meniscus disappeared. The temperature was then decreased slowly until the meniscus reappeared. This was repeated several times while the tube was shaken intermittently. Typical data for an individual sample tube appears in Table VII. With the

TABLE VII

CRITICAL TEMPERATURE OF WATER

Measurement	Millivolt Reading	
	Increasing Temperature	Decreasing Temperature
1.	20.425	
·2.		20.425
3.	20.425	
4.		20.425

thermocouple corrections applied to this reading, the measured critical temperature was 374.2 ± 0.1 °C. This is in excellent agreement with accepted values.

This procedure of reading the temperature as the meniscus disappeared and reappeared was employed in all measurements. Averages were taken where variations occurred. Such was generally the case for two-component systems but the variations were normally less than 0.005 millivolt.

The importance of the appropriate fraction filling of the sample tube was noted. If a tube were above or below the proper fraction filling, the meniscus would disappear out the top or bottom of the tube at a temperature other than the accepted critical temperature value. The fraction filling parameter was even more important in critical temperature determinations for binary solutions.

Solution Preparation and Analysis

All sulfuric acid solutions were prepared from reagent grade concentrated sulfuric acid by dilution with demineralized distilled water. Each solution was analyzed for total sulfate content. This was done by titrating samples of the diluted acid with dilute standard sodium hydroxide solution. A Fisher Titrimeter was used to titrate each solution to a pH of seven and the mole fraction of sulfur trioxide was calculated. The density of each solution was determined by interpolation of handbook data.

TABLE VIII

ACID SOLUTION ANALYSES

% H_2SO_4	% SO_3	% H_2O	Moles SO_3	Moles H_2O	Total Number of Moles	Mole Fraction SO_3	Density g./cc.
9.857	8.047	91.953	0.1005	5.1040	5.2045	0.0193	1.065
19.933	16.271	83.729	0.2032	4.6475	4.8507	0.0419	1.139
29.057	23.719	76.281	0.2963	4.2341	4.5304	0.0654	1.211
38.579	31.494	68.506	0.3934	3.8025	4.1959	0.0938	1.291
47.578	38.842	61.158	0.4852	3.3946	3.8798	0.1251	1.372
57.114	46.623	53.377	0.5824	2.9628	3.5452	0.1643	1.467
66.026	53.918	46.082	0.6735	2.5578	3.2313	0.2084	1.565
75.603	61.737	38.263	0.7711	2.1238	2.8949	0.2664	1.676
84.890	69.296	30.704	0.8656	1.7043	2.5699	0.3368	1.778
94.825	77.401	22.599	0.9668	1.2544	2.2212	0.4353	1.833
100.000	81.631	18.369	1.0196	1.0196	2.0392	0.5000	1.831
	84.93	15.07				0.5591	

Solutions Below 0.5 Mole Fraction SO_3

The first binary aqueous solution used was approximately ten
per cent sulfuric acid. Numerous sample tubes were prepared and coded.
All tubes were coded with four numbers. The first and second,
respectively, indicated the month and day of the tube preparation and
critical temperature measurement. The third indicated the solution
number (approximate per cent sulfuric acid) and the fourth numbered the
individual sample tube. The fraction filling of each tube was deter-
mined by measuring the total length of the tube and the length of the
liquid portion to the nearest hundredth of a millimeter. The center of
the tube was marked with ink as a reference point.

The temperature of the disappearance and reappearance of the
meniscus in each tube was measured and an average taken if variations
occurred. The millivolt reading was converted to degrees centigrade and
corrections applied from the thermocouple calibration curves. The tube
in which the meniscus disappeared at the center of the tube was
considered to have the correct fraction filling and thus to correspond
to the correct critical temperature. Table IX summarizes the data for
0.0193 mole fraction of sulfur trioxide.

In working with the 19.933% sulfuric acid solution the
technique was improved somewhat by measuring the distance in millimeters
between the point at which the meniscus disappeared and reappeared and
the center of the tube. This distance was then added to or subtracted
from one-half the total length of the tube and this was divided by the
total tube length to give the fraction filling of the tube at the

TABLE IX

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.0193$$

Sample	f_r	f_c vs. 0.5	T_m
3-26-10-2	0.425	$f_c > 0.5$	$393.4 \pm 1.0\ °C.$
3-26-10-4	0.415	$f_c > 0.5$	400.6
3-26-10-1	0.413	$f_c > 0.5$	399.7
3-26-10-3	0.405	$f_c > 0.5$	402.9
3-19-10-1	0.400	$f_c > 0.5$	404.1
3-26-10-8	0.393	$f_c = 0.5$	404.2
3-15-10-2	0.381	$f_c < 0.5$	406.9
Accepted Value	0.393		404.2 $°C.$

f_r: fraction filling at room temperature, 26 $°C.$

f_c: fraction filling at the temperature at which the meniscus disappeared and reappeared.

T_m: the temperature at which the meniscus disappeared and reappeared.

critical temperature. Ideally, this would be 0.500. The data are summarized in Table X.

Figure V shows a plot of the fraction filling at room temperature against the distance between the center of the tube and the position at which the meniscus disappeared and reappeared. Assuming a linear relationship, we see an initial fraction filling at room temperature of 0.396 would result in the meniscus disappearing at the center of the tube.

In Figure VI the fraction filling at room temperature is plotted against the fraction filling at the critical temperature. This indicates a room temperature filling of 0.396 would give a desired fraction filling at the critical temperature of 0.500. It should be pointed out that the scattering in these graphs is not unreasonable when the actual values and the method involved are considered.

Figure VII indicates the variation of temperature with the room temperature fraction filling. The correct value of this filling now indicates the correct critical temperature for this solution. This refinement in method permitted the critical temperature measurement without the endless work required to prepare a sample tube that corresponded exactly to the correct room temperature fraction filling.

In the next two concentrations the tubes prepared included one in each case which gave what was considered a reliable critical temperature measurement. This meant that in each case a tube was prepared in which the room temperature fraction filling just happened to be the value which corresponded to a value of 0.500 when the meniscus vanished.

TABLE X

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.0419$$

Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_c
5-9-20-4	83.90	0.407	3	0.536	443.5 $\pm$ 1.0 °C.
5-9-20-3	61.81	0.405	3	0.548	441.1
5-9-20-6	61.82	0.393	0.5	0.492	451.5
5-9-20-1	58.89	0.392	6	0.398	452.7
5-9-20-11	61.71	0.391	1	0.484	448.2
5-9-20-9	59.15	0.382	6	0.399	451.3
5-9-20-8	61.98	0.380	7	0.387	449.1
5-9-20-2	49.18	0.364	6.5	0.368	454.6
5-9-20-10	76.42	0.348	15	0.304	462.2
5-9-20-12	76.77	0.347	15	0.305	463.9
5-9-20-5	61.54	0.339	13	0.289	461.5
5-9-20-7*	67.15	0.331	12	0.321	471.6*
Accepted Value		0.396			447.4 °C.

* Excessive time was consumed in this determination and the apparent corrosion was the reason for the unusually high temperature.

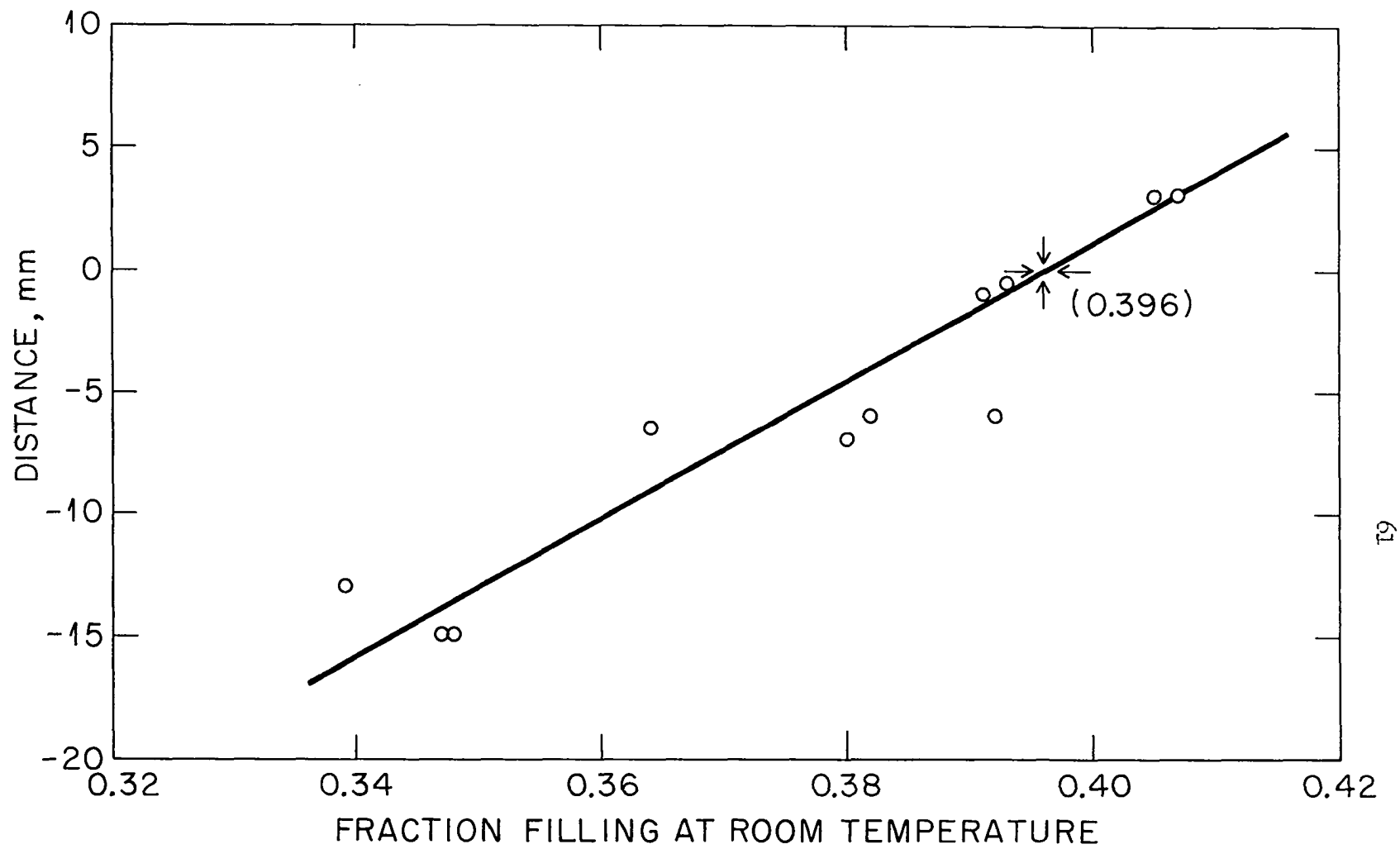Figure $\overline{V}$
POSITION OF VANISHING MENISCUS AS A
FUNCTION OF FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3^=}$ 0.0419
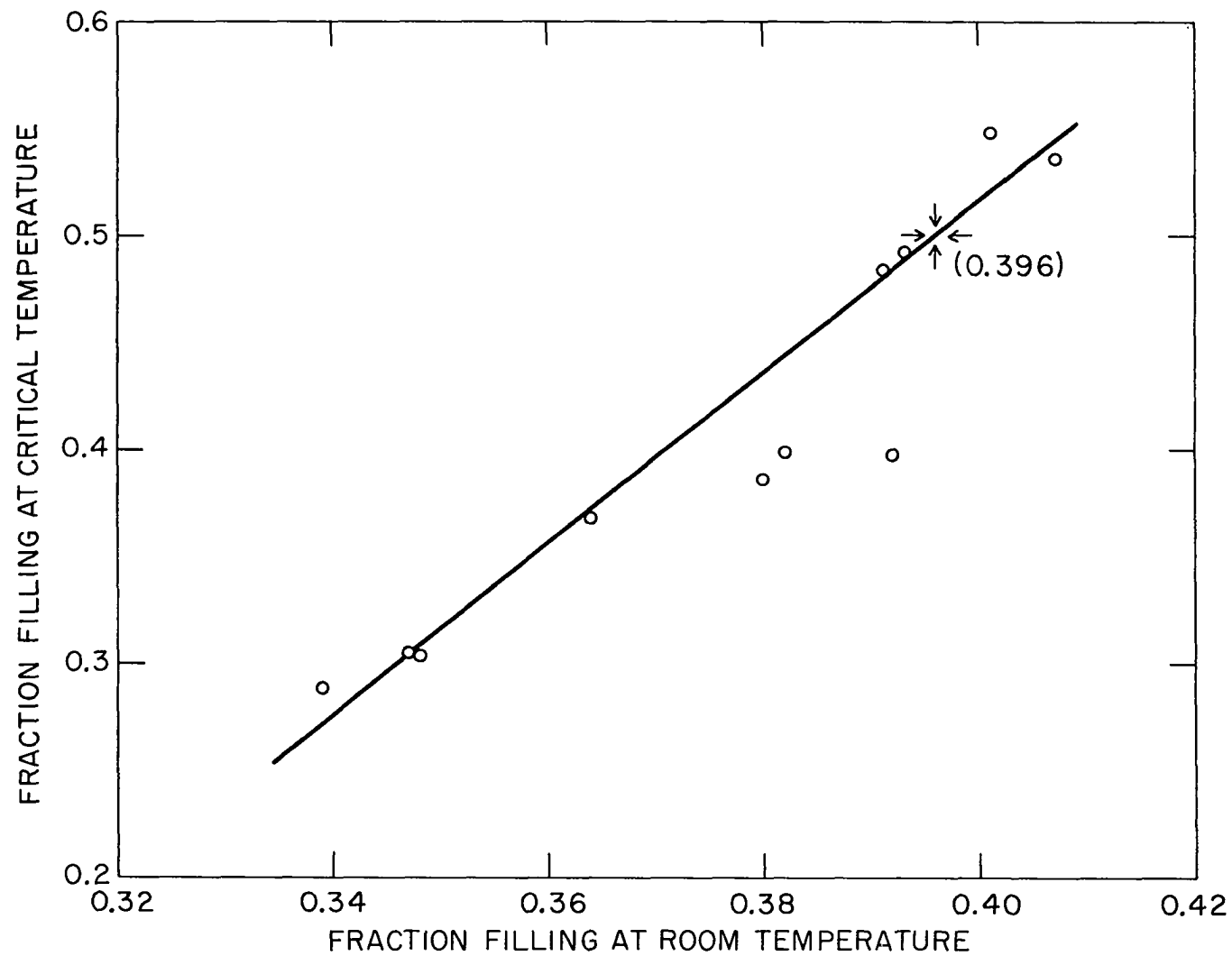
Figure VI
FRACTION FILLING AT CRITICAL TEMPERATURE
IN RELATION TO FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.0419$

Figure $\underline{VII}$
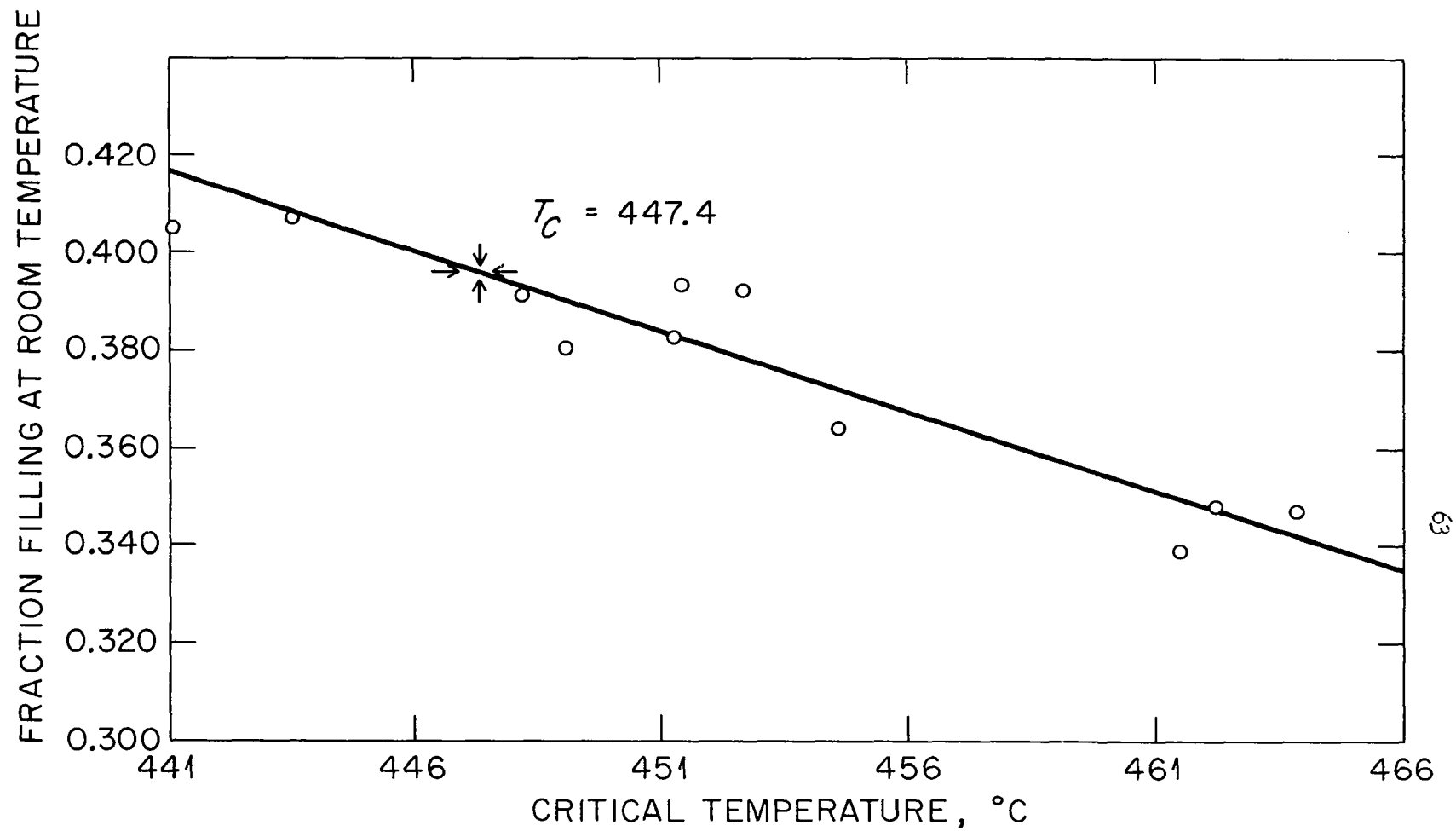
CRITICAL TEMPERATURE AS A FUNCTION OF FRACTION FILLING
AT ROOM TEMPERATURE

$X_{SO_3} = 0.0419$

Note the fact that there is less temperature variation here than for an equal difference in fraction filling in the more dilute solutions. Tables XI, XII, and XIII summarize the data for mole fractions of 0.0654, 0.0938, and 0.1251, respectively.

TABLE XI

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.0654$$

Sample	f_r	f_c vs. 0.5	T_m
3-20-30-1	0.392	$f_c > 0.5$	480.2 ± 1.0 °C.
3-20-30-2	0.376	$f_c = 0.5$	482.8
Accepted Value	0.376		482.8 °C.

TABLE XII

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.0938$$

Sample	f_r	f_c vs. 0.5	T_m
3-19-40-1	0.343	$f_c < 0.5$	525.4 ± 1.0 °C.
3-28-40-1	0.353	$f_c = 0.5$	526.1
3-28-40-2	0.342	$f_c < 0.5$	533.8
Accepted Value	0.353		526.1 °C.

TABLE XIII

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.1251$$

Sample	f_r	f_c sv. 0.5	T_m
3-28-50-2	0.350	$f_c > 0.5$	555.5 $\pm$ 1.0 $^oC.$
3-28-50-1	0.343	$f_c > 0.5$	557.4
3-27-50-2	0.336	$f_c = 0.5$	562.0
3-27-50-1	0.326	$f_c < 0.5$	568.3
Accepted Value	0.336		562.0 $^oC.$

Table XIV summarizes the data for 0.1643 mole fraction of
sulfur trioxide. Note the general agreement among sample tubes prepared
and measured on four different days. There is a slight difference in the
room temperature filling which would result in 0.5 fraction filling at
the critical temperature as determined by the graph in Figure VIII and
that in Figure IX. However, the variation is not large and Figure X
shows that in terms of temperature it represents less than one degree.

Table XV and Table XVI summarize data for mole fractions of
0.2084 and 0.2664, respectively.

Tables XVII and XVIII give data from a 0.3368 mole fraction
solution. Figures XI, XII, and XIII show the data in graphical form.
Here is a good example of how the critical temperature can be determined

TABLE XIV

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.1643$$

Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_m
5-1-60-3*	76.62	0.361	1	0.487	586.4 ± 1.0 °C.
5-1-60-2	-	0.356	-	-	585.8
4-30-60-4	100.10	0.354	9	0.590	586.8
5-1-60-6	77.80	0.340	0.2	0.497	592.3
5-1-60-4	81.10	0.342	2	0.525	593.0
4-30-60-2	101.85	0.339	6	0.559	589.9
3-20-60-2	-	0.337	-	-	589.4
3-28-60-1	-	0.336	-	-	588.6
5-1-60-5	80.56	0.336	3	0.463	591.7
5-1-60-1	82.00	0.333	2.5	0.530	592.8
5-1-60-8	76.76	0.330	2	0.474	591.5
3-28-60-2	-	0.323	- -	-	594.6
3-20-60-1	-	0.309	-	-	594.5
4-30-60-3	113.16	0.301	10	0.412	599.4
5-1-60-7	92.35	0.285	-	-	626.5
4-30-60-1	-	0.262	-	-	606.9
Accepted Value		0.333			592.2 °C.

* Questionable point.
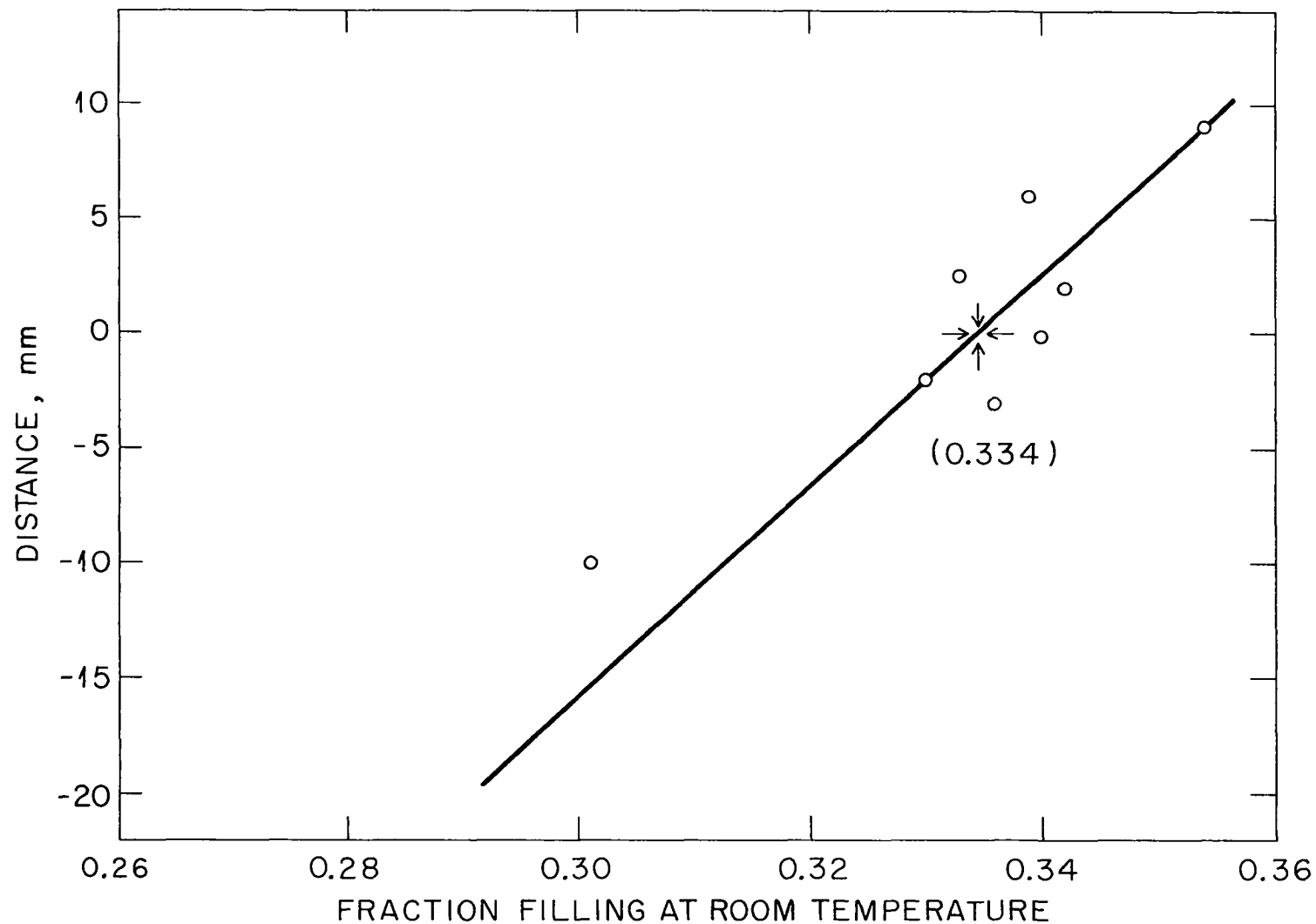
Figure VIII
POSITION OF VANISHING MENISCUS AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.1643$
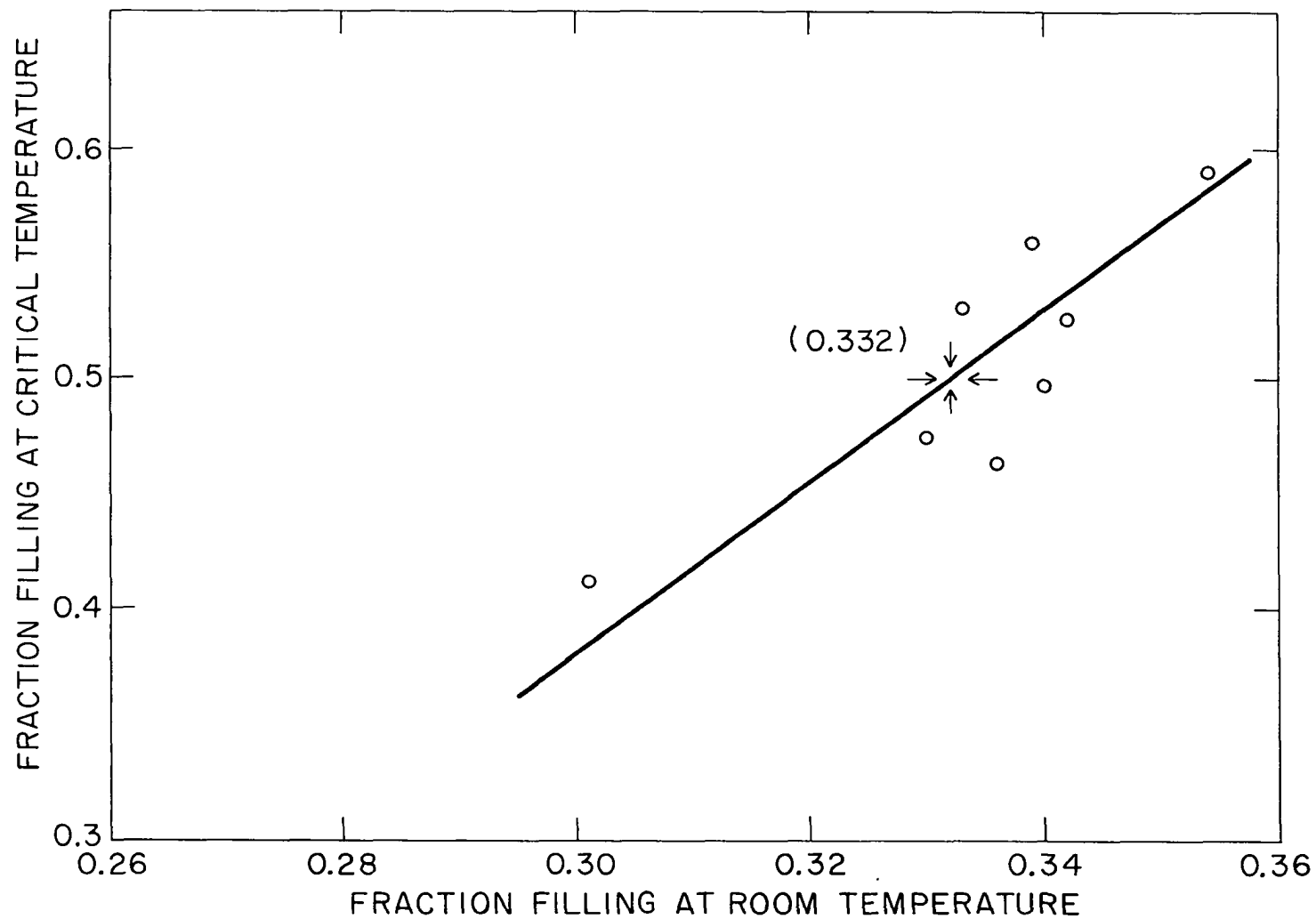
Figure IX

FRACTION FILLING AT CRITICAL TEMPERATURE IN RELATION TO
FRACTION FILLING AT ROOM TEMPERATURE
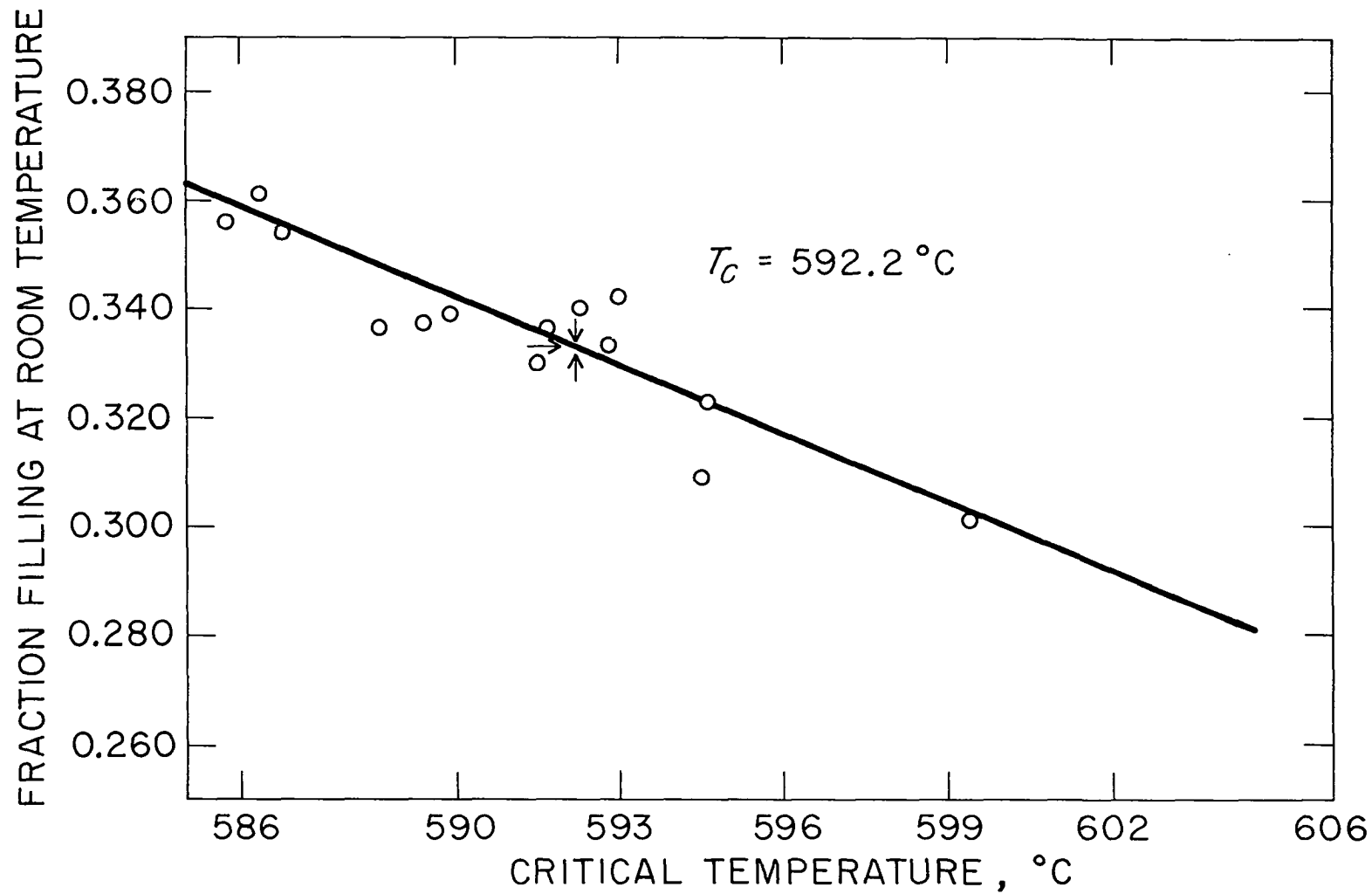
$$X_{SO_3} = 0.1643$$

Figure X
CRITICAL TEMPERATURE AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.1643$

TABLE XV

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.2084$$

Sample	f_r	f_c vs. 0.5	T_m
3-21-70-1	0.352	$f_c > 0.5$	$614.6 \pm 1.0 \ ^oC.$
3-21-70-2	0.345	$f_c > 0.5$	615.0
3-21-70-3	0.336	$f_c > 0.5$	616.6
3-21-70-4	0.314	$f_c = 0.5$	621.0
3-21-70-5	0.284	$f_c < 0.5$	626.3
Accepted Value	0.314		621.0 $^oC.$

TABLE XVI

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.2664$$

Sample	f_r	f_c vs. 0.5	T_m
3-22-80-1	0.334	$f_c > 0.5$	$643.4 \pm 1.0 \ ^oC.$
3-22-80-2	0.293	$f_c = 0.5$	646.8
Accepted Value	0.293		646.8 $^oC.$

71

TABLE XVII

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.3368$$

Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_m
5-2-90-4	84.59	0.318	-	-	664.1 ± 1.0 °C.
5-2-90-6	83.36	0.296	3	0.536	665.2
5-2-90-1	103.09	0.283	0	0.500	665.5
5-3-90-2	94.67	0.279	-	-	666.0
5-3-90-4	84.87	0.267	2	0.524	666.3
5-2-90-7	119.81	0.258	11	0.408	666.7
5-2-90-3	106.46	0.241	-	-	668.3
5-2-90-8	101.69	0.240	-	-	667.4
5-3-90-5	94.04	0.233	-	-	667.8
5-3-90-6	93.48	0.233	-	-	667.6
5-3-90-1	112.07	0.223	-	-	665.6
5-3-90-3	94.46	0.215	-	-	668.3
5-2-90-5	114.20	0.211	-	-	668.4
5-2-90-2	117.93	0.209	-	-	669.3
Accepted Value		0.283			665.4 °C.

TABLE XVIII

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.3368$$

Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_m
5-22-90-4	83.30	0.314	10	0.620	$663.9 \pm 1.0\ °C.$
5-22-90-5	80.71	0.310	8	0.599	664.0
5-22-90-1	83.81	0.309	6	0.572	663.3
5-22-90-2	76.64	0.293	0.5	0.507	665.0
5-22-90-6	74.80	0.281	1.5	0.480	664.9
5-22-90-3	78.81	0.272	3.5	0.456	666.0
5-22-90-8	83.68	0.270	4	0.452	665.4
5-22-90-10	112.29	0.257	7	0.438	666.4
5-22-90-9	75.58	0.255	7	0.407	666.3
5-22-90-7	84.76	0.242	8	0.406	667.4
Accepted Value		0.283			665.4 $°C.$
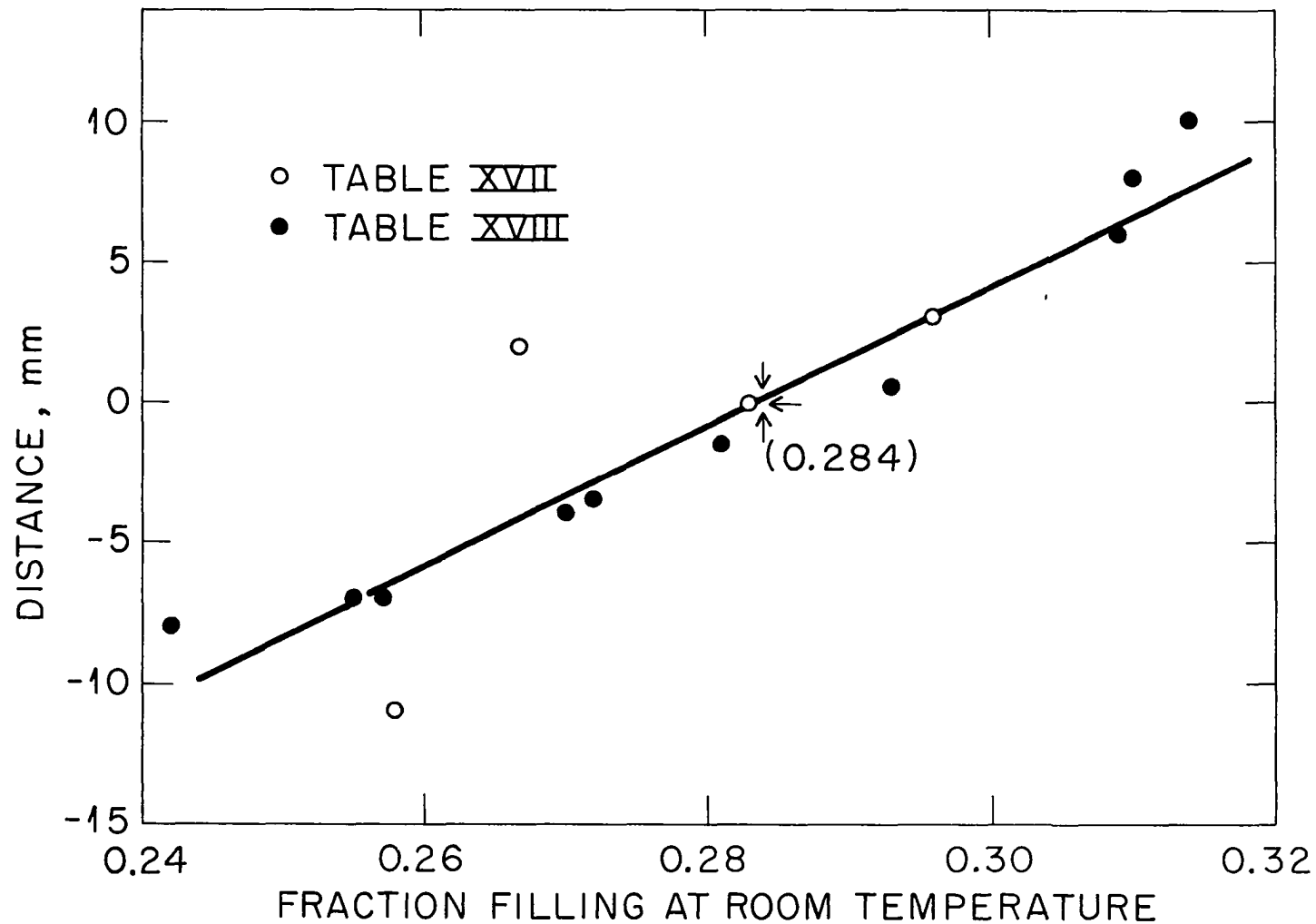
Figure XI
POSITION OF VANISHING MENISCUS AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.3368$

Figure XII
FRACTION FILLING AT CRITICAL TEMPERATURE IN RELATION TO
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.3368$

Figure XIII
CRITICAL TEMPERATURE AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.3368$

with more and more precision provided the time is available. It should

be noted that the temperature variation is still less than in previous

work with solutions having a lower concentration of sulfur trioxide.

Therefore, the critical temperature for the higher concentrations can

be determined with greater accuracy than for lower concentrations.

This is even more evident in Table XIX and Figures XIV, XV,

and XVI which show that concentrated sulfuric acid is almost independent

of the initial fraction filling.

Solutions Above 0.5 Mole Fraction SO_3

The problems involved in preparing solutions on the sulfur

trioxide rich side were formidable. Such concentrations could be

prepared only by adding measured amounts of water to pure sulfur

trioxide. Problems of mixing fixed quantities of each and of analyzing

the solutions after mixing were numerous. For instance, the large

amount of heat generated on mixing and the volatility of the sulfur

trioxide made handling difficult.

Pure sulfur trioxide was readily prepared from Baker and

Adamson reagent grade Sulfan B. This was liquid sulfur trioxide

containing a stabilizer. Pure sulfur trioxide was distilled using warm

water around the distilling flask to supply heat for vaporization and ice

water around the receiving vessel for condensation. The distillation was

carried out in an all glass system because of the highly corrosive nature

of the sulfur-trioxide. Ground glass connections were used but were not

entirely satisfactory. Leakage occurred unless a sealing lubricant was

used; however, contamination always resulted even with minute quantities

TABLE XIX

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.5453$$

| Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_m
5-7-95-12	81.56	0.295	5	0.561	666.3 $\pm$ 1.0 °C.
5-7-95-11	80.31	0.289	4	0.550	666.5
5-7-95-3	83.41	0.269	4	0.452	666.3
5-7-95-2	81.94	0.262	6	0.427	666.2
5-7-95-5	81.12	0.258	10	0.377	666.4
5-7-95-4	76.02	0.253	10	0.368	666.4
5-7-95-6	86.72	0.252	10	0.385	666.3
5-7-95-1	101.17	0.252	15	0.352	666.3
5-7-95-9	84.95	0.232	-	-	666.8
5-7-95-8	98.93	0.186	-	-	664.3
Accepted Value		0.280			666.4 °C.
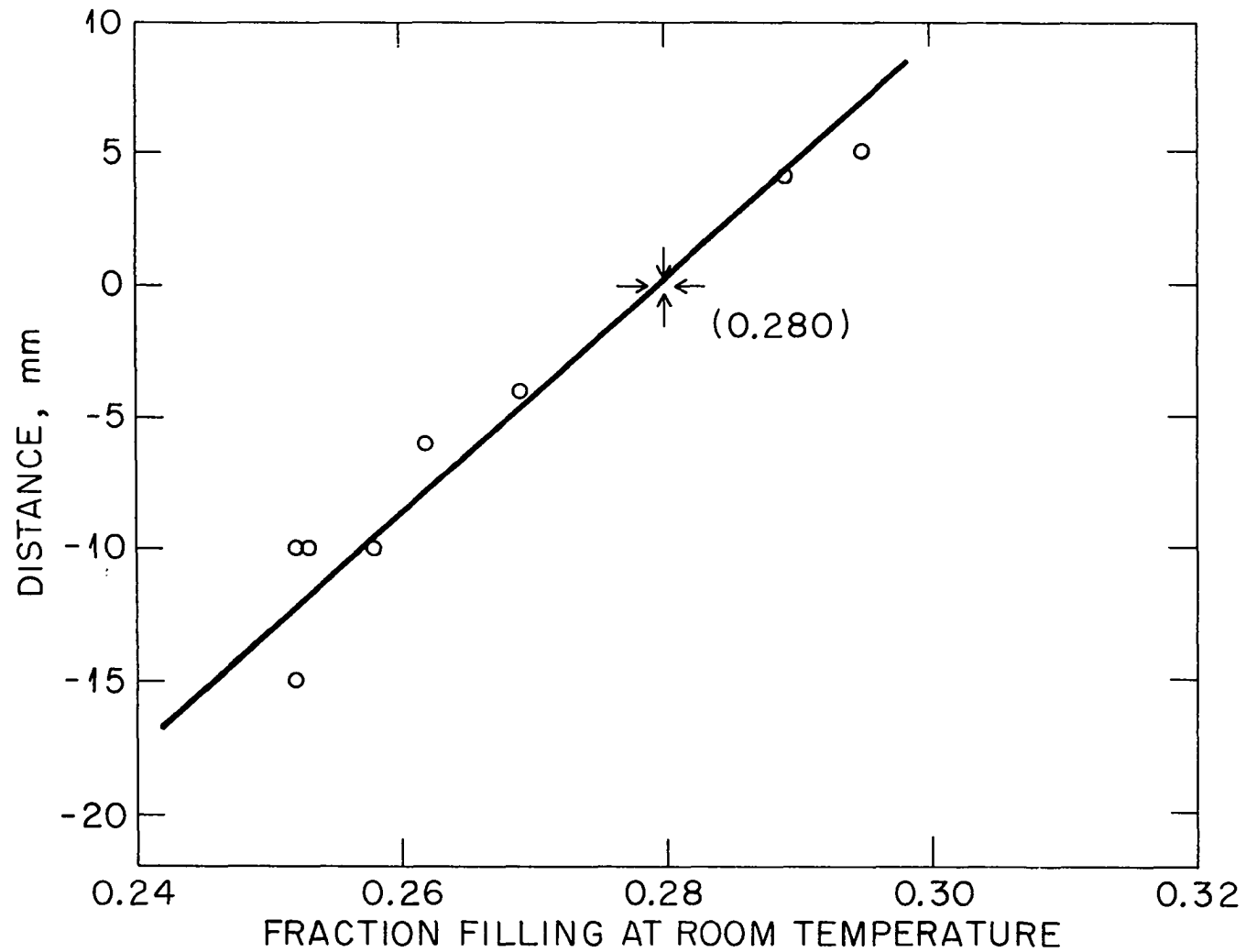
Figure XIV
POSITION OF VANISHING MENISCUS AS A FUNCTION OF
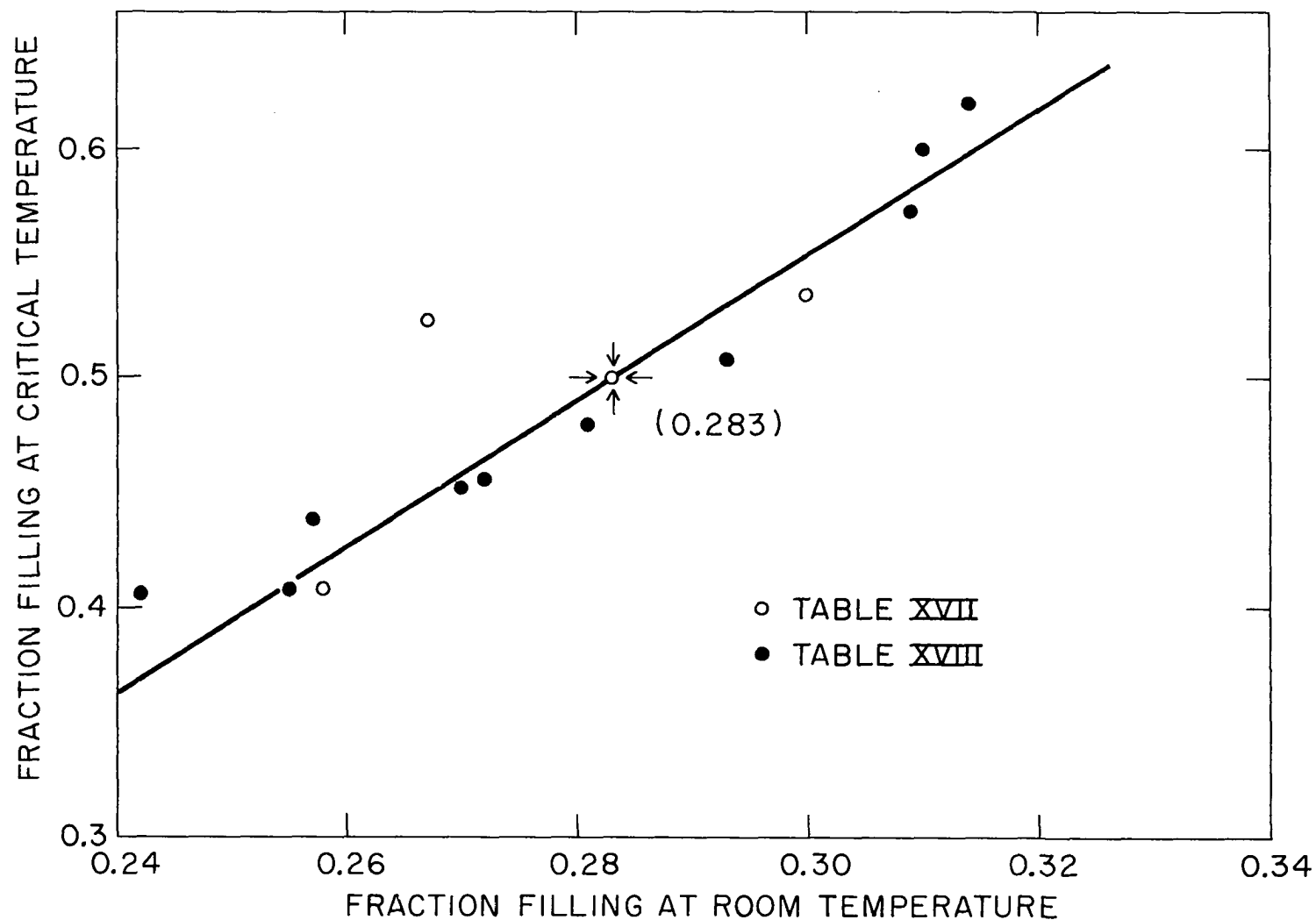FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO} = 0.4353$
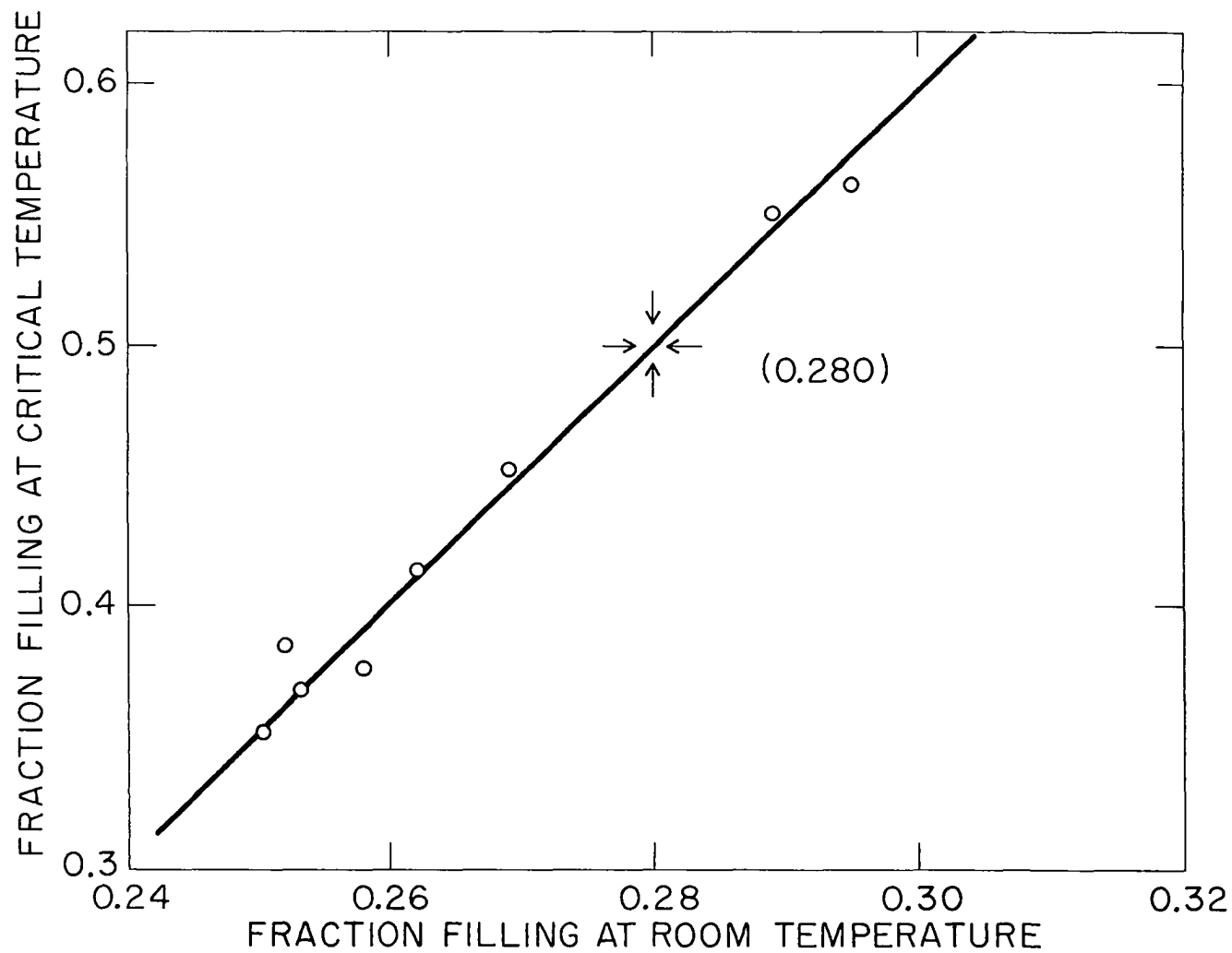
Figure XV

FRACTION FILLING AT CRITICAL TEMPERATURE IN RELATION TO
FRACTION FILLING AT ROOM TEMPERATURE

$$X_{SO_3} = 0.4353$$

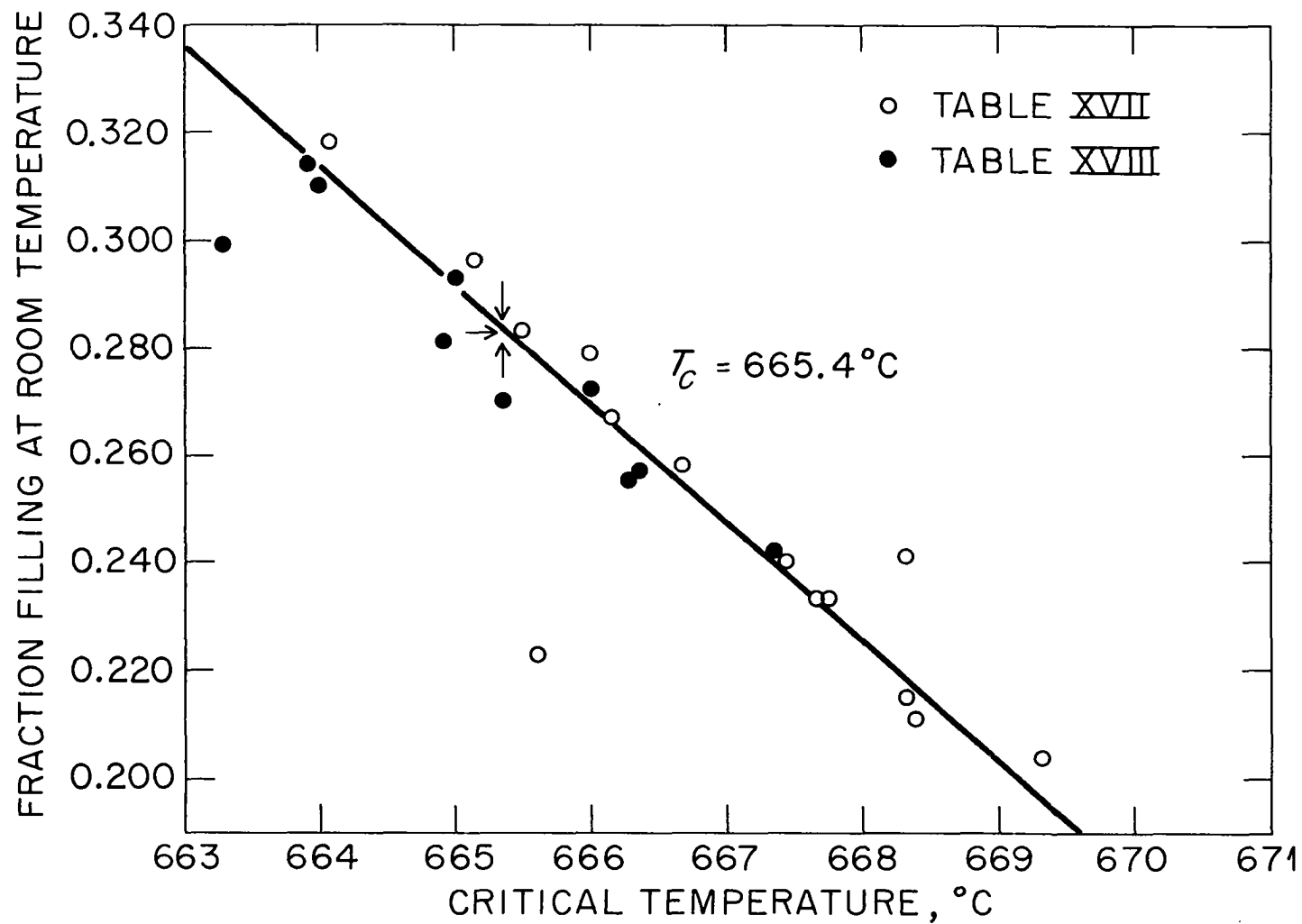FIGURE XVI
CRITICAL TEMPERATURE AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
X_{SO_3} = 0.4353

of lubricant. The sulfur trioxide solidified in very long white
needle-like crystals. While standing at room temperature intricate
flowers of crystal clusters formed from various imperfections on the
glass container wall.

Various techniques were used in attempts to fill the quartz
tubes with sulfur trioxide. Attempts were made to distill and
condense the trioxide directly into the sample tube but were unsuccessful
due to the small tube bore. Even evacuation of the air in the tube and
distillation apparatus before distillation did not help. Suction of
liquid into the tube before either end was sealed was also unsuccessful.
Sealing resulted in vaporization and sufficient build up of pressure to
blow the liquid phase out of the tube. Some success in filling came by
sealing one end and placing the cool end in the liquid phase. As the
hot end cooled the liquid was drawn into the tube. However, attempts
to seal the other end resulted in loss of the sulfur trioxide.

It was also very difficult to keep the sulfur trioxide in a
pure state. Dust in the air rapidly contaminated the purified sample
and resulted in a darkening of the crystals.

As a result of these difficulties, only one point on the
sulfur trioxide rich side was obtained. This resulted from work with
reagent grade fuming sulfuric acid.

Sample tubes were prepared in a manner similar to those of
lower concentrations. Care was necessary in keeping the tubes cold
during sealing to prevent loss of the excess sulfur trioxide. Many
tubes were made before a few were successfully sealed without loss of

sulfur trioxide and with fraction fillings in the proper range.

Samples of the fuming acid were diluted in ice water to prevent loss of sulfur trioxide and the resulting solution was analyzed as previously described. Some sample tubes were analyzed after the critical temperature had been determined. The tubes were weighed and broken under a known quantity of ice water. The solution was titrated and the broken glass filtered and weighed. The process was not ideal due to frequent losses of sulfur trioxide during the process.

Table XX summarizes the data for 0.5591 mole fraction of sulfur trioxide. Note that the critical temperature is again becoming dependent upon the fraction filling of the sample tube. The data are graphed in Figures XVII, XVIII, and XIX.

Table XXI summarizes the critical temperature data and Figure XX shows the critical temperature of various concentrations plotted as a function of the mole fraction of sulfur trioxide.

Corrosive Effect of Sulfuric Acid on Glass

It was obvious that the effect of water and sulfuric acid solutions at high temperatures on pyrex made it undesirable and a more inert substance necessary. Pure quartz and high percentage quartz glass proved adequate because of their corrosion resistant properties. Limited observations indicated the corrosion rate on Vycor (a high percentage quartz) tubing was no different than that of pure quartz.

Even with quartz tubing corrosion was evident and had to be considered. The corrosion was noticeably more rapid in more dilute solutions. Tubes heated slowly to temperature or held over ten minutes

TABLE XX

EXPERIMENTAL CRITICAL TEMPERATURE DATA

$$X_{SO_3} = 0.5591$$

Sample	Total Tube Length mm.	f_r	Distance mm.	f_c	T_m
5-8-F-10	69.12	0.364	4	0.558	632.3 $\pm$ 1.0 °C.
5-8-F-8	73.41	0.350	4	0.554	634.3
5-8-F-7	76.62	0.341	3	0.539	635.6
5-8-F-2	94.12	0.324	3	0.468	637.3
5-8-F-1	100.00	0.312	3.5	0.465	639.9
5-8-F-5	99.30	0.286	6	0.440	646.4
5-8-F-4	100.11	0.255	18	0.320	650.5
5-8-F-6	100.12	0.241	20	0.300	652.3
5-8-F-3	100.28	0.239	-	-	653.7
Accepted Value		0.331			637.2 °C.
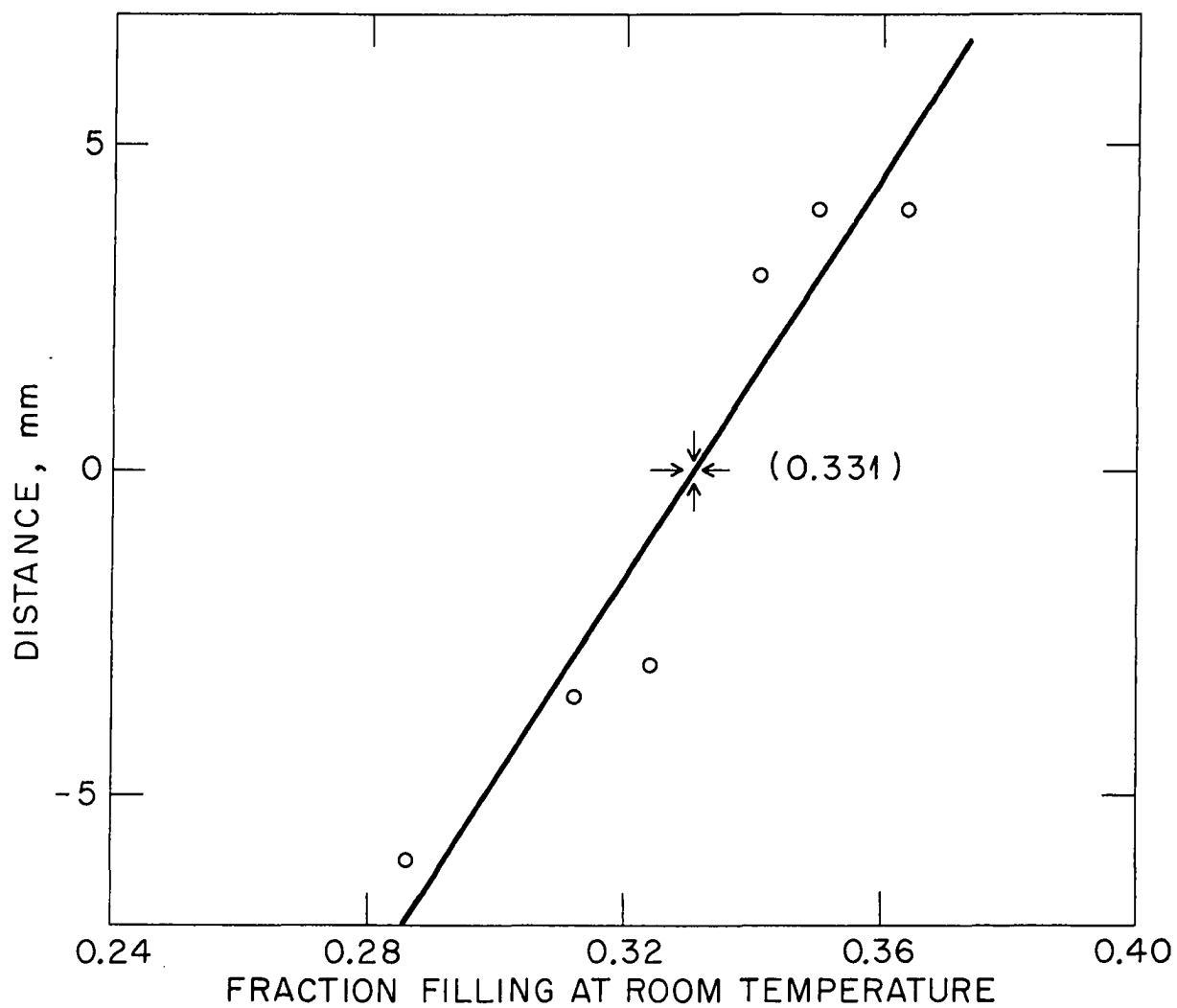
Figure XVII
POSITION OF VANISHING MENISCUS AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.5591$
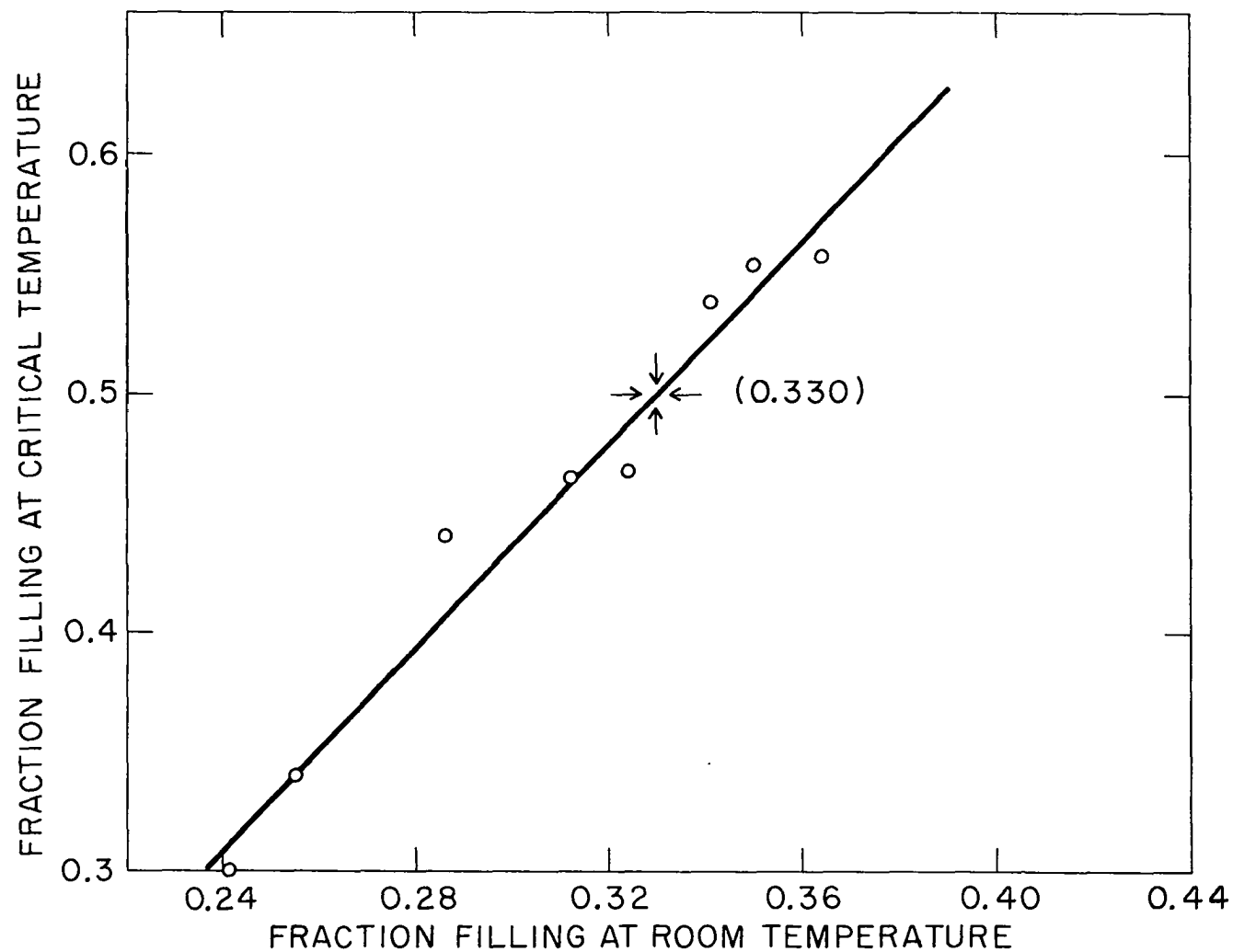
Figure XVIII
FRACTION FILLING AT CRITICAL TEMPERATURE IN RELATION TO
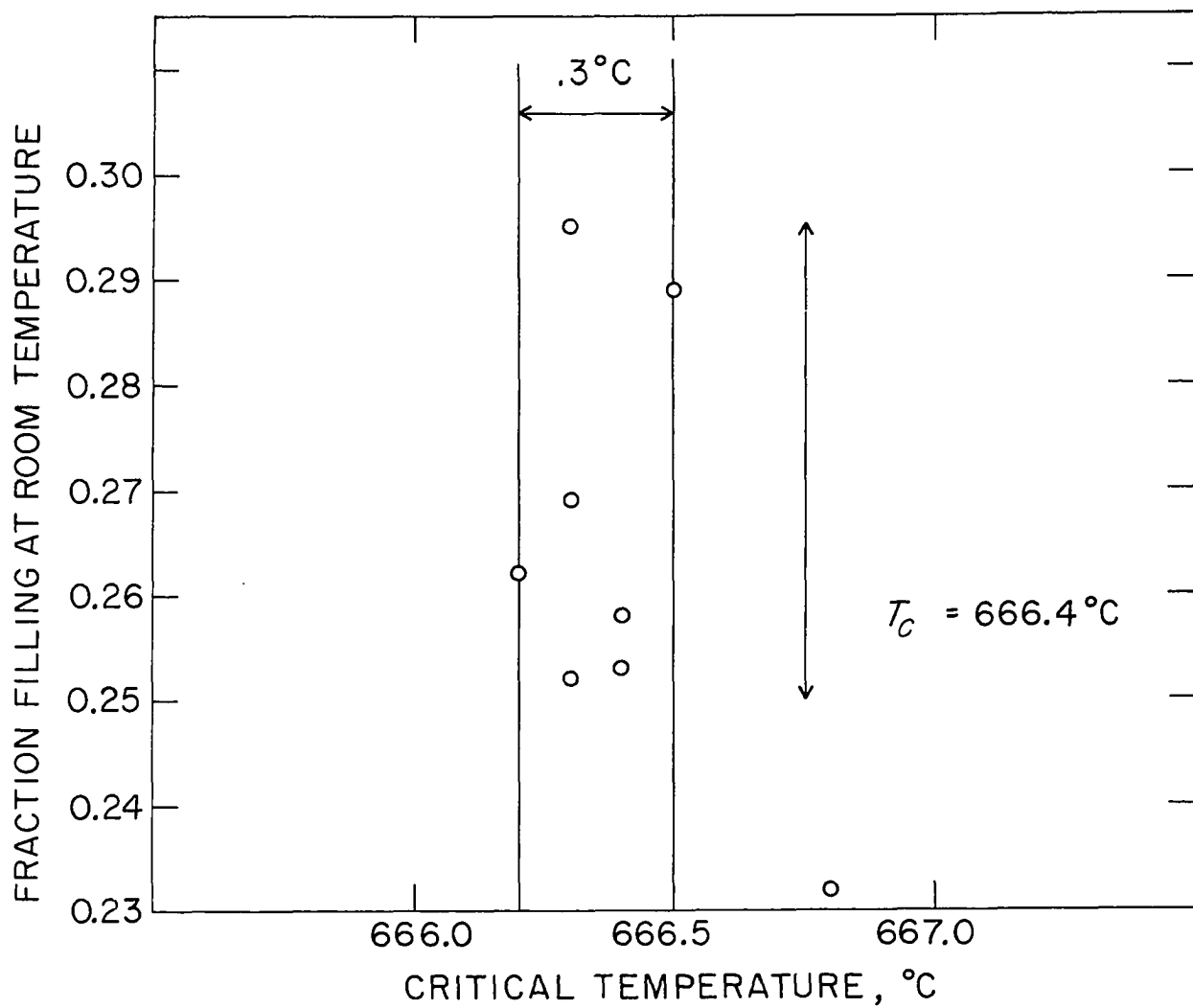FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.5591$
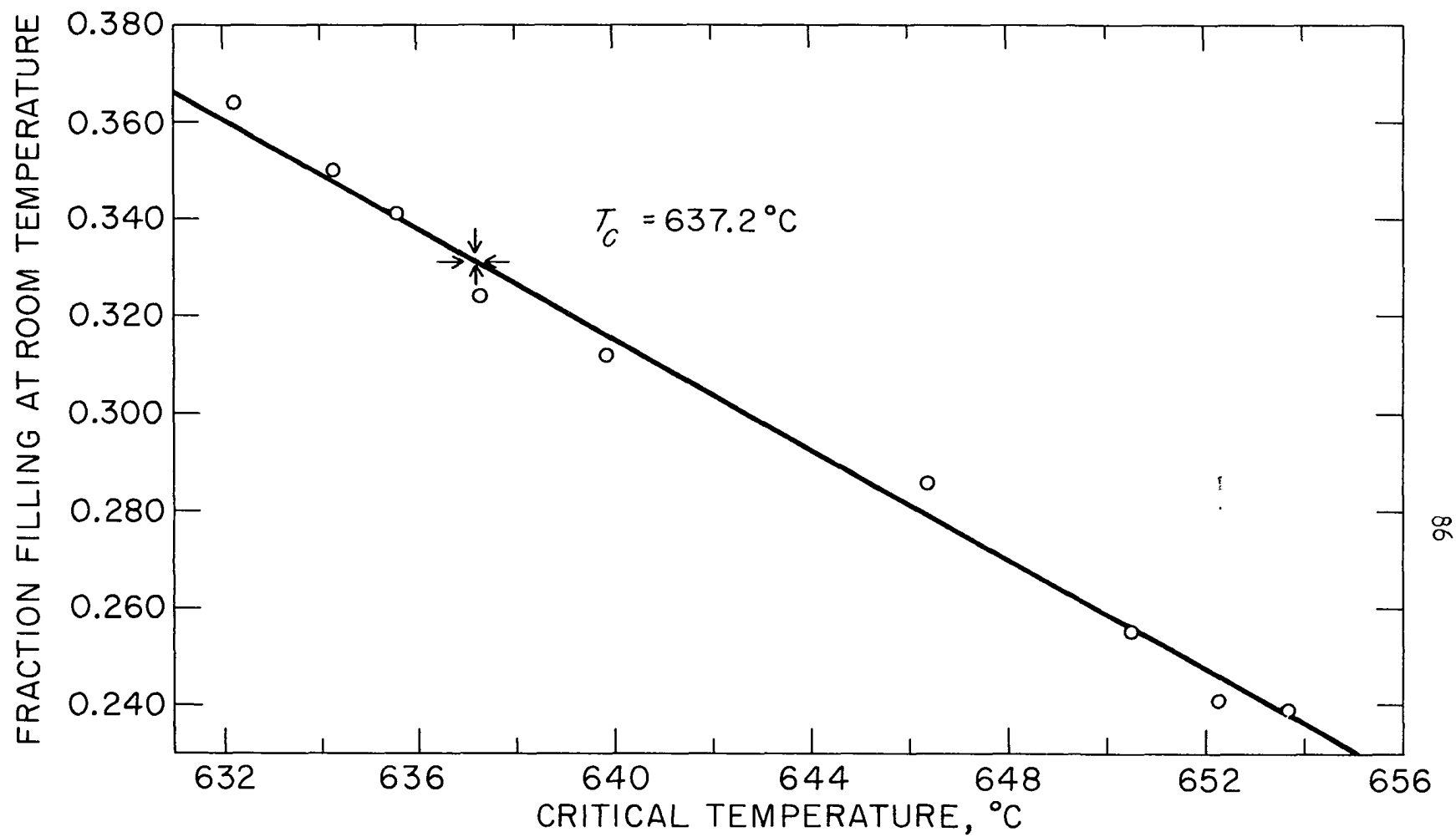
Figure XIX
CRITICAL TEMPERATURE AS A FUNCTION OF
FRACTION FILLING AT ROOM TEMPERATURE
$X_{SO_3} = 0.5591$

TABLE XXI

SUMMARY OF CRITICAL TEMPERATURES

x_{SO_3}	f_r °	T_c
0.0000	0.32	374.2 °C. °°
0.0193	0.393	404.2
0.0419	0.396	447.4
0.0654	0.376	482.8
0.0938	0.353	526.1
0.1251	0.336	562.0
0.1643	0.333	592.2
0.2084	0.314	621.0
0.2664	0.293	646.8
0.3368	0.283	665.4
0.4353	0.280	666.4
0.5591	0.331	637.2
1.0000	0.336	218.3 °°°

°   Fraction filling at room temperature for which f_c = 0.5

°° Reference 2.

°°° Reference 149.
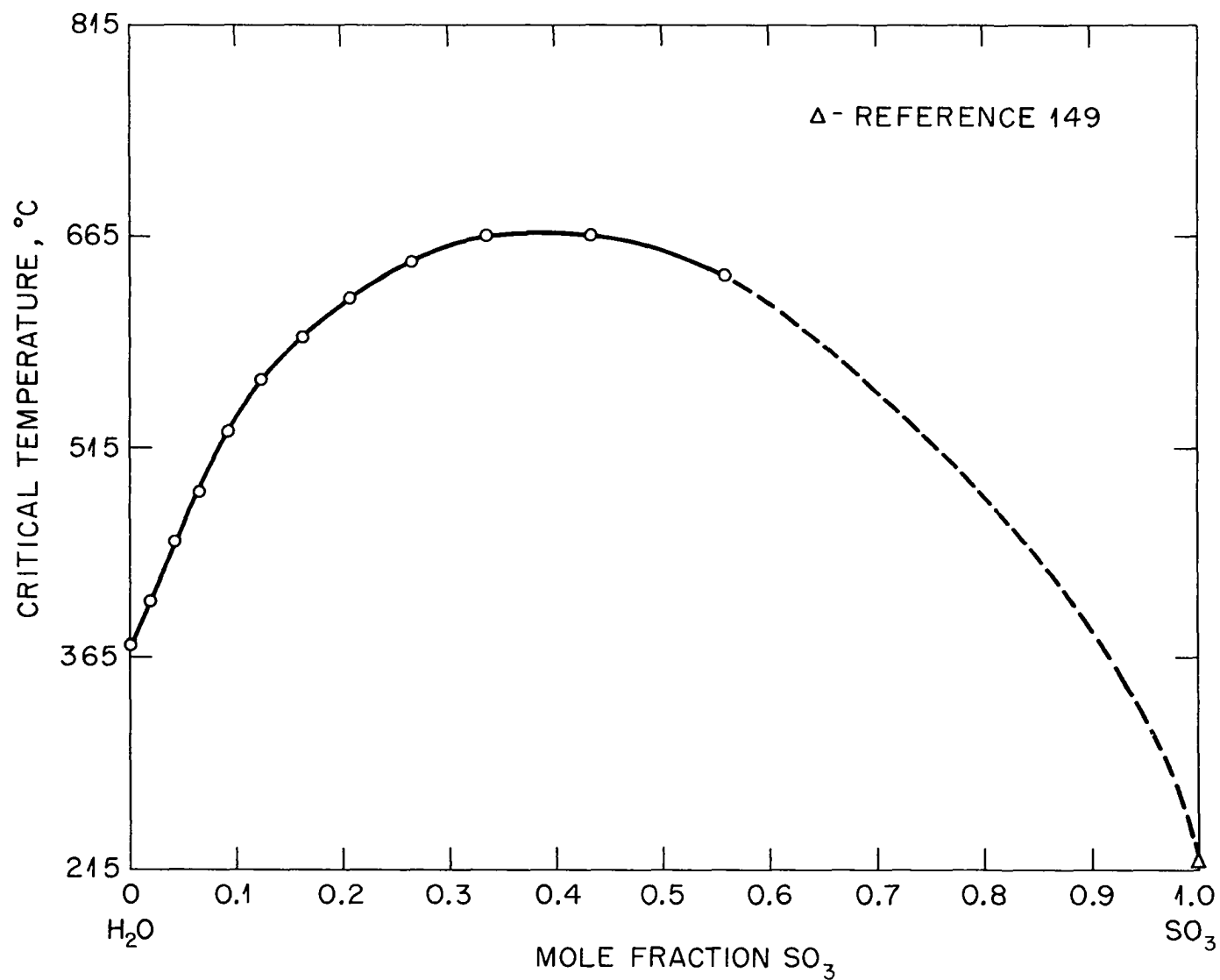
Figure XX
CRITICAL TEMPERATURES
SYSTEM $SO_3 - H_2O$

at high temperatures could not be expected to give a dependable

critical temperature measurement. Representative corrosion data

appear in Table XXII and graphically in Figure XXI.

Therefore, certain precautions were necessary and the following

procedure was followed.in making critical temperature measurements.

First, rough determinations were made to locate the approximate critical

temperature. Then a sample tube was placed in the furnace while it

maintained a temperature a few degrees below the approximate critical

temperature. Several temperature readings as the meniscus vanished and

reappeared could be made in five minutes or less. The tube was then

removed, quenched in ice water, and examined under a microscope for

signs of possible corrosion. If corrosion were evident the tube was

discarded; otherwise, the data were deemed satisfactory and were recorded.

TABLE XXII

CORROSIVE EFFECT OF SULFURIC ACID ON QUARTZ

Sample	Time	Increase in Critical Temperature
	$X_{SO_3} = 0.0193$	
3-15-10-2	0.08 hr.	1.2 °C.
3- 26-10-8	0.25	2.5
3-26-10-8	0.75	4.2
3-15-10-2	1.60	4.8
3-15-10-2	2.10	5.7
3-15-10-2	19.00	7.9
	$X_{SO_3} = 0.0419$	
3-15-20-1	0.33	1.4
3-15-20-1	0.75	2.4
3-15-20-1	18.00	6.4
3-15-20-1	65.00	14.9
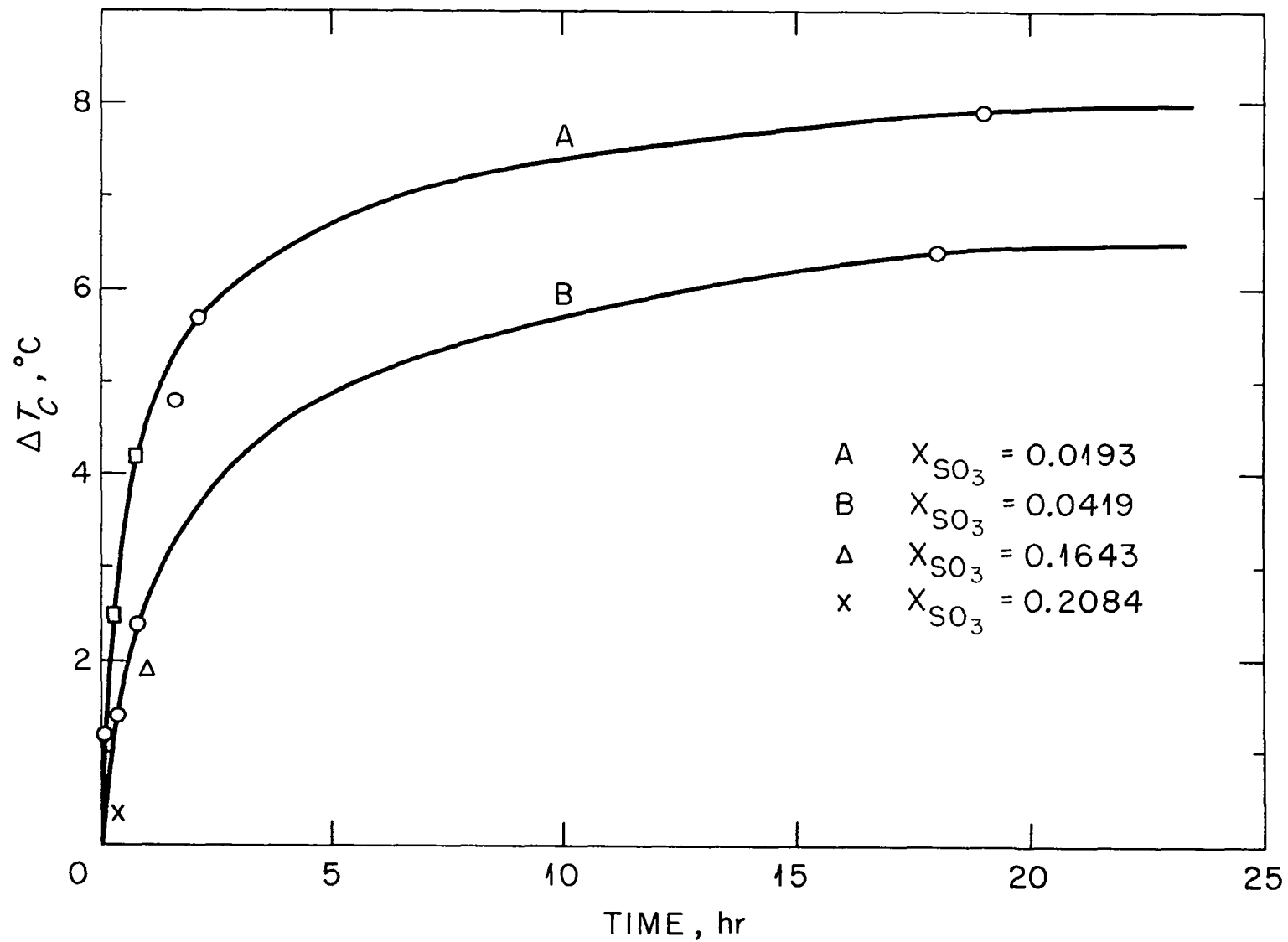
Figure XXI

CORROSION RATES OF H₂SO₄ ON QUARTZ

Chart axes and legend:

Y-axis: ΔT_C, °C

X-axis: TIME, hr

Legend:
A $X_{SO_3} = 0.0193$
B $X_{SO_3} = 0.0419$
Δ $X_{SO_3} = 0.1643$
x $X_{SO_3} = 0.2084$

CHAPTER III

CRITICAL PRESSURE MEASUREMENTS

The measurement of vapor pressures at relatively high temper-
ature is frequently difficult. When such measurements are made in the
critical temperature region and particularly on aqueous solutions the
difficulties are multiplied. When the solutions chosen are highly
corrosive the total problems involved have apparently resulted in very
limited, if any, experimental work.

In such cases the usual procedures for vapor pressure measure-
ments are unsatisfactory. For instance, the direct use of a mercury
piston is limited to cases where chemical reaction between mercury and
the system is negligible. Other fluid pressure transmitters, such as
organic oils, decompose in the higher temperature ranges. In addition,
under extreme conditions of temperature and pressure there are un-
certainties in volume and composition. Other fluids, such as sodium-
potassium alloys, require extensive equipment and safety precautions.
Simplicity in procedure has seemed impossible.

However, some pressure measurements have been made on enclosed
systems at high temperatures. Osborne, Stimson, Fiock, and Ginnings[150]
developed a method involving the displacement of a restrained diaphragm.
The measurements depended upon the visual observation of the effect of

pressure on a moveable diaphragm. The diaphragm was not included in the thermostated region of the system; therefore, it was not a 'system' in a thermodynamic sense and would be unsuitable for use with binary aqueous systems.

A relatively simple method for determining the pressure of isolated systems was independently developed by D. M. Richardson.[151] The method was used to measure unsaturated steam pressures in connection with volumetric water adsorption studies.[152] Modifications of this principle were made to permit the measurement of critical pressures in this work.

The current method involved the isolation of the aqueous system in a corrosion resistant container and the use of a special diaphragm to transmit pressure from the aqueous system to a pressure transmitting fluid isolated from the corrosive solution. Individual problems and their solution will be discussed as each part of the apparatus is described.

Apparatus

High Pressure Bomb

A container for the aqueous system was needed which would withstand high temperatures and pressures and not be corroded by sulfuric acid under such conditions. A special high pressure corrosion resistant bomb was constructed from stainless steels and platinum. Figures XXII and XXIII show sketches of the bomb.

The center section of the bomb was 4.000 inches long and was

A. THRUST BOLTS
B. THRUST RING
C. RETAINER PLATE
D. DIAPHRAGM
E. PLATINUM PLATE
F. PRESSURE CONNECTION
G. BLEED HOLE
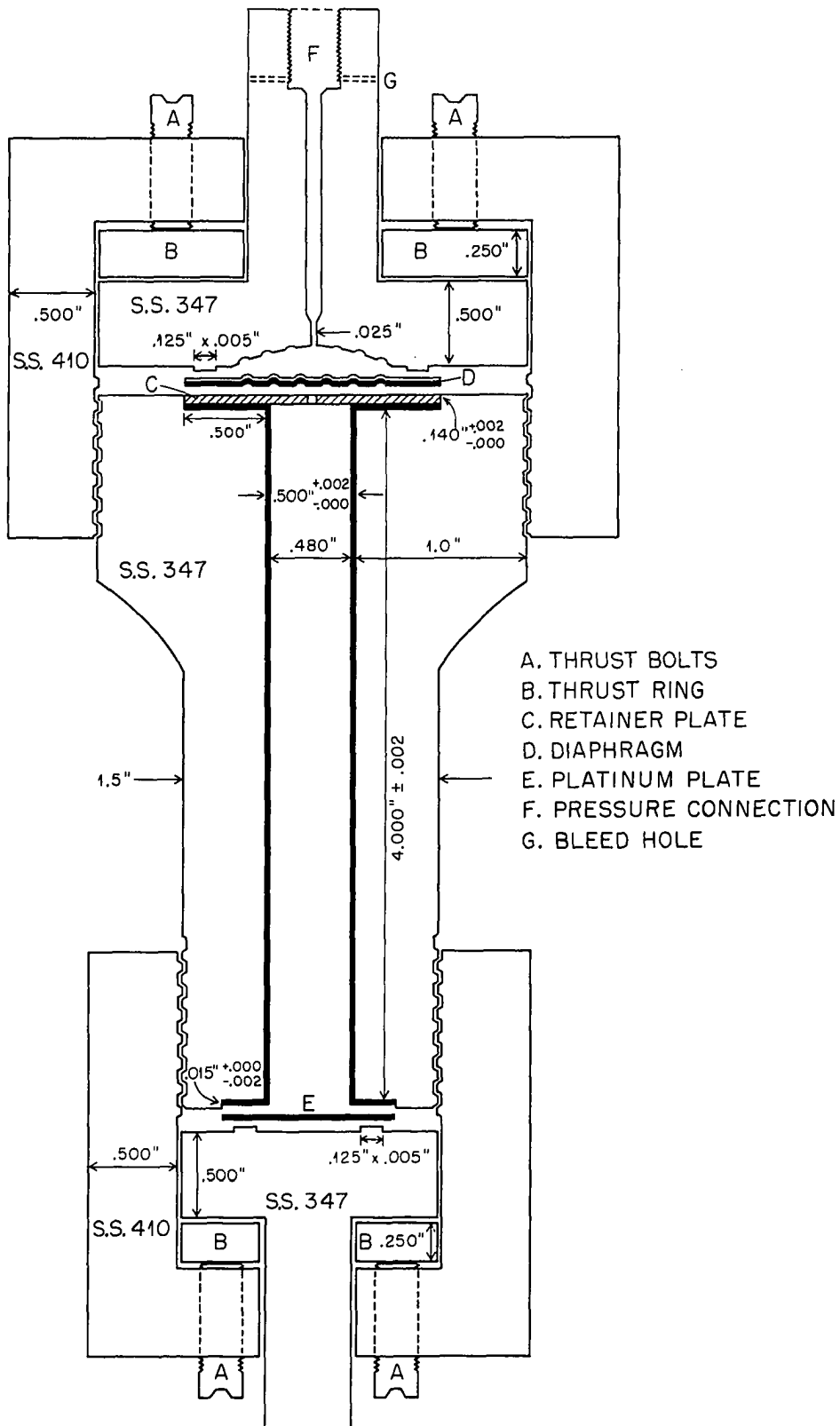
FIGURE XXII
HIGH PRESSURE BOMB

.500"

.480"

.500" O.D.

4.000"

.250"

PLATINUM
LINER
.010 Thickness

1.500 " +.000
      -.005

.005" S.S.347
.005" Platinum

BIMETALLIC
DIAPHRAGM

1.500 " +.000
      -.005

.125" Thickness
85% Platinum
15% Iridium

INNER
DIAPHRAGM
SUPPORT

6 Holes
.020" in Diameter

1.000 " +.000
      -.005

.010" Thickness

PLATINUM
CIRCULAR
PLATE
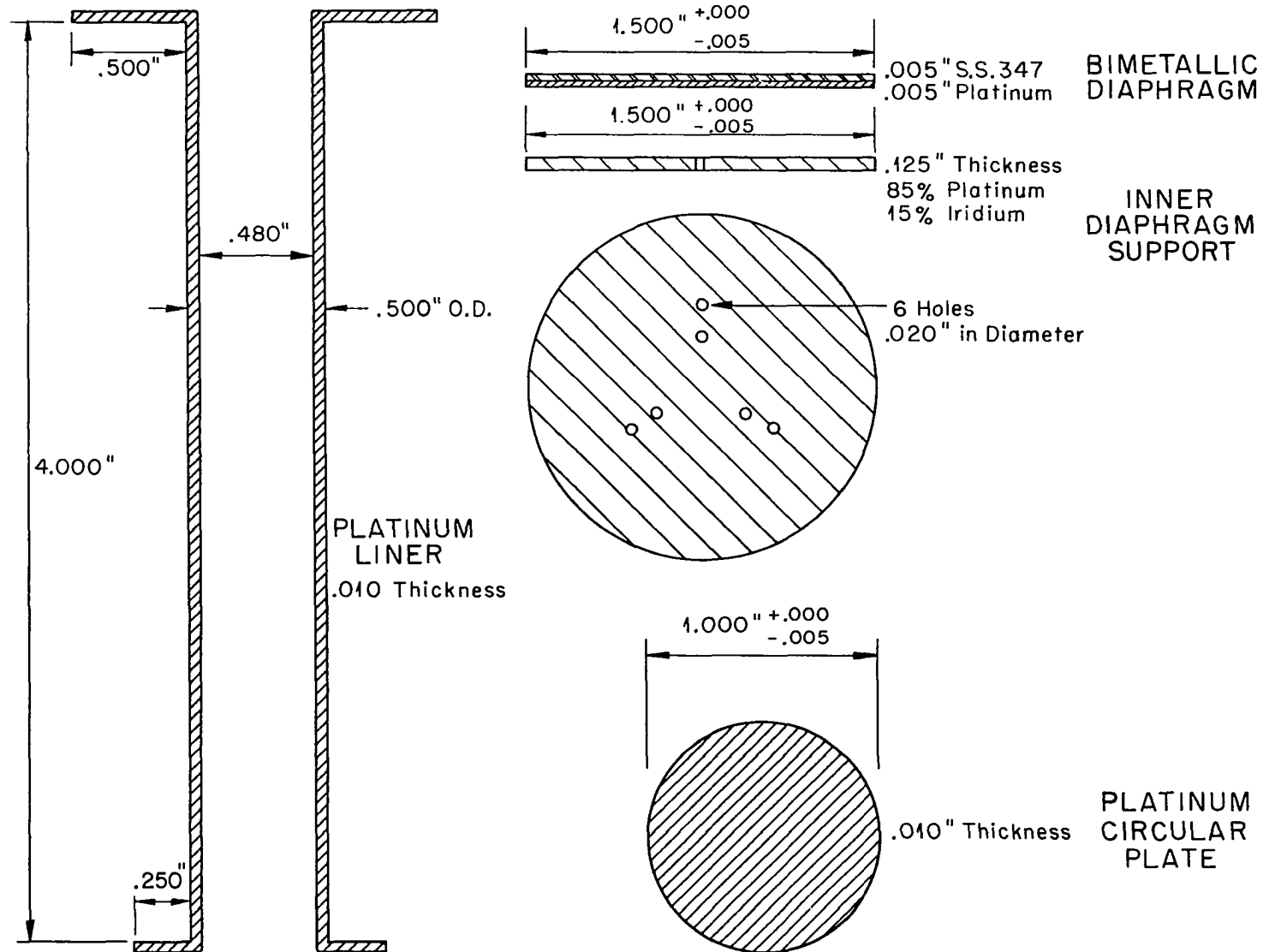
FIGURE XXIII

PLATINUM PARTS FOR HIGH PRESSURE BOMB

constructed from stainless steel type 347. It had an inside diameter of 0.500 inch and its wall dimensions gave sufficient strength for safe work at 33,000 psi. and temperatures of 650 °C. A 0.010 inch thick platinum liner was inserted inside the stainless steel container because of the rapid corrosion of stainless steel by sulfuric acid. The steel gave strength and the platinum liner gave the corrosive protection necessary.

The top of the center section was fitted with a retainer plate against which the diaphragm would rest when external pressure was applied in excess of the internal pressure of the aqueous system. The circular plate was 1.500 inches in diameter and 0.125 inch thick. It was rolled and machined from an 85% platinum-15% iridium alloy. Six small holes were drilled through the center to permit pressure transmission to the diaphragm. A platinum wire O-ring was positioned between the retainer plate and the platinum liner of the bomb. Pressure upon the plate was localized on the ring and formed a reliable seal.

The head and thrust ring for the bottom end of the bomb were machined from stainless steel type 347 while the cap was formed from stainless steel type 410. This use of two different stainless steels reduced the chance of binding of the threads during use. The use of acme threads further decreased the probability of binding. The cap screwed into place and the tightening of six thrust bolts against the thrust ring forced a circular 1.000 inch by 0.010 inch platinum disc against the platinum liner and effectively sealed the container while keeping only platinum exposed to the action of the liquid and vapor inside the bomb. The bomb was filled at this end because it could be

readily sealed and did not require removal of the diaphragm or resealing at the stainless steel interface.

Likewise, the thrust ring and head for the top of the bomb were machined from stainless steel type 347 and the cap from stainless steel type 410. The six bolts and thrust ring distributed force evenly to the 0.125 inch raised ring on the bomb head which formed the pressure point for sealing the platinum-iridium plate to the platinum side of the diaphragm and the bomb head to the stainless steel side of the diaphragm. The center of the bomb head was specially constructed so that the cup shape and grooves held the diaphragm in position. A 0.025 inch diameter hole connected the standard 0.250 inch autoclave high pressure fitting to the back side of the pressure transfer diaphragm. Figure XXIV shows a profile cut of the bomb head.

The diaphragm was cut from a bimetallic sheet of stainless steel type 347 and platinum. The sheet consisted of 0.005 inch stainless steel and 0.005 inch platinum bonded by the General Plate Division of Metals and Controls Corporation of Attleboro, Massachusetts. The fact that the system under investigation was sulfuric acid limited one side of the diaphragm to a non-corrosive metal such as platinum. The fact that the other side of the diaphragm was exposed to mercury at high temperatures and pressures limited its composition to stainless steel. Therefore, the diaphragm had to be constructed of two well bonded metals.

A die machined under the same specifications as the bomb head was used to stamp three concentric corrugations into the diaphragm. The specifications for the die corresponded to those for the head of the

DEPTH OF CUT
(inches)

RADIAL DISTANCE
FROM CENTER
(inches)

.6875

$\frac{1}{2}$ "

$\frac{1}{8}$ "

.5625

.000

.002   .4375

BOMB HEAD   .004
S.S. 347 $\frac{1}{8}$ "

.007   .3125

$\frac{1}{8}$ "   .012

.019   .1875

.024

$\frac{3}{16}$ "   .028

.03125   0.0000

No.72 Hole   .028

$\frac{3}{16}$ "   .024

.019   .1875

.012

$\frac{1}{8}$ "   .007   .3125

BOMB HEAD   .004
S.S. 347 $\frac{1}{8}$ "

.002   .4375

.000

.5625

$\frac{1}{8}$ "

.6875

$\frac{1}{2}$ "
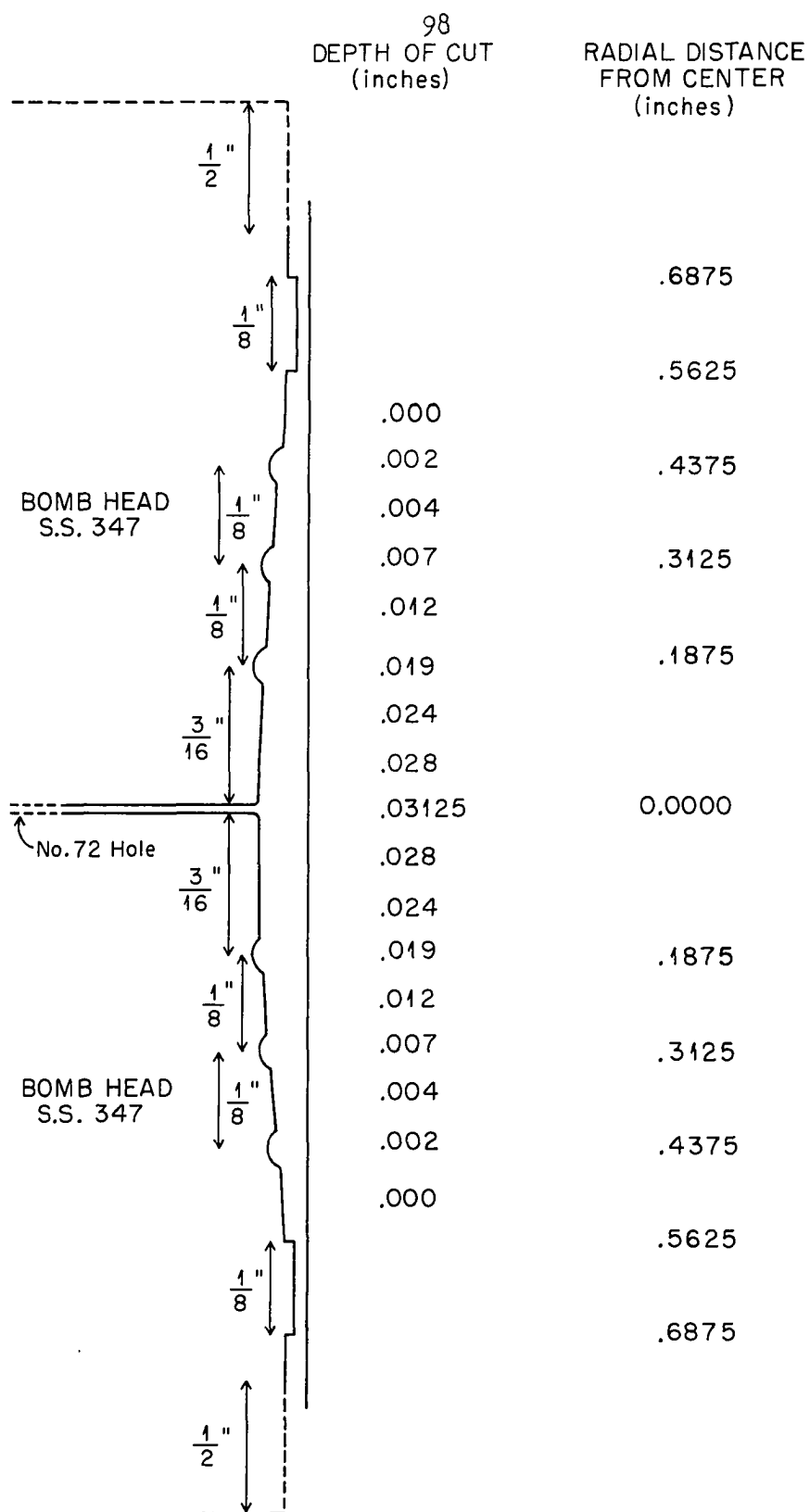
FIGURE XXIV
DIAPHRAGM SUPPORT PROFILE

bomb and will be found in Table XXIII. The corrugations reduced stress localization and prevented non-uniform diaphragm displacement and 'cricket' snapping sharply from concave to convex. This tendency was further minimized by use of a flat retainer wall on one side of the diaphragm. As a result, there was smooth displacement of the diaphragm between its limiting boundaries.

In principle, the flexible diaphragm could move freely from one restraining surface to the other. With the internal system at a given temperature the vapor pressure of the system would hold the diaphragm positioned in the head of the bomb. The volume of the mercury system backing up the diaphragm could be decreased by small increments. This would result in small increments of pressure increase on the outer side of the diaphragm. When the external pressure became infinitesimally greater than the internal pressure the diaphragm would begin to move. With further attempts to decrease the volume of the mercury system the pressure would remain the same but the diaphragm would move toward the inner retainer wall. When it came to rest against the fixed surface the pressure of the mercury system would again rise rapidly as its volume was decreased by increments. Thus, with an ideal diaphragm, the pressure of the enclosed system would be indicated by the pressure plateau of the external system.

In actual practice a level plateau was not realized. The spring constant of a practical diaphragm caused some tilting of the plateau. However, the increment increase in external pressure was very small when the diaphragm was free to move as compared to the increase

TABLE XXIII

DIAPHRAGM SUPPORT PROFILE

(Stepwise cuts to obtain smooth surface upon emery polishing)

Radial Distance from Center Inches	Depth of cut Inches
0 to 1/16	0.03125
1/16 to 1/8	0.028
1/8 to 3/16	0.024
3/16 to 1/4	0.019
1/4 to 5/16	0.012
5/16 to 3/8	0.007
3/8 to 7/16	0.004
7/16 to 1/2	0.002
1/2 to edge of flange	0.000

Diaphragm Support Corrugations

1/32-inch diameter grooves, 1/64-inch deep,

concentric at radii of 3/16 , 5/16 , and 7/16 inch.

when it was in either of the two fixed positions.

In practical use consideration had to be given to the decrease in volume of the enclosed system as the diaphragm moved inward. Since the diaphragm displacement volume was extremely small compared to the total volume of the internal system, no significant limitation in accuracy was imposed by this effect.

Pressure Equipment

The reverse side of the diaphragm was exposed to pressure from the external mercury system through a small hole from the back side of the diaphragm through the head of the bomb to a standard autoclave high pressure fitting. This fitting connected the bomb to the external system by means of a stainless steel capillary tube. Figure XXV shows schematically the external pressure system.

All tubing in the system, other than the capillary connection to the bomb, was one-quarter inch stainless steel type 347. This was capable of withstanding pressures in excess of 30,000 psi. All connections, valves, crosses, tees, and fittings, were standard high pressure equipment from Autoclave Engineers, Inc.

The mercury reservoir was a standard high pressure bomb that had been fitted with an additional opening at the bottom. Provision was made for placing the external system under an initial pressure of 1200 psi. by admitting a compressed gas such as nitrogen to the top of the reservoir. With a highly compressible transmitting agent it might be necessary to use an initial boost in pressure, but such was not the case when compressing mercury.
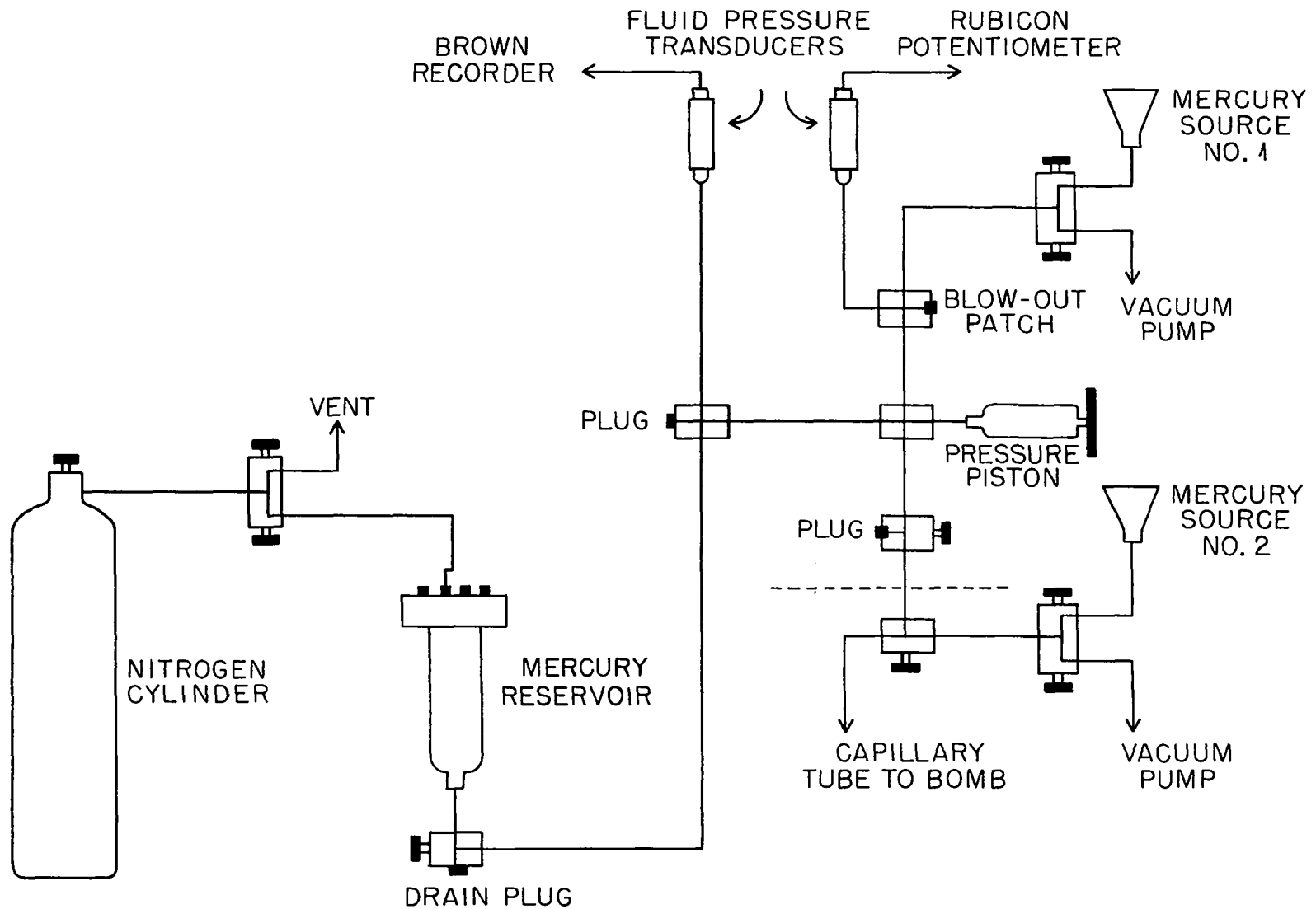
FIGURE XXV
SCHEMATIC DIAGRAM OF PRESSURE SYSTEM

The small increments of volume reduction necessary to increase
the pressure were obtained by using a pressure generator made by the
High Pressure Equipment Co. of Erie, Pennsylvania. Figure XXVI pictures
the design of the generator. The total displacement capacity of the
generator was 7.5 cc. and required 14.5 revolutions of the generator
handle. Therefore, the volume reduction of the mercury could be con-
trolled by controlling the number of revolutions. With a slightly
compressible substance only a small volume displacement was needed to
give a substantial increase in pressure.

Thus, an accurate way of measuring the volume reduction was
needed. This was accomplished by mounting a mirror behind the generator
handle and a clear plastic protractor in front of the mirror. The
operator could view the image of the handle in the mirror and read its
position on the protractor to $\pm 1^{\circ}$ of arc.

Pressure was always applied in increments corresponding to a
10° rotation on the generator handle. This represented approximately
50 psi. pressure change on a closed and immovable system. However, when
connected to the diaphragm this increase would drop to one or two psi.
per 10° of rotation when the diaphragm was moving.

The actual pressure on the external system was measured by
Baldwin SR-4 pressure transducers in two ways. One Baldwin cell in the
system sent its potential to a Brown recorder which continuously recorded
the pressure. The recorder was constructed with five 1000 psi. scales
so that more accurate readings could be recorded from 0 to 5000 psi.
The output from the other Baldwin cell was determined by a Rubicon

I C.

WORKING PRESSURE 20,000 psi
CAPACITY 7 $\frac{1}{2}$ cc

10"

1"

1"

"O" RING PRP-902

2 HOLES $\frac{13}{32}$" DRILL

"O" RING - PRP - 902 - 14

STROKE LENGTH 3"

$\frac{SS}{316}$

$\frac{7}{16}$"

F-H4

8"
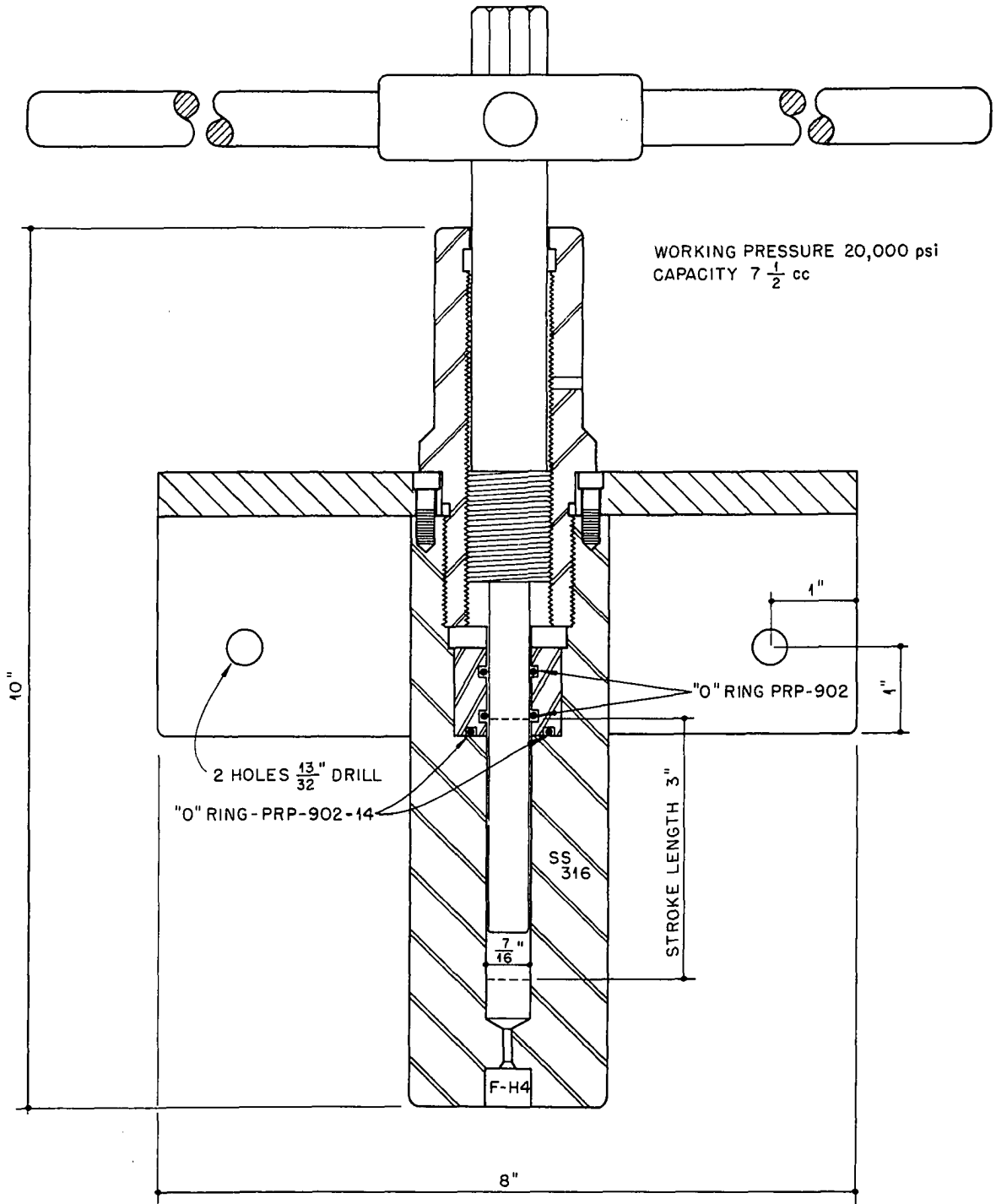
FIGURE XXVI
PRESSURE GENERATOR ASSEMBLY

potentiometer and was used for all pressure readings as recorded in the experimental data.

Since the Baldwin cells were limited to 5000 psi. a safety blowout patch was introduced into the external system to prevent possible damage to the Baldwin cells.

After the assembly of the external pressure system, a vacuum pump was connected to evacuate the lines for twenty-four hours. After evacuation the valve connecting the system with mercury source No. 1 (Figure XXV) was opened. This permitted mercury to enter and fill the system completely. The valve was closed and the rapid increase in pressure caused by a slight displacement of the pressure generator handle indicated the system was full of mercury with very little, if any, air trapped in the lines.

To prevent the delay caused by refilling the external system with mercury each time the capillary tube to the bomb was disconnected, a portion of the system was arranged so that it could be isolated from the major part of the system. The dotted line in Figure XXV shows how one valve could isolate most of the mercury system from the capillary tube connection. When it was necessary to disconnect the capillary line the vacuum pump was attached to this portion and the mercury was drawn off into a mercury trap. When it was desirable to refill this portion mercury from source No. 2 was introduced into the evacuated lines. Upon opening only one valve the whole system was again connected.

Furnace

Several problems arose concerning the method of heating the bomb. It was desirable to have as uniform heating as possible since no thermocouple wells could be placed inside the bomb because of the corrosive nature of the acid solution and the necessity of a platinum lining. Probably the best way to have obtained uniform heating would have been to use a large metal heating block which would have distributed heat evenly. The material and construction of such a block presented difficulties. Aluminum would melt before the maximum temperatures were obtained and copper was subject to rapid oxidation at high temperatures. Silver would have given good conductance but the expense was prohibitive. Materials stable at high temperatures were found, in general, to be very poor heat conductors. The odd shape of the bomb would have made it necessary to break any heating block into parts before fitting around the bomb. This would have meant air gaps and combined with available metals which were poor heat conductors, no advantages would have been gained over a standard air furnace. The matter of induction heating was also considered but was undesirable because of the lack of temperature control, particularly in the lower temperature ranges. The final solution appeared to be an air furnace large enough for the bomb and constructed so that it could be regulated to give equal temperatures throughout the area of the bomb.

A modified air furnace was constructed by the Marshall Products Co. of Columbus, Ohio, according to their regular specifications but with dimensions that would accomodate our bomb. The furnace was fifteen

inches long with twelve inch outside diameter and five inch inside diameter. It operated on 110 volts to a maximum temperature of 1000 °C. There were ten binding posts provided on the furnace shunt panel to permit localized control of temperature. By the use of shunts the temperature of that portion of the furnace located between any two of the binding posts could be varied considerably. Therefore, it was possible to attain temperature uniformity along the length of the furnace.

The furnace was placed on a platform of fire brick and the bottom packed firmly with a layer of Fibroflax thermal insulation (fibrous aluminum silicate) and asbestos cloth to prevent air drafts up the furnace. The bomb was positioned in the center of the furnace on a stainless steel rack. Two 0.125 inch stainless steel semi-circular plates and 2.0 inch semi-circular fire brick were placed on top of the rack to close the top of the furnace. Fibroflax insulation was firmly packed in all openings and a heavy layer placed over the furnace top.

Numerous calibrated thermocouples placed in various positions in the furnace were used to measure temperature gradients. Approximately a four degree gradient was noted between the extreme ends of the bomb rack. The temperature variation over the center section of the bomb was about one degree. However, the temperature variation inside the sealed bomb was considerably less. The temperature variation at the center of the bomb cavity over periods of fifteen minutes was about 0.05 °C. This was the limit of accuracy of the temperature measurement.

Instrumentation

The furnace temperature was controlled by regulating the applied voltage. This was done by two twenty ampere variacs operating on 115 volt alternating current. One variac was used to supply the major portion of the current for 'base heat'. The second supplied additional current through an 18:1 stepdown transformer for the 'control heat'.

When a given furnace temperature was required the 'base heat' variac supplied current sufficient to hold the temperature ten or fifteen degrees below the desired reading. The 'control heat' variac then added sufficient current for the remaining few degrees. This current was controlled by the on-off action of an Adlake mercury relay.

The relay, in turn, was activated by a modified Electron-O-Therm. A Sola constant voltage transformer supplied power to the Electron-O-Therm which in normal operation is a bridge operated instrument using a Wheatstone bridge with a resistance thermometer in one arm. A modification, indicated in Figure XXVII, was made by installing an auxillary Wheatstone bridge having a controller in one arm and a resistance thermometer in one arm. The signal from this bridge was amplified in the Electron-O-Therm and the current output sent through a mercury relay coil. However, the plunger in this relay was removed and a one ohm resistor placed in series with the remaining coil. The voltage across this resistor was then amplified and used to operate a Pyr-O-Vane. The Pry-O-Vane was a d'Arsonval millivolt vane-type controller which measured the voltage across the one ohm resistor, amplified the signal, and operated the mercury relay controlling the heater power. Experimentation showed

20a VARIAC "BASE HEAT"

18:1 STEP DOWN TRANS.

115 v a-c

TO FURNACE

T.C. FROM FURNACE

BROWN CIRCULAR CHART RECORDER-CONTROLLER 0-800°C I.C.

115 v a-c

ADLAKE RELAY "ALARM"

20a VARIAC "CONTROL HEAT"

115 v a-c

SOLA CONSTANT VOLTAGE TRANS.

MODIFIED ELECTRON-O-THERM CONTROLLER

BROWN PYR-O-VANE CONTROLLER

115 v a-c

ADLAKE RELAY "CONTROL"

65 Ω

1300 Ω

500 Ω

1100 Ω

"FURNACE TEMP. CONTROL POINT ADJ."

Pt. RESISTANCE THERM.

FIGURE XXVII

SCHEMATIC DIAGRAM OF INSTRUMENTATION

PART 1

109

that the use of the Pyr-0-Vane in place of the regular mercury relay in the Electron-0-Therm gave increased sensitivity and smoother control action.

One arm of the auxillary bridge consisted of a platinum resistance thermometer made by winding very fine platinum wire on insulated spools and encasing in platinum. The control thermometer entered the top of the furnace through a hole in the fire brick and stainless steel plate. The other arm contained a series of resistors which could be adjusted for furnace temperature control.

The furnace temperature was recorded continually on a Brown circular chart recorder. The 0 ° - 800 ° C. recorder operated on an iron-constantan thermocouple. The recorder also acted as a controller through the use of an Adlake relay 'alarm'. This mercury relay could be adjusted to break the circuit suppling all current to the furnace if any specified temperature were exceeded. This acted as a safety control on the 'base heat' as well as a secondary safety control on the 'control heat'.

Other temperature measurements were made with four platinum-platinum (10% rhodium) thermocouples positioned at various points in the furnace. The thermocouples went directly to copper lead wire in an oil bath immersed in an ice-water bath. All lead wires were united through a Leeds and Northrup thermocouple switch to a common copper lead connected to the Rubicon Type B potentiometer. A Weston standard cell, four No. 6 dry cells, and a Leeds and Northrup Type 2430 galvanometer were auxillary equipment with the potentiometer. Figure XXVIII shows a schematic diagram.
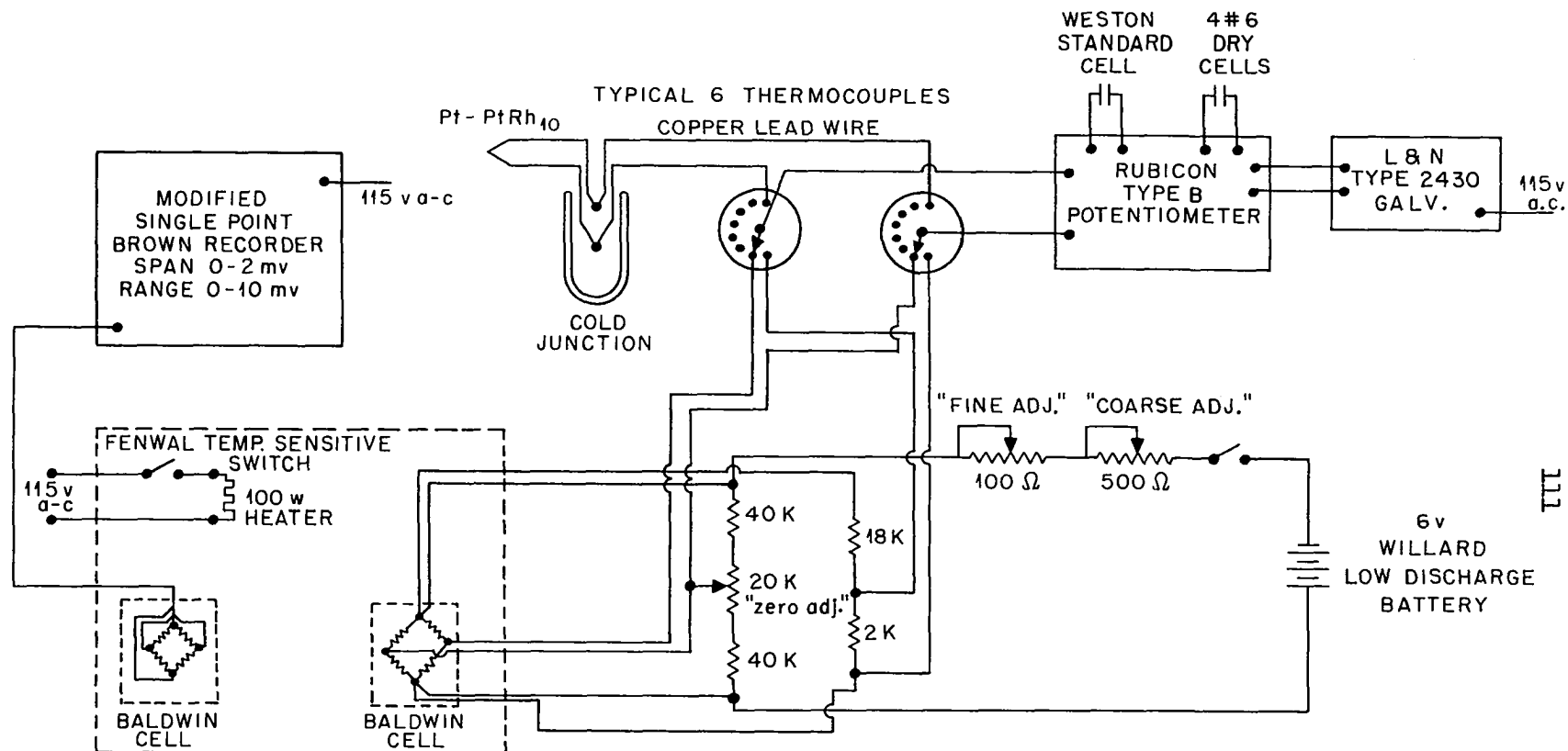
FIGURE XXVIII
SCHEMATIC DIAGRAM OF INSTRUMENTATION
PART 2

The pressure measuring instrumentation is also indicated in Figure XXVIII. The two Baldwin cells used for measuring pressures were enclosed in a metal case which was equipped for temperature control. A 100 watt heater was regulated by a Fenwal Thermoswitch which, with good circulation due to a small rotary fan, held the temperature fluctuation to about one degree. One Baldwin cell activated a single point Brown recorder modified to include the voltage supply for the Baldwin cell. A range stepping switch and circuit were installed to permit recording of zero to ten millivolts in two millivolt steps. This allowed continuous recording of pressures from 0 to 5000 psi. with each 1000 psi. units recording over the full pressure scale. Input voltage to the other Baldwin cell was supplied by a six volt Willard low discharge battery. Coarse and fine adjustments permitted control of the input voltage to the exact value desired. Adjustments were also possible on the voltage output for zero pressure. Both input to and output from this cell were measured on the Rubicon potentiometer. Pressure measurements were recorded to the nearest unit psi. with a precision of $\pm$ 0.5 psi. The Baldwin cells were guaranteed to $\pm$ 5.0 psi. but experience has shown them to be considerably better.

Bomb Modifications

During initial calibration runs with water certain difficulties arose which resulted in some modifications to the bomb. The trouble resulted from the bomb design which called for sealing two platinum surfaces and two stainless steel surfaces at the same pressure point. Thus, a very soft material and a reasonably hard material required

sealing under a common pressure. No trouble was experienced in making platinum-to-platinum seals but leaks did develop around the steel-to-steel seal behind the diaphragm. This allowed mercury to escape and penetrate under the edge of the platinum diaphragm.

After cooling and opening of the bomb, examination showed mercury had apparently amalgamated with the platinum. The outside edge of the platinum side of the diaphragm and the platinum-iridium plate were black and rough in appearance. Further examination showed mercury inside the bomb on the underneath side of the platinum-iridium plate. However, the plate was not black and it was thought this mercury entered when the bomb was opened at room temperature.

The entire platinum lined section of the bomb was then treated to remove the excess mercury and to determine the damage due to amalgamation. The bomb was first sealed in a pyrex glass container and heated under a high vacuum for 12.5 hours at 190 °C. This was done to remove excess mercury without further amalgamation since mercury and platinum do not react at lower temperatures.[153] Mercury was collected in the cold trap during this initial heating. The temperature was increased to 350 °C. for 7 hours and then to 450 °C. for 13 hours. The bomb was held under vacuum until room temperature was reached.

Examination of the platinum-iridium plate showed definite attack around the edges where mercury had reached the platinum while at 350 °C. Microscopic examination showed a cracked spongy looking surface. However, the underneath side of the plate appeared to be damaged in no way. The plate was cut down and polished to remove the damaged surface

and a new platinum liner was made since the original liner was damaged

in removing the retainer plate.

Certain modifications were made in the bomb head to prevent a

recurrence of this trouble. These appear in Figure XXIX. The bomb head

was cut down to allow more clearance around the edge to insure that all

pressure from the thrust bolts was concentrated at the sealing surface.

The previously flat sealing surface was machined into an arc and a

negative bite cut into the arc to effect better sealing. A cut was

made on the edge of the bomb head to permit welding of the diaphragm in

position. This insured exact positioning of the diaphragm and retained

any mercury that might leak under the steel to steel seal. To prevent

pressure build up on the weld, a small bleed hole was drilled to permit

the escape of mercury should a leak occur. The one-quarter inch thrust

bolts were replaced with three-eights inch bolts.

Figure XXX shows a photograph of the outside of the high

pressure cell, Figure XXXI shows a closer view of the instrumentation,

and Figure XXXII shows the external pressure system, furnace, bomb, and

instrumentation on the inside of the high pressure cell.

Experimental Data

Calibration of Baldwin SR-4 Pressure Transducers

The first step in the experimental work was the calibration

of the Baldwin cells. One cell was calibrated with the Brown recorder

as the instrument was standardized. The other cell, whose output was

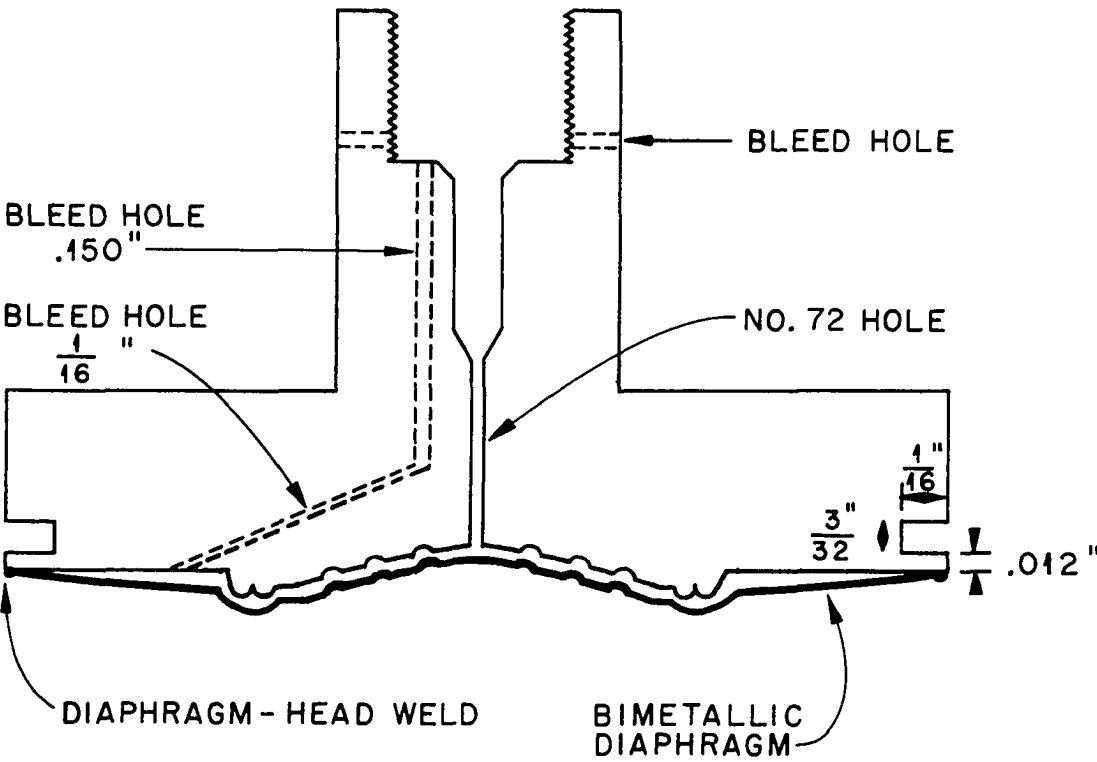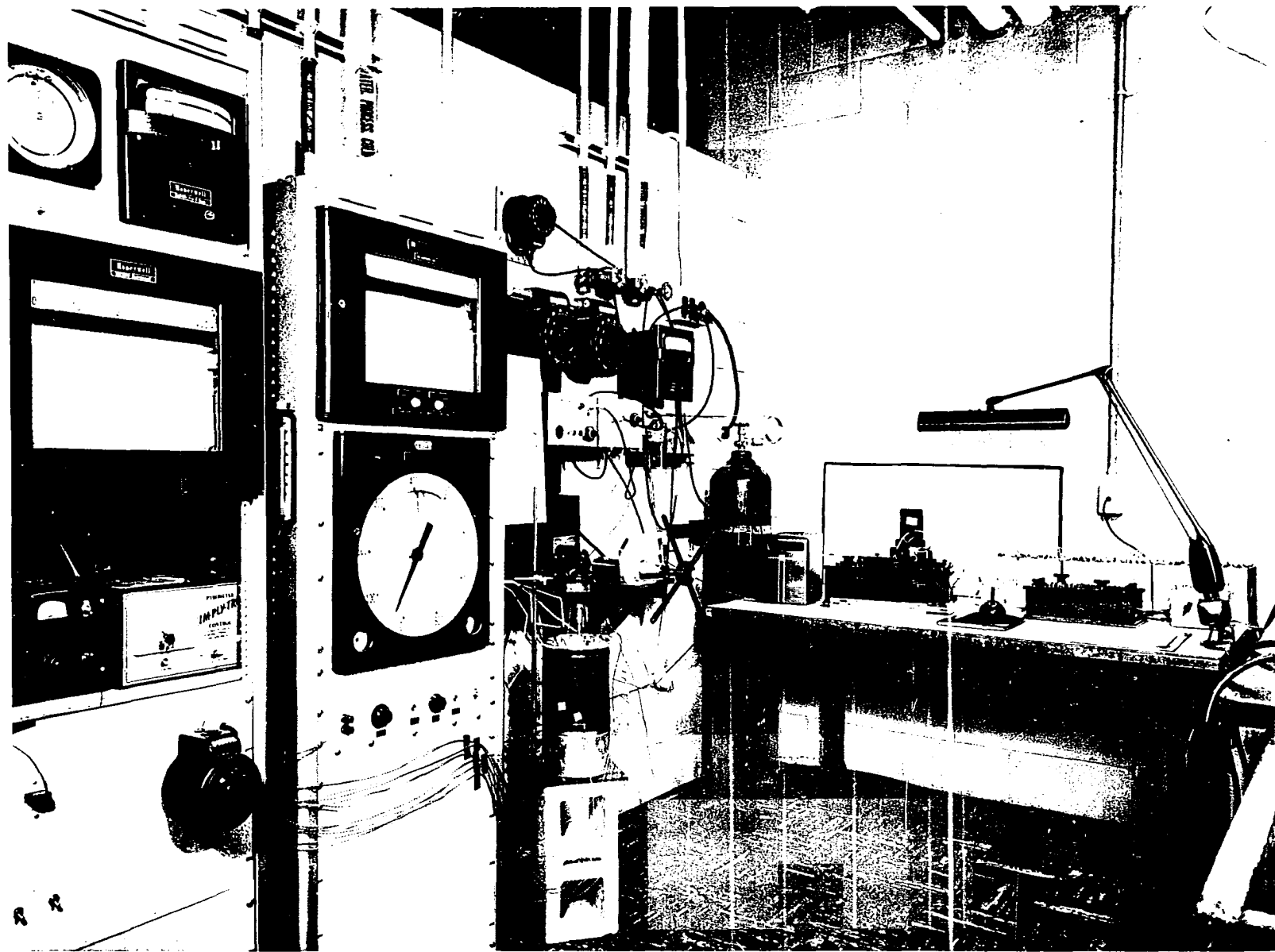measured by the Rubicon potentiometer, was connected to the external

FIGURE XXIX
BOMB HEAD MODIFICATIONS

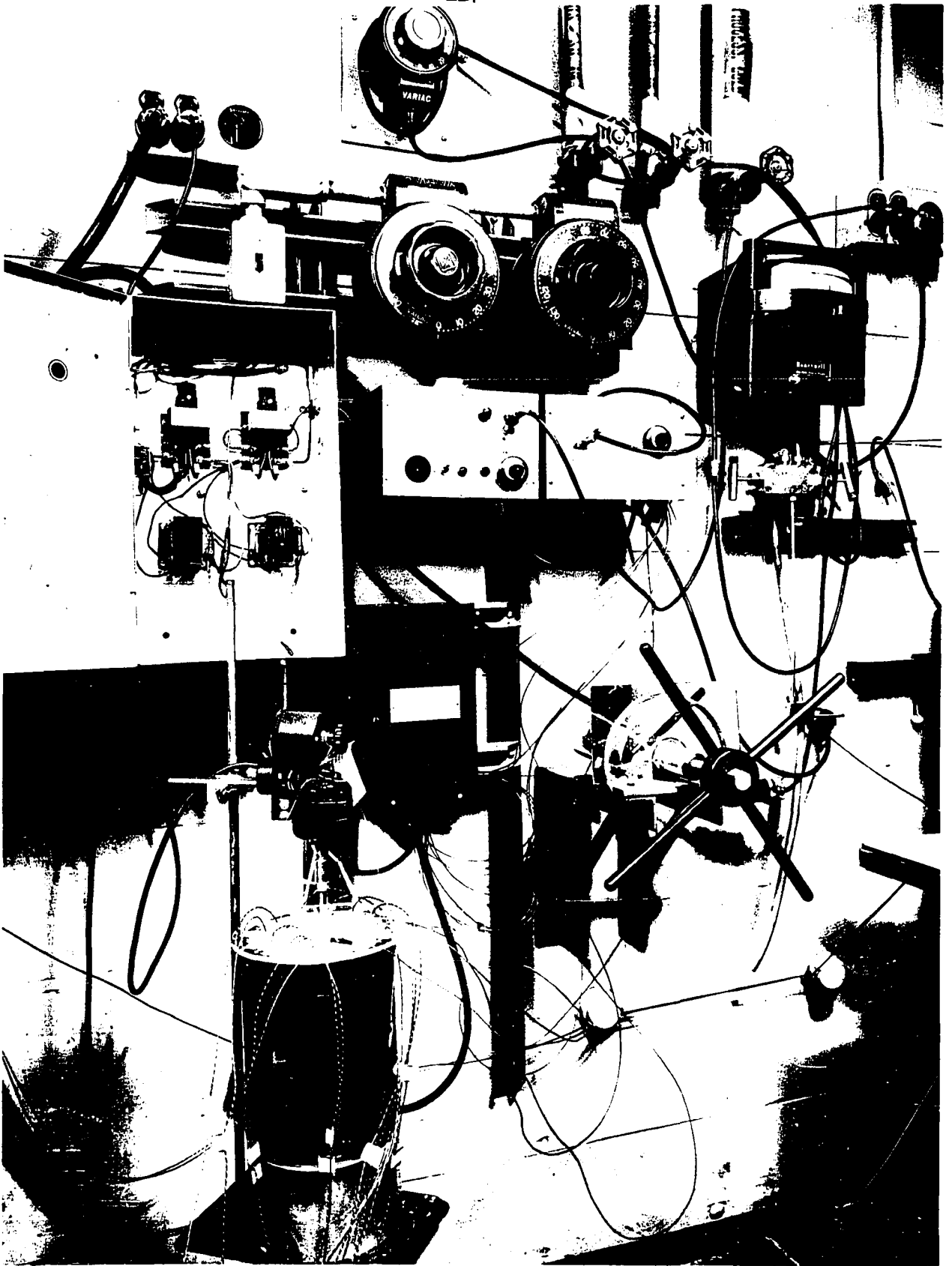FIGURE XXX
HIGH PRESSURE CELL - EXTERIOR

FIGURE XXXI
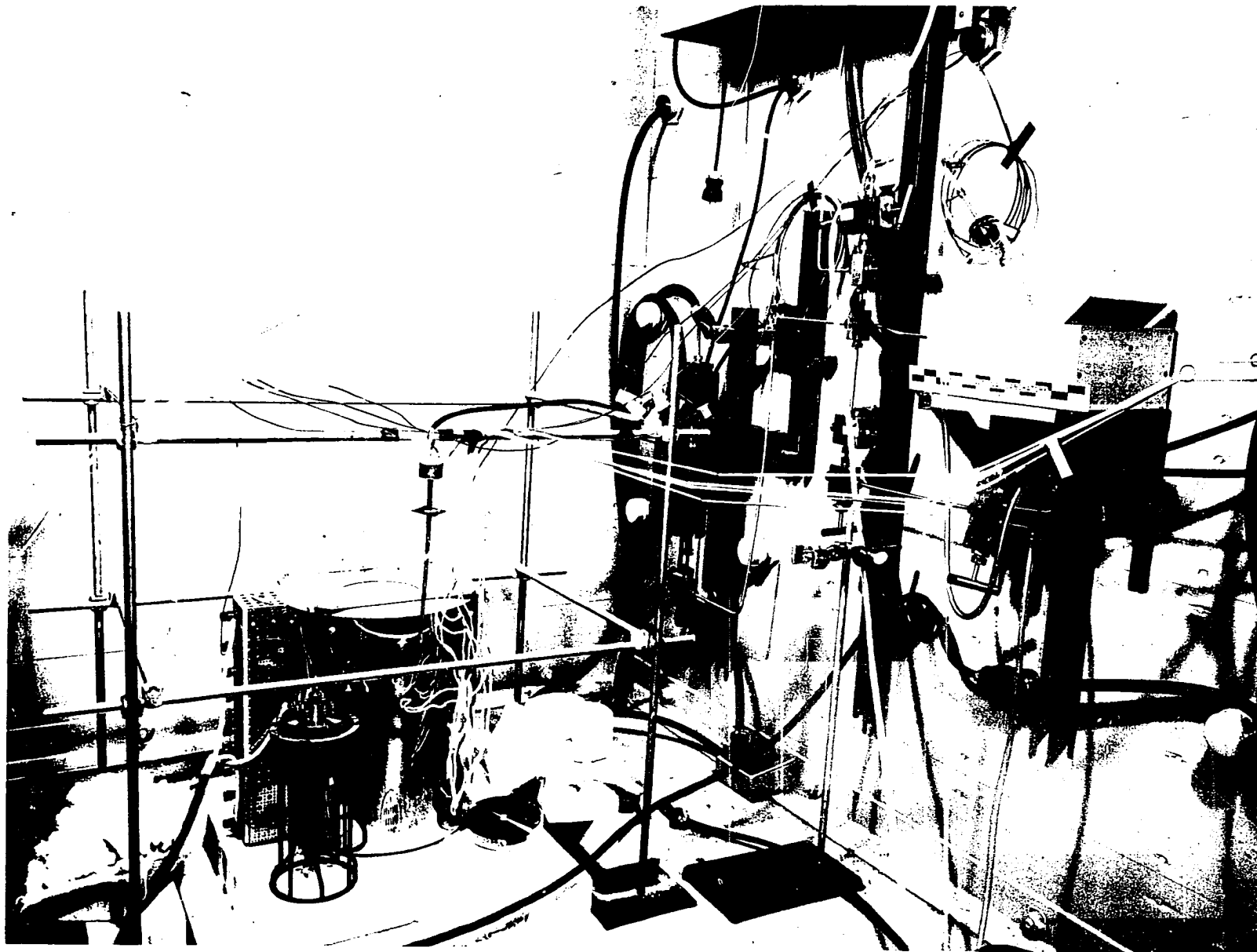HIGH PRESSURE CELL - INSTRUMENTATION

FIGURE XXXII
HIGH PRESSURE CELL - INTERIOR

pressure system and was calibrated in place just as it was to be used.

The calibration was made with a Dead Weight Gage using mercury and oil as pressure transmitting agents. The Dead Weight Gage was connected to the top of a ten milliliter standard high pressure bomb equipped with pressure fittings at each end. The bottom end of the bomb was connected by capillary tubing to the external mercury system at the same point as the platinum lined bomb when in use. The ten milliliter bomb held the interface between the oil of the Dead Weight Gage and the mercury of the external pressure system.

The connection of the Dead Weight Gage at this point during the calibration of the Baldwin cell eliminated the necessity of making pressure corrections for the weight of the mercury in the external system or for other errors which might arise from the nature of the system itself.

The calibration runs revealed that a very good Baldwin cell had been installed. Table XXIV shows the reproducibility of the cell at various pressures. Two checks were made under increasing pressure and two under decreasing pressure. It should be pointed out that the second column indicates greater reproducibility than the first. This is probably due to the increased sensitivity of the cell which usually results from the first few minutes of cell use.

Table XXV shows the hysteresis effect evident during standardization. The effect is not serious but is of sufficient magnitude to warrant the use of different calibration curves with increasing and decreasing pressures. Note again the apparent increase in sensitivity of the cell with use.

TABLE XXIV

REPRODUCIBILITY IN BALDWIN CELL READINGS

Applied Pressure from Dead Weight Gage psi.	Reproducibility*	
	Increasing Pressure	Decreasing Pressure
0 psi.		
500	0.20 %	0.09 %
1000	0.14	0.07
1500	0.09	0.03
2000	0.06	0.05
2500	0.02	0.03
2750	0.06	0.02
3000	0.08	0.04
3250	0.06	0.02
3500	0.08	0.02
3750	0.05	0.05
4000	0.09	0.04
4250	0.09	0.00
4500	0.06	0.00
4750	0.05	0.01
5000	0.04	0.02

*Reproducibility: Difference between the millivolt readings of two consecutive calibration runs expressed as per cent of the full scale millivolt value.

TABLE XXV

HYSTERESIS EFFECT IN BALDWIN CELL READINGS

Applied Pressure from Dead Weight Gage psi.	Hysteresis*	
	Run 1	Run 2
0 psi		
500	0.11 %	0.22 %
1000	0.11	0.18
1500	0.16	0.22
2000	0.19	0.20
2500	0.24	0.19
2750	0.24	0.16
3000	0.28	0.16
3250	0.24	0.16
3500	0.23	0.13
3750	0.22	0.12
4000	0.21	0.08
4250	0.18	0.09
4500	0.13	0.07
4750	0.09	0.03
5000	0.03	0.01

*Hysteresis: The difference beween the millivolt reading measured with increasing pressure and with decreasing, expressed as per cent of the full scale millivolt value.

Determination of Pressure-Temperature Isochore of Water

The second step in the experimental work was to investigate the characteristics of the pressure measuring apparatus and to determine how well pressure measurements of a well defined system could be reproduced. Since we were interested in the two-component system sulfur trioxide-water, it was natural to use one of these components in calibration runs. Water was the choice because the pressures involved near the critical temperature were in the pressure range expected for the two-component system and the pressure-temperature isochore for water had been well established by Keenan and Keyes.[154]

The preparation of the bomb for pressure measurements began with the positioning of the diaphragm in the bomb head and the sealing of the top end of the bomb. The diaphragm was positioned by hand in the depression in the bomb head and the head placed on the center section of the bomb. The cap was lowered slowly over the head and screwed down until firm. There was doubt as to whether or not the diaphragm remained properly positioned during this operation but there was no way to determine its position after the cap was in place. The thrust bolts were tightened in a symmetrical pattern with a torque wrench to assure even pressure through the thrust ring to the sealing surface.

The bomb was then inverted and a sample of highly purified water added through the bottom opening. The water used was first distilled from a potassium permanganate solution to remove organic material and then from a phosphoric acid solution to remove traces of ammonia. The vapor was condensed in a platinum lined condenser and was

collected in a carbon dioxide free atmosphere. A specific volume of water, based on the calculated volume of the bomb, was added so that the liquid fraction filling was 0.32 at room temperature.

A platinum disc was placed over the bomb opening and the head held firmly against the disc. The cap was screwed in place carefully to prevent the disc from vibrating out of position. A torque wrench was used again to apply torque to the thrust bolts in a symmetrical and even manner.

The bomb was then placed in the furnace and the capillary connection made between the bomb and the external pressure system. Thermocouples and the resistance thermometer were positioned and the furnace closed. After filling the capillary line with mercury as previously described, the furnace was brought to the desired temperature over a twenty-four hour period. The temperature controller was then adjusted to the desired setting and sufficient time allowed for temperature equilibrium to be established. It was apparent from the data collected that the final few degrees of temperature adjustment could be made in two hours.

When equilibrium had been attained, the following procedure was employed in making measurements. Four consecutive temperature readings were recorded as the Pyr-O-Vane controller went through two on-off cycles. The numerical average was recorded as the temperature of the system. Although there was some temperature fluctuation on the outside of the bomb, there was apparently very little fluctuation inside the bomb during the time required to make measurements. If there had

been a temperature variation inside, random scattering of pressures
would have been observed as the pressure is very sensitive to temperature
change in this region. Nevertheless, in all probability there was a
slight temperature gradient between the outside and inside of the bomb.
A correction for this was not applied to the temperature reading but was
incorporated with a correction factor for the pressure reading.

Next, the input voltage to the Baldwin cell was adjusted to
exactly 5.0000 volts and the output voltage for zero pressure was
adjusted to the same value as that used during calibration of the Baldwin
cell. The mercury piston handle was then turned to decrease the volume
of the mercury system and increase the pressure to a point about 200 psi.
below the known pressure of water at the regulated temperature. A
pressure reading was taken on the Rubicon potentiometer and the handle
of the piston turned an additional 10 $^\circ$ of arc. Another millivolt reading
was taken and the process repeated until the pressure had increased about
400 psi. over the original reading. The temperature was rechecked to
see that no significant change had occurred. The complete experimental
procedure required approximately thirty minutes. Typical data recorded
on two experiments are tabulated in Tables XXVI and XXVII.

The millivolt pressure readings were converted to psi. values
and were plotted as a function of the volume reduction of the mercury
system as shown in Figures XXXIII and XXXIV. The break in the curves
was not horizontal, as expected for an ideal system, but had a slight
positive slope. However, the break was very definite and indicated the
diaphragm was moving as the external pressure slightly exceeded the

TABLE XXVI

DATA FOR PRESSURE MEASUREMENT NO. 1-2

Temperature Readings

Pyr-O-Vane on	346.27 °C.
Pyr-O-Vane off	346.54
Pyr-O-Vane on	345.96
Pyr-O-Vane off	346.32
Average Temperature	346.27 °C.

Pressure Readings

Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	2.2040	2084 psi.	17	2.3985	2279 psi.
2	2.2490	2129	18	2.4010	2281
3	2.2920	2172	19	2.4035	2284
4	2.3265	2206	20	2.4060	2286
5	2.3450	2225	21	2.4085	2289
6	2.3600	2240	22	2.4105	2291
7	2.3705	2251	23	2.4130	2293
8	2.3755	2256	24	2.4150	2295
9	2.3790	2259	25	2.4175	2298
10	2.3830	2263	26	2.4230	2303
11	2.3850	2265	27	2.4310	2311
12	2.3870	2267	28	2.4405	2321
13	2.3895	2270	29	2.4510	2331
14	2.3920	2272	30	2.4645	2345
15	2.3940	2274	31	2.4855	2366
16	2.3960	2276	32	2.5230	2403

TABLE XXVII

DATA FOR PRESSURE MEASUREMENT NO. 1-3

Temperature Readings

Pyr-O-Vane off	349.43 °C.
Pyr-O-Vane on	348.91
Pyr-O-Vane off	349.33
Pyr-O-Vane on	349.01
Average temperature	349.17 °C.

Pressure Readings

| Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	2.2120	2092 psi.	18	2.4785	2359 psi.
2	2.2575	2137	19	2.4805	2361
3	2.3035	2183	20	2.4840	2364
4	2.3535	2233	21	2.4865	2367
5	2.3980	2278	22	2.4890	2369
6	2.4225	2303	23	2.4900	2370
7	2.4390	2319	24	2.4925	2373
8	2.4500	2330	25	2.4950	2375
9	2.4545	2335	26	2.4980	2378
10	2.4590	2339	27	2.5030	2383
11	2.4615	2342	28	2.5120	2392
12	2.4635	2344	29	2.5230	2403
13	2.4665	2347	30	2.5330	2413
14	2.4700	2350	31	2.5450	2425
15	2.4715	2352	32	2.5610	2441
16	2.4740	2354	33	2.5935	2474
17	2.4765	2357	34	2.6280	2508
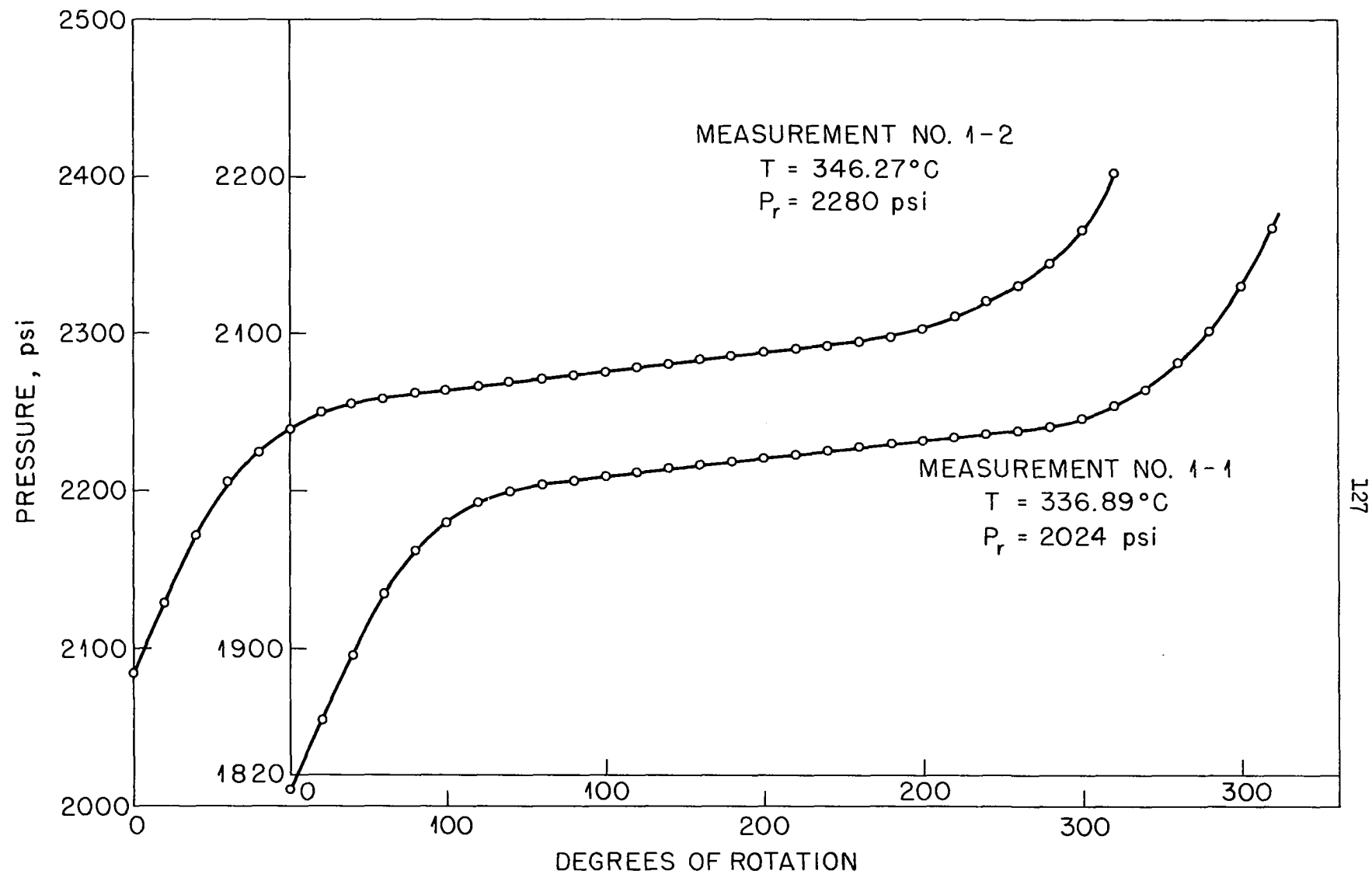
FIGURE XXXIII
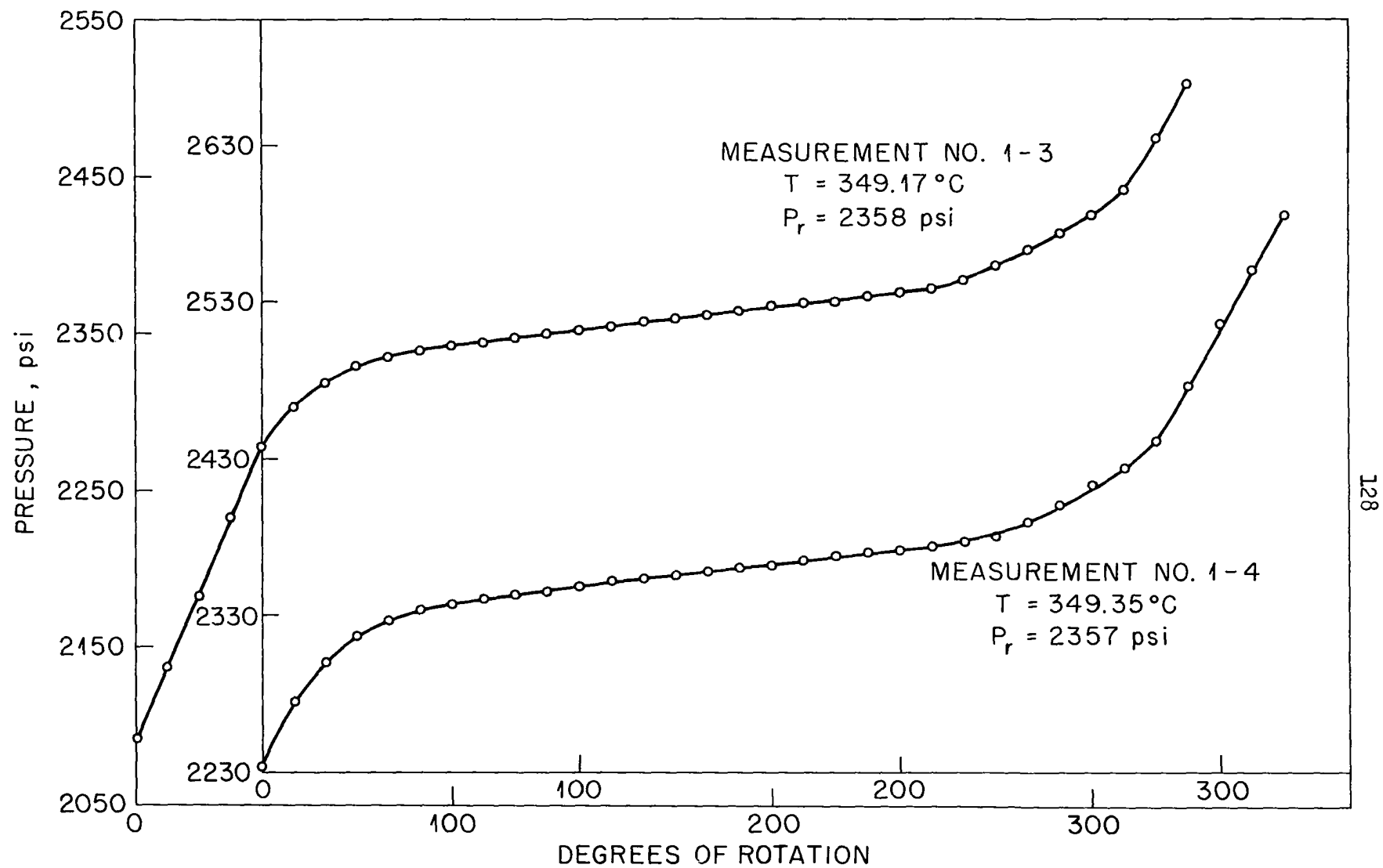PRESSURE AS A FUNCTION OF VOLUME REDUCTION

FIGURE XXXIV
PRESSURE AS A FUNCTION OF VOLUME REDUCTION

internal pressure of the system. The failure of the curve to show a
perfectly horizontal section was assumed to be caused by a spring
constant of the diaphragm. As the diaphragm was moved from its initial
position it became more and more distorted. This degree of distortion
should determine the pressure in excess of the internal pressure of the
system which was necessary to move the diaphragm. The pressure recorded
as corresponding to our fixed temperature was taken from the center
section of the curve which showed an increase of two, or less, psi. per
unit of volume decrease. The pressure at each end of this section was
noted and the numerical average recorded.

Since this metallic diaphragm was assumed to have a character-
istic spring constant, the external pressure measured was assumed to be
the sum of the internal pressure of the vapor and the pressure necessary
to overcome the spring constant of the diaphragm. Therefore, a pressure
correction was applied to the external pressure reading to correct for
the spring constant. Data obtained (Table XXVIII) in experiments using
this particular diaphragm were used to calculate this correction factor
for the spring constant. The standard pressure as determined by Keenan
and Keyes, P_o , was subtracted from each experimental pressure measure-
ment, P_r . These deviations were reasonably constant, completely random
in scatter, and in no way related to any variable in the system. There-
fore, the numerical average of these deviations was used as the
correction factor. When the correction factor was applied to each
measurement, corrected values, P_m , were obtained. It should be noted
that a correction factor determined in this manner incorporates any

TABLE XXVIII

TEMPERATURE-PRESSURE ISOCHORE OF WATER
DIAPHRAGM NO. 1

Measurement No.	T	P_r	P_o	P_m	$P_m - P_o$
	°C.	psi.	psi.	psi.	psi.
1-1	336.89	2024	2037	2040	3
1-2	346.27	2280	2290	2296	6
1-3	349.17	2358	2373	2374	1
1-4	349.35	2357	2379	2373	-6
1-5	354.87	2541	2545	2557	12
1-6	368.33	2967	2993	2983	-10
1-7	373.90	3181	3202	3197	-5
1-8	374.27	3196		3212	
1-9	374.86	3238		3254	
1-10	375.13	3260		3276	
1-11	377.10	3288		3304	
1-12	382.62	3526		3542	

P_r - pressure read from pressure-volume isotherm

P_o - pressure from Keenan and Keyes

P_m - pressure reading, P_r , corrected for diaphragm spring constant

correction which might be necessary due to the temperature gradient mentioned earlier. The corrected values showed less than 0.5% deviation from Keenan and Keyes' values.

It was noted in work with diaphragm No. 1 that all P_r measurements were lower than the P_o values. With the spring constant to overcome, the external pressure values should be greater than the P_o values. This discrepancy was believed to be due to improper positioning of the diaphragm when the bomb was assembled. The bomb was probably sealed with the diaphragm 'floating', that is, positioned in the center of the space between the bomb head and retainer plate, rather than firmly against the bomb head. As the internal pressure increased a certain force would be required to move the diaphragm against the bomb head. Therefore, when the external system measured one atmosphere the internal pressure would be greater by this amount. The external pressure required to move the diaphragm from the bomb head to the retainer plate would now be less, by an equivalent amount, than it would if the diaphragm had been firmly positioned in the bomb head originally.

After cooling to room temperature the bomb was opened at both ends and prepared for the second run. A new diaphragm was inserted and care taken to position the diaphragm firmly in the bomb head. A new sample of water was added to give a fraction filling of 0.32 and both ends were resealed as previously described.

The bomb was given an initial twenty-four hours to reach a temperature near 350 °C. before the temperature controller was adjusted to a fixed point and an additional fifteen hours allowed for the

establishment of equilibrium. Most temperatures after that were given only two to three hours to reach equilibrium but each time only a few degrees change was involved. This was apparently satisfactory as the data proved to be as reliable as previously.

Data were collected and the same procedure followed to obtain a correction factor for the spring constant of the new diaphragm. In this case all P_r values were greater than the P_0 values and indicated improper diaphragm positioning might have been a factor in the lower values recorded in the first series of experiments. Tables XXIX and XXX summarize the data for two measurements and Figures XXXV and XXXVI show several pressure-volume isotherms. Table XXXI summarizes all data obtained using diaphragm No. 2.

The third series of experiments was made with still another diaphragm, No. 3, which was welded to the head of the bomb. This assured proper positioning. Experimental techniques were the same and the same procedure was used for calculating a correction factor for the spring constant of the diaphragm. Tables XXXII and XXXIII show typical data for two measurements involving this diaphragm and Figures XXXVII and XXXVIII show typical pressure-volume isotherms. Table XXXIV summarizes data for all measurements.

The spring constant correction factor for this diaphragm was -55 psi. as compared to -40 psi. for diaphragm No. 2 and +16 psi. for diaphragm No. 1. This further supports the theory of a 'floating' diaphragm in the first series of measurements. In addition, the graphs in Figures XXXVII and XXXVIII show two interesting facts. First, the

TABLE XXIX

DATA FOR PRESSURE MEASUREMENT NO. 2-3

Temperature Readings

Pyr-O-Vane off	346.28 °C.
Pyr-O-Vane on	345.85
Pyr-O-Vane off	346.18
Pyr-O-Vane on	345.90
Average temperature	346.05 °C.

Pressure Readings

Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	2.2760	2156 psi.	17	2.4475	2328 psi.
2	2.3195	2199	18	2.4485	2329
3	2.3655	2246	19	2.4495	2330
4	2.3895	2270	20	2.4500	2330
5	2.4060	2286	21	2.4510	2331
6	2.4190	2299	22	2.4515	2332
7	2.4255	2306	23	2.4530	2333
8	2.4295	2310	24	2.4550	2335
9	2.4330	2313	25	2.4565	2337
10	2.4360	2316	26	2.4600	2340
11	2.4385	2319	27	2.4660	2346
12	2.4395	2320	28	2.4800	2360
13	2.4415	2322	29	2.4960	2376
14	2.4435	2324	30	2.5230	2403
15	2.4450	2325	31	2.5525	2433
16	2.4465	2327	32	2.5860	2466

TABLE XXX

DATA FOR PRESSURE MEASUREMENT NO. 2-6

Temperature Readings

Pyr-O-Vane off	346.91 °C.
Pyr-O-Vane on	346.27
Pyr-O-Vane off	346.59
Pyr-O-Vane on	346.27
Average temperature	346.51 °C.

Pressure Readings

Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	2.3030	2183 psi.	17	2.4470	2327 psi.
2	2.3500	2230	18	2.4485	2329
3	2.3855	2266	19	2.4495	2330
4	2.4030	2283	20	2.4505	2331
5	2.4195	2300	21	2.4515	2332
6	2.4245	2305	22	2.4520	2332
7	2.4275	2308	23	2.4530	2333
8	2.4310	2311	24	2.4540	2334
9	2.4340	2314	25	2.4560	2336
10	2.4365	2317	26	2.4640	2344
11	2.4385	2319	27	2.4750	2355
12	2.4405	2321	28	2.4920	2372
13	2.4425	2323	29	2.5115	2392
14	2.4440	2324	30	2.5390	2419
15	2.4450	2325	31	2.5740	2454
16	2.4455	2326			

CURVE I
MEASUREMENT NO. 2-3
T = 346.05 °C
P_r = 2325 psi

CURVE II
MEASUREMENT NO. 2-5
T = 346.28 °C
P_r = 2328 psi

CURVE III
MEASUREMENT NO. 2-6
T = 346.51 °C
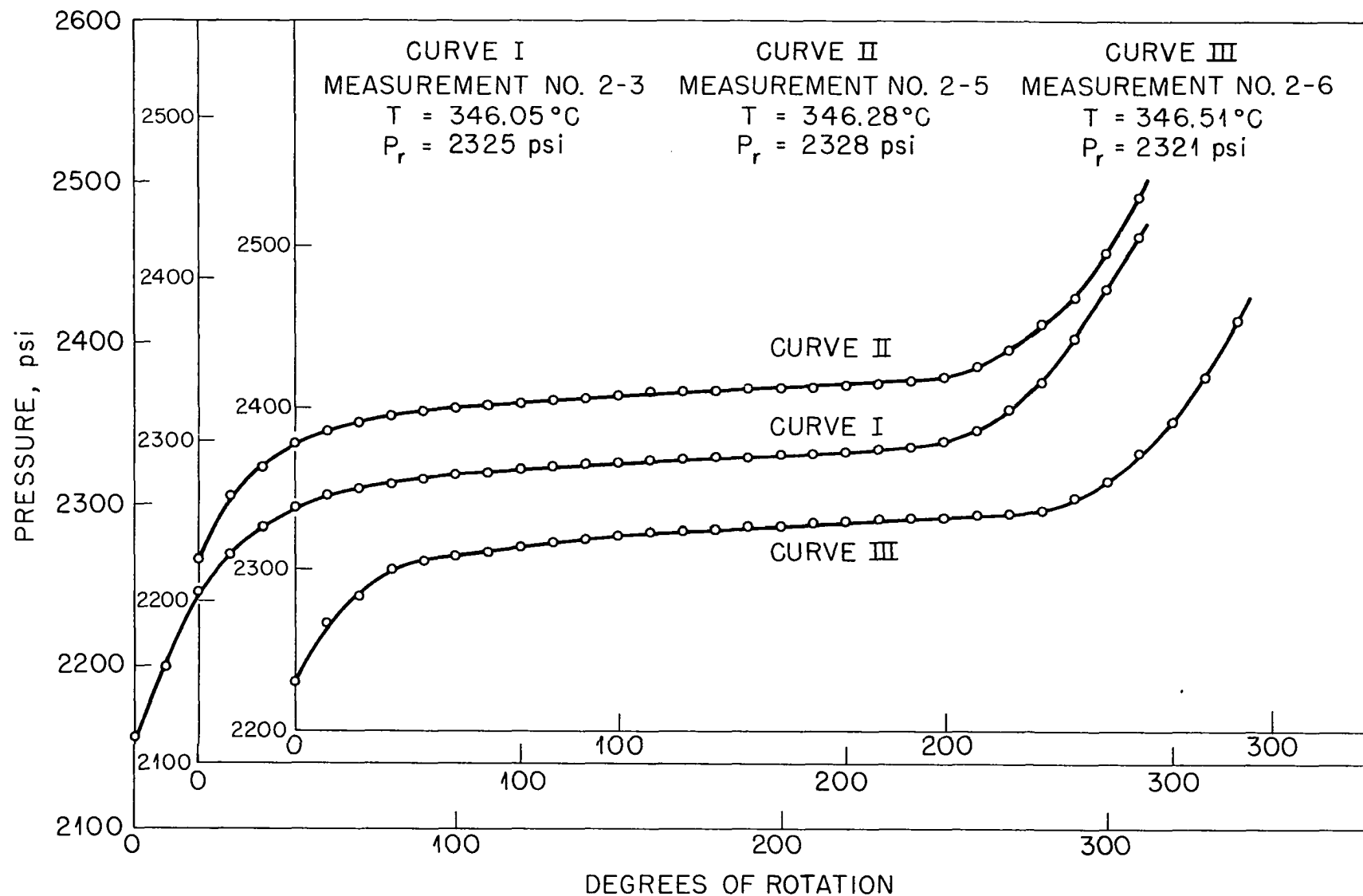P_r = 2321 psi

DEGREES OF ROTATION

FIGURE XXXV

PRESSURE AS A FUNCTION OF VOLUME REDUCTION
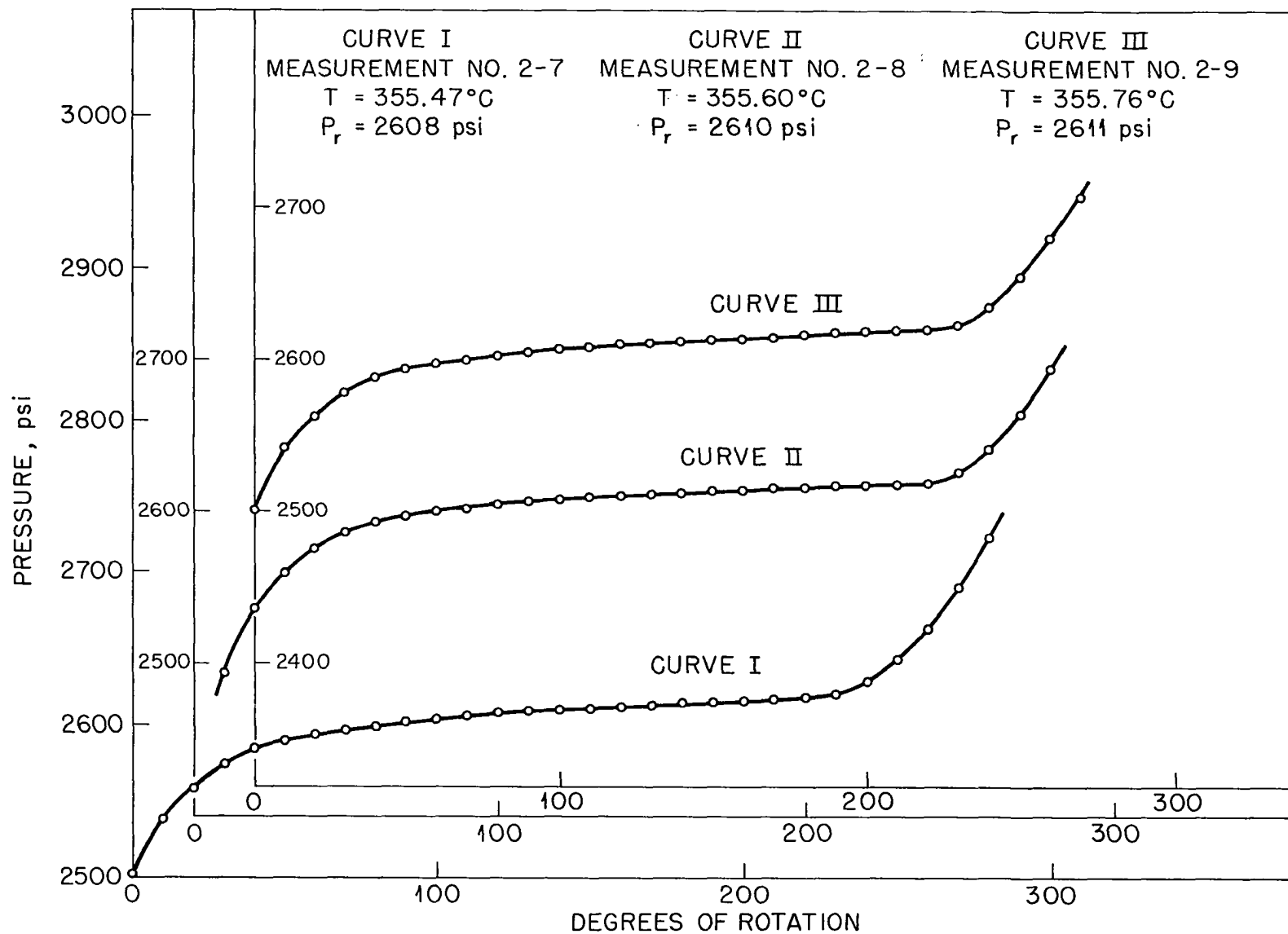
FIGURE XXXVI
PRESSURE AS A FUNCTION OF VOLUME REDUCTION

TABLE XXXI

TEMPERATURE-PRESSURE ISOCHORE OF WATER
DIAPHRAGM NO. 2

Measurement No.	T	P_r	P_o	P_m	$P_m - P_o$
	°C.	psi.	psi.	psi.	psi.
2-1	345.75	2338	2276	2298	22
2-2	345.88	2322	2279	2282	3
2-3	346.05	2325	2284	2285	1
2-4	346.06	2320	2284	2280	-4
2-5	346.28	2328	2291	2288	-3
2-6	346.51	2321	2297	2281	-16
2-7	355.47	2608	2564	2568	4
2-8	355.60	2610	2568	2570	2
2-9	355.76	2611	2573	2571	-2
2-10	365.57	2925	2895	2885	-10

TABLE XXXII

DATA FOR PRESSURE MEASUREMENT NO. 3-13

Temperature Readings	
Pyr-O-Vane off	370.69 °C.
Pyr-O-Vane on	370.30
Pyr-O-Vane off	370.69
Pyr-O-Vane on	370.40
Average temperature	370.52 °C.

Pressure Readings

Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	2.9630	2843 psi.	24	3.2310	3111 psi.
2	3.0090	2889	25	3.2320	3112
3	3.0630	2943	26	3.2320	3112
4	3.1130	2993	27	3.2325	3113
5	3.1460	3026	28	3.2330	3113
6	3.1660	3046	29	3.2340	3114
7	3.1830	3063	30	3.2350	3115
8	3.1940	3074	31	3.2360	3116
9	3.2020	3082	32	3.2370	3117
10	3.2060	3086	33	3.2375	3118
11	3.2090	3089	34	3.2380	3118
12	3.2115	3092	35	3.2385	3119
13	3.2140	3094	36	3.2385	3119
14	3.2160	3096	37	3.2390	3119
15	3.2175	3098	38	3.2395	3120
16	3.2195	3099	39	3.2405	3121
17	3.2210	3101	40	3.2415	3122
18	3.2225	3103	41	3.2430	3123
19	3.2235	3104	42	3.2485	3128
20	3.2250	3105	43	3.2590	3139
21	3.2265	3107	44	3.2720	3152
22	3.2285	3109	45	3.2890	3169
23	3.2300	3110	46	3.3030	3183

TABLE XXXIII

DATA FOR PRESSURE MEASUREMENT NO. 3-20

Temperature Readings

Pyr-O-Vane off	374.16 °C.
Pyr-O-Vane on	373.79
Pyr-O-Vane off	373.95
Pyr-O-Vane on	373.69
Average temperature	373.90 °C.

Pressure Readings

Reading	Millivolt	Pressure	Reading	Millivolt	Pressure
1	3.1700	3050 psi.	24	3.3835	3263 psi.
2	3.2210	3101	25	3.3840	3263
3	3.2690	3149	26	3.3845	3264
4	3.3015	3181	27	3.3845	3264
5	3.3230	3203	28	3.3845	3264
6	3.3370	3217	29	3.3845	3264
7	3.3490	3229	30	3.3850	3264
8	3.3560	3236	31	3.3850	3264
9	3.3610	3241	32	3.3855	3265
10	3.3635	3243	33	3.3855	3265
11	3.3655	3245	34	3.3860	3265
12	3.3675	3247	35	3.3860	3265
13	3.3705	3250	36	3.3860	3265
14	3.3735	3253	37	3.3860	3265
15	3.3750	3254	38	3.3860	3265
16	3.3760	3255	39	3.3860	3265
17	3.3775	3257	40	3.3870	3266
18	3.3790	3258	41	3.3930	3272
19	3.3800	3259	42	3.4050	3284
20	3.3810	3260	43	3.4200	3299
21	3.3815	3261	44	3.4350	3314
22	3.3825	3262	45	3.4520	3331
23	3.3835	3263			
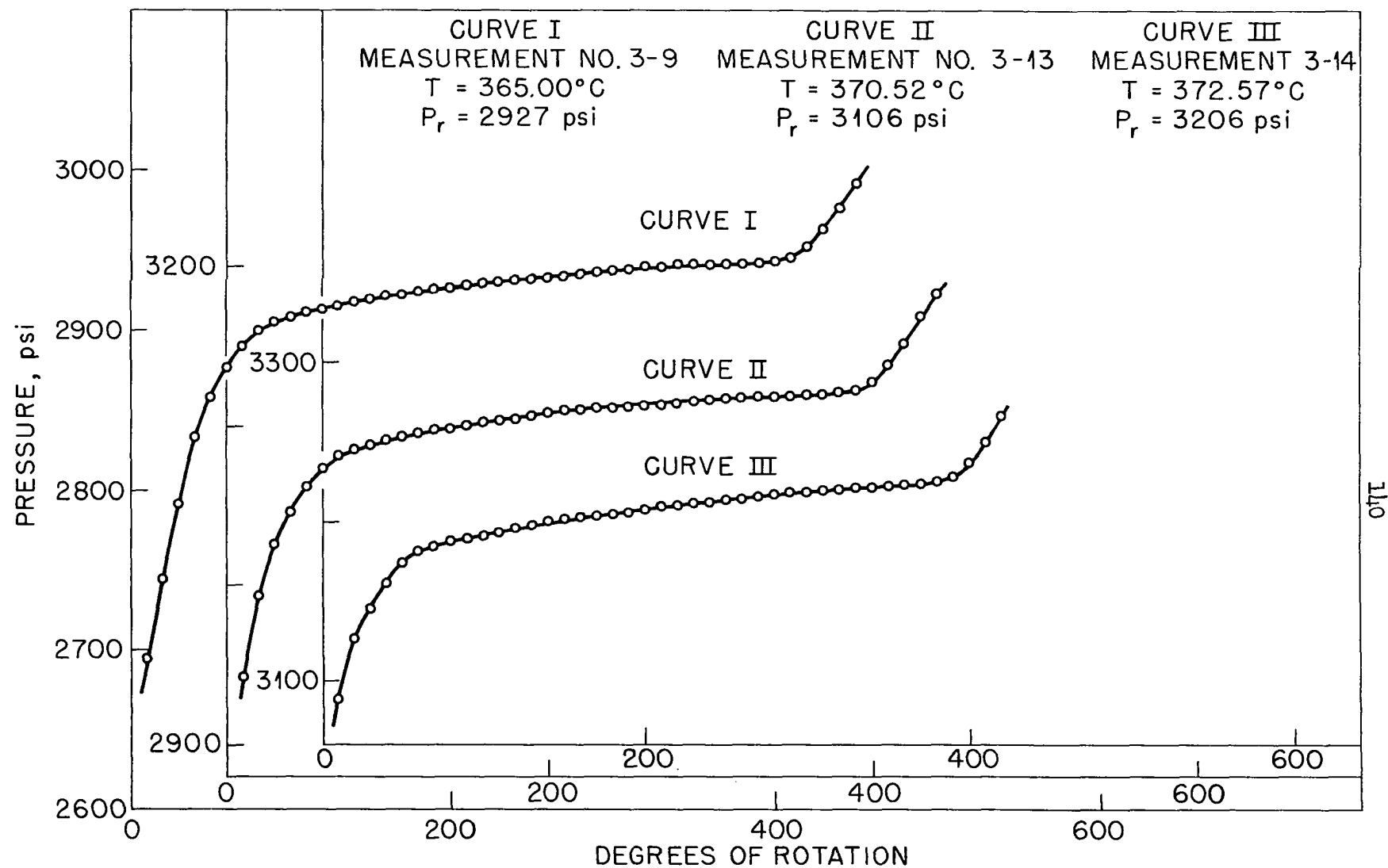
FIGURE XXXVII
PRESSURE AS A FUNCTION OF VOLUME REDUCTION
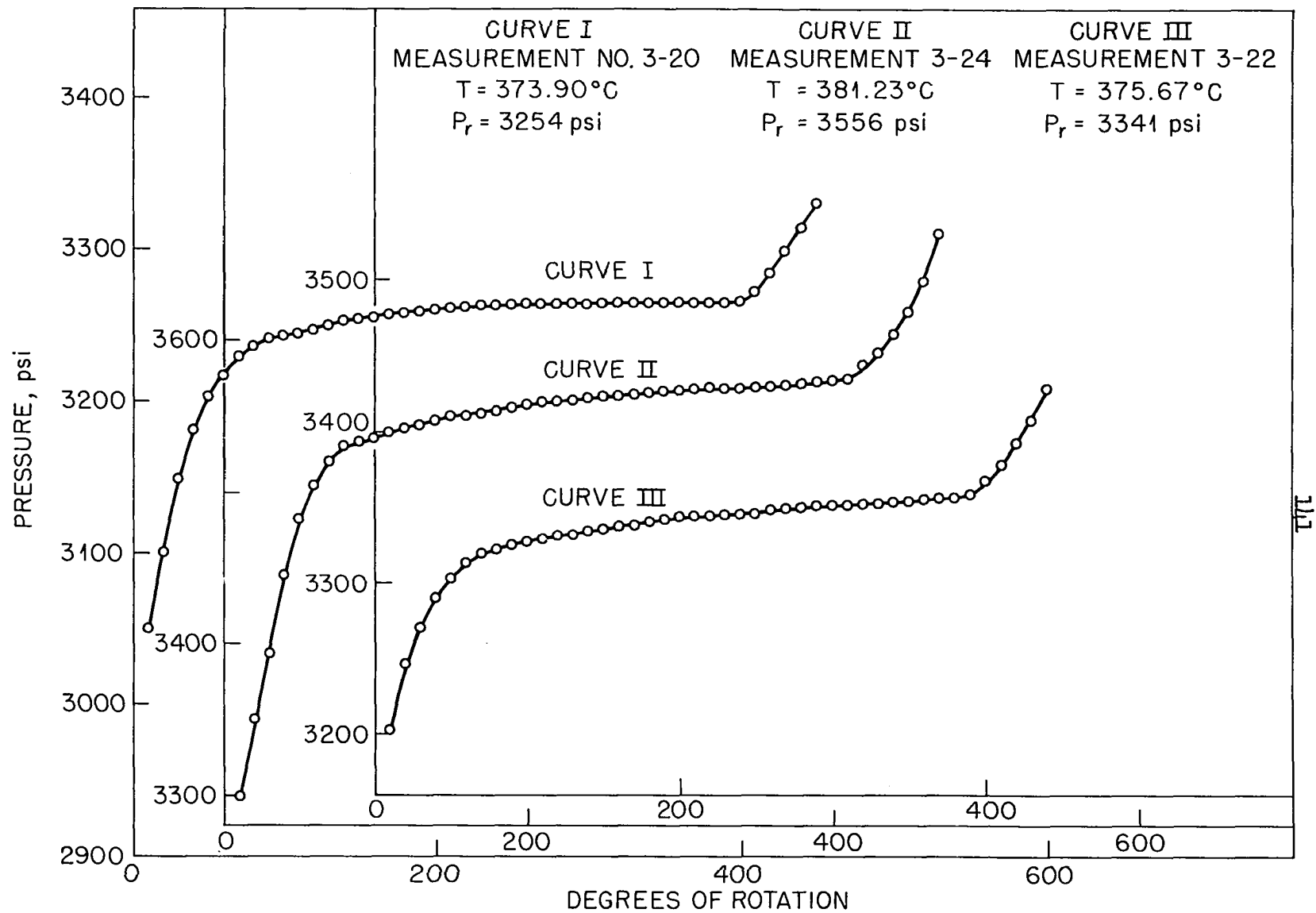
FIGURE XXXVIII
PRESSURE AS A FUNCTION OF VOLUME REDUCTION

TABLE XXXIV

TEMPERATURE-PRESSURE ISOCHORE OF WATER
DIAPHRAGM NO. 3

Measurement No.	T	P_r	P_o	P_m	$P_m - P_o$
	°C.	psi.	psi.	psi.	psi.
3-1	345.82	2319	2277	2264	-13
3-2	345.89	2317	2279	2262	-17
3-3	346.37	2348	2293	2293	0
3-4	354.71	2603	2540	2548	8
3-5	354.96	2605	2548	2550	2
3-6	355.60	2587	2568	2532	-36
3-7	356.06	2633	2582	2578	-4
3-8	364.63	2940	2863	2885	23
3-9	365.00	2927	2876	2872	-4
3-10	365.36	2953	2888	2898	10
3-11	369.44	3099	3033	3044	11
3-12	369.50	3120	3035	3065	30
3-13	370.52	3106	3072	3051	-21
3-14	372.57	3206	3148	3151	3
3-15	372.85	3217	3159	3162	3
3-16	373.05	3228	3166	3173	7
3-17	373.22	3232	3173	3177	4
3-18	373.67	3242	3189	3187	-2
3-19	373.83	3246	3195	3191	-4
3-20	373.90	3254	3198	3199	1
3-21	375.91	3336		3281	
3-22	375.67	3341		3286	
3-23	376.09	3342		3287	
3-24	381.23	3556		3501	
3-25	382.44	3587		3532	

length of the break in the pressure curve is noticeably longer than in previous work. Curves resulting from the use of diaphragm No. 1 had a plateau of about 145 $^{\circ}$ of rotation. With diaphragm No. 2 this increased to about 185 $^{\circ}$ or rotation and with diaphragm No. 3 to about 310 $^{\circ}$ of rotation. This means that the diaphragm volume displacement is roughly doubled from No. 1 to No. 3 and again indicates better diaphragm positioning. Second, the sharp break in the pressure curve on the right side indicates the diaphragm moved uniformly and all parts came to rest firmly against the retainer wall at the same time.

This sharp break gives a rapid and convenient means of reading a consistant P_r value even without plotting the curve. The method of determining and applying the spring constant correction factor to obtain corrected values makes the method of reading P_r merely a matter of choice. However, consistancy is necessary throughout all measurements of a given series. Since the mid-point of the plateaus was determined for P_r values in the other data, the same technique was used here.

All experimental points are shown on the pressure-temperature isochore for water in Figure XXXIX. The data for Keenan and Keyes is indicated by the solid line. Agreement between the two is very good with only an occasional value off as much as 1.0%. Many experimental points are within 0.5% of the standard curve. This indicates that the experimental technique and apparatus are suitable for pressure measurements in this temperature and pressure range and, with further improvement, the apparatus is probably capable of producing data in which the average error is less than 0.1%.
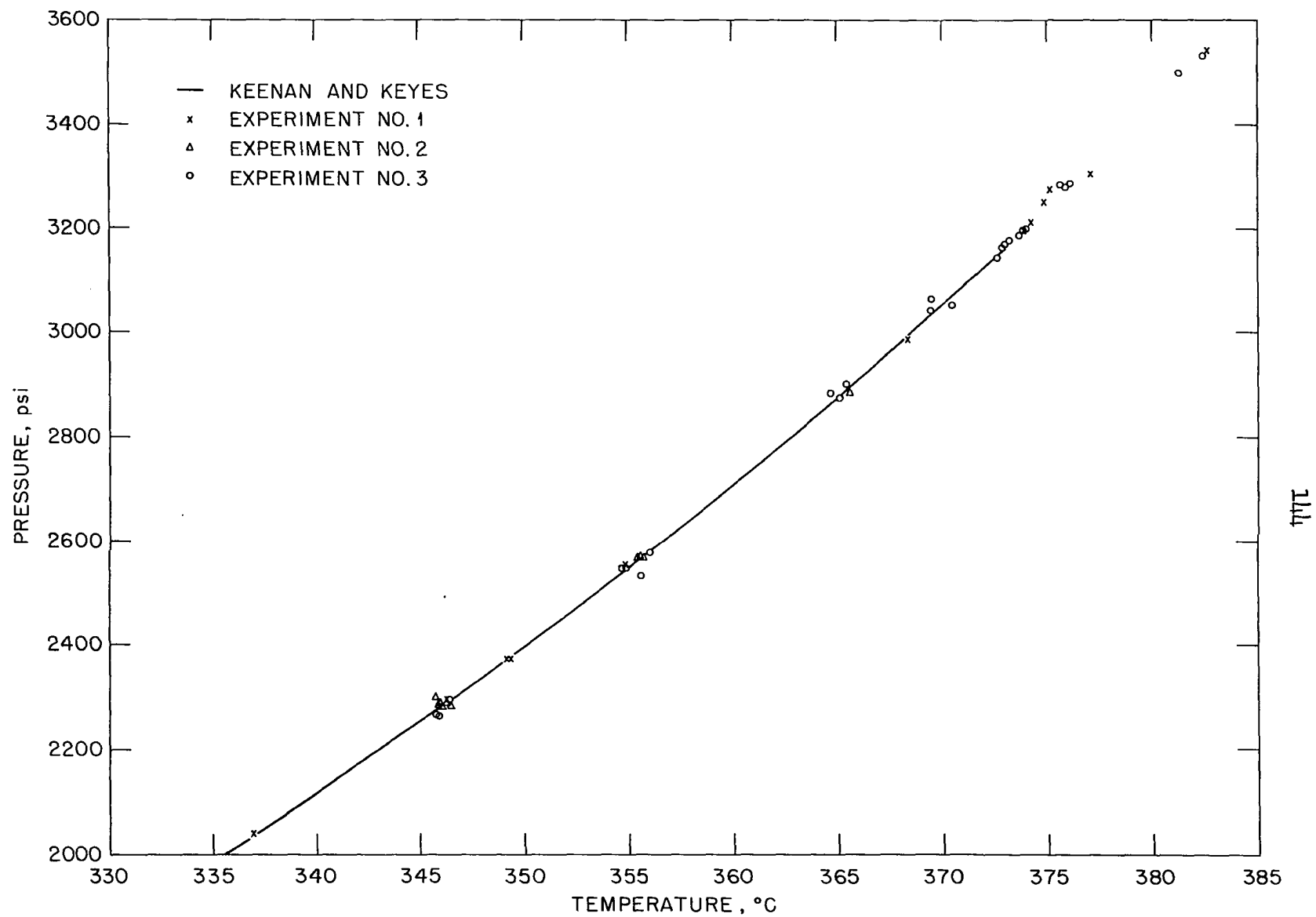
FIGURE XXXIX
PRESSURE-TEMPERATURE ISOCHORE OF WATER

CHAPTER IV

DISCUSSION AND SUMMARY

Temperature Measurement

It was obvious from the beginning of the experimental work on critical temperature measurements of the system sulfur trioxide - water that there were marked differences between this system and the usual one-component system. Even when limited to constant volume experiments, critical temperature measurements of one-component systems would, in general, present no difficulties. Various fraction fillings of liquid at room temperature could be heated to the temperature at which only one phase remained and the temperature at this point plotted as a function of the fraction filling. A curve would be obtained in which the critical temperature of the one-component system was the maximum on the curve. However, with a two-component system such was not the case.

A review of the graphs in Chapter II in which the fraction filling is plotted as a function of the temperature shows that a curve is not obtained but, in general, a straight line. The critical temperature has been defined as the temperature at which the meniscus disappears at the center of the tube and is not, necessarily, the maximum temperature at which two phases coexist.

Let us consider what happens to a liquid sample when heated

from room temperature to the temperature at which the meniscus disappears. First, consider a sample tube with a low concentration of sulfur trioxide, for example, fifteen mole per cent. As the tube is heated part of the liquid is vaporized to a vapor with a composition different from that of the liquid. It is probable that the vapor is rich in water and that the liquid thus becomes richer in sulfur trioxide. The lower the fraction filling the more water will vaporize and the richer the liquid will become in sulfur trioxide. Thus, as the fraction filling is decreased the remaining liquid becomes richer in sulfur trioxide and the temperature at which the meniscus disappears increases.

Suppose the sample tube contains a solution of eighty mole per cent, that is, on the sulfur trioxide rich side of the temperature-concentration diagram. As the temperature is increased on a sample the vapor becomes richer in sulfur trioxide and the liquid composition changes so that the mole fraction of trioxide decreases. Therefore, as the fraction filling of a sample tube is decreased, the vapor space is increased and the liquid composition shifts to a lower mole fraction value. This means the temperature at which the meniscus disappears increases with decreasing fraction fillings. This is substantiated in Figure XIX.

Now assume a liquid sample whose composition is near fifty mole per cent of sulfur trioxide. The vapor phase now has a composition very near that of the liquid and, thus, the liquid composition does not vary appreciably as the fraction filling is varied. The temperature would be expected to be nearly constant regardless of the initial room temperature fraction filling of a sample tube. This is noted in Figure XVI.

A review of all temperature vs. fraction filling at room temperature graphs will show a marked difference in the slopes of the curves at low sulfur trioxide concentrations, at concentrations near fifty mole per cent, and at higher concentrations. At low concentrations the liquid composition would change rapidly if the vapor phase were chiefly water. At higher concentrations the liquid composition would change rapidly if the vapor were chiefly sulfur trioxide. At concentrations near fifty mole per cent the liquid composition would not change materially if sulfur trioxide and water vaporized in approximately a 1:1 ratio.

Unfortunately, no mean was available during this research for sampling the liquid and vapor phases. However, our hypothesis is supported by our experimental data, by vapor-liquid equilibrium data at lower temperatures,[155] and by recent work by G. P. Luchinskii.[156] In Luchinskii's work pressures and vapor compositions of the sulfur trioxide - water system were measured in the temperature range from 20 to 200 °C. and at the boiling point. The vapors of liquids with less than 85% sulfuric acid consisted of water only, but over liquids containing over 35% free sulfur trioxide they consisted of sulfur trioxide, and over those from 85% sulfuric acid to 35% free sulfur trioxide they consisted of sulfuric acid with water and sulfur trioxide. Although these data were obtained at somewhat lower temperatures than the critical region, they add support to our hypothesis. Only the abstract of this work is available at the present time.

Although no means were available for sampling, the experimental method used did permit calculation of the critical densities from a know-

ledge of the room temperature densities of each solution and the fraction filling. Table XXXV summarizes the densities of the single phase remaining when the meniscus disappeared at the center of the tube. Figure XXXX shows the dependence of the critical density upon the mole fraction of sulfur trioxide.

The critical temperature data reveal another interesting item. Figure XX shows the maximum in a critical temperature vs. composition curve to be near forty mole per cent of sulfur trioxide. This is a shift from the position of the maximum boiling point at one atmosphere. Luchinskii[156] indicates a slight shift in the single azeotropic point in the temperature range of his work which is in the same direction as that indicated by the maximum critical temperature.

Pressure Measurement

The pressure apparatus developed for use with corrosive substances was satisfactory for pressure measurements in the critical region to a reproducibility of about 0.5%. The many difficulties encountered in construction and operation were successfully overcome and the development and use of a bimetallic diaphragm were new and significant contributions.

The characteristics of metallic pressure transmitting diaphragms, particularly stainless steel, are under study at the present time by the Instrument Division of the Oak Ridge National Laboratory. It is too early to be certain of results but indications are that such diaphragms will be satisfactory. The characteristics of bimetallic diaphragms have not been studied systematically but this work indicates that they will be equally satisfactory.

TABLE XXXV

CRITICAL DENSITIES OF SULFURIC ACID

x_{SO_3}	d_r g/cc	f_r	d_c g/cc
0.000	0.997	0.321	0.320
0.0193	1.065	0.393	0.419
0.0419	1.139	0.396	0.451
0.0654	1.211	0.376	0.455
0.0938	1.291	0.353	0.456
0.1251	1.372	0.336	0.461
0.1643	1.467	0.333	0.489
0.2084	1.565	0.314	0.491
0.2664	1.676	0.293	0.491
0.3368	1.778	0.283	0.503
0.4353	1.833	0.280	0.513
0.5000	1.831		
0.5591	1.784	0.331	0.591
1.0000	1.884	0.336	0.633

d_r : room temperature density

f_r : room temperature fraction filling

d_c : density of homogeneous phase remaining as meniscus disappeared at the center of the sample tube.
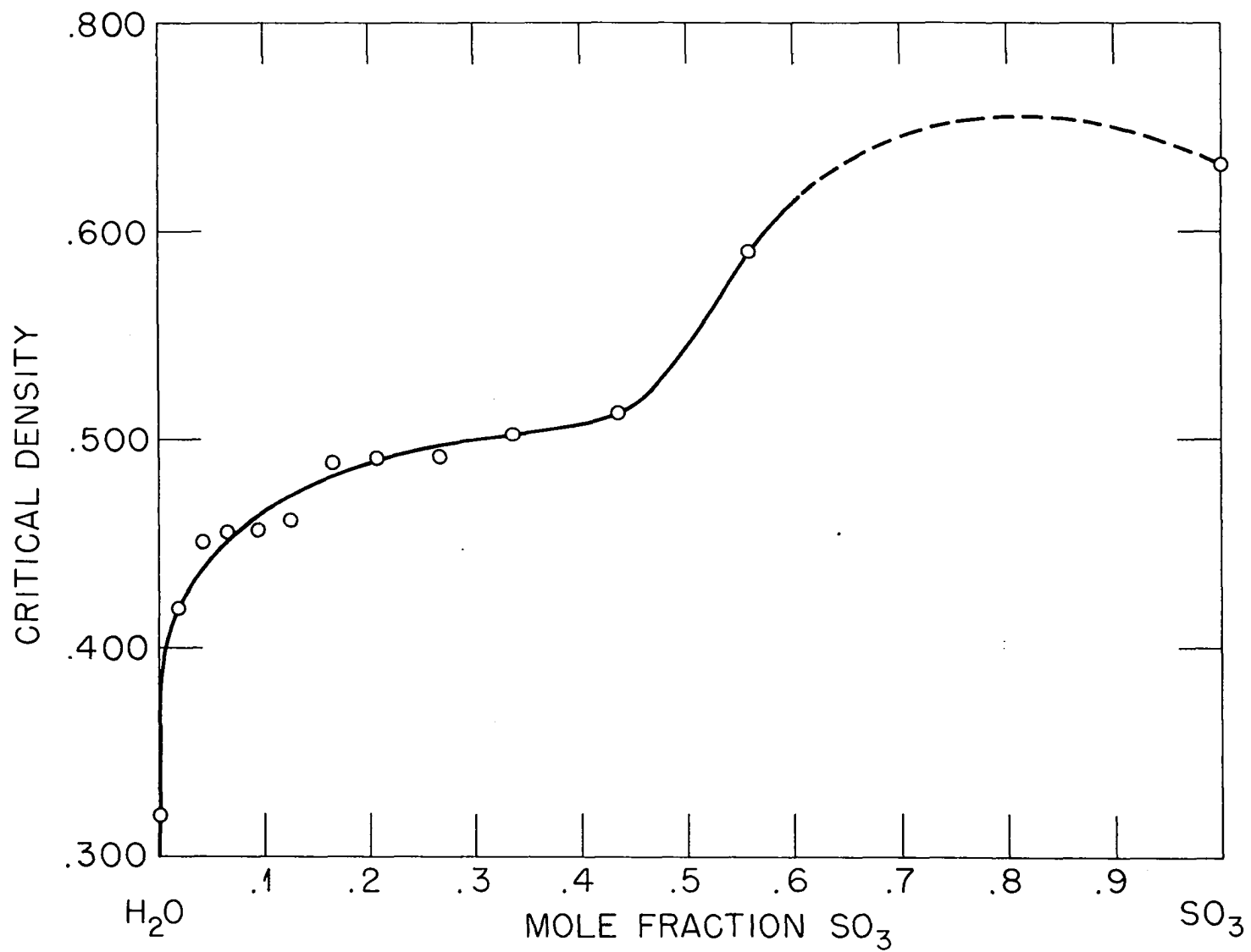
FIGURE XXXX
CRITICAL DENSITY OF SYSTEM SO_3-H_2O

150

Phase Relationships

The experimental work done and the apparatus developed have made a contribution to the overall problem of making pressure-volume-temperature-composition studies of binary systems. As previously stated, the normal experimental procedure was believed to be unsatisfactory for a system such as sulfur trioxide - water at the extreme conditions of temperature and pressure involved in the critical region. Since no satisfactory technique was devised for making all physical measurements in one combined operation, the equipment and technique for two separate measurements were developed.

Therefore, obtaining a general picture of the pressure-volume-temperature-composition relationships in the critical region requires a somewhat different approach than if all pressure-volume-temperature-composition measurements could be made on one system at the same time. First, temperature must be related to concentration and to fraction filling. Then pressure must be related to temperature, concentration, and fraction filling. Then the four variables may be interrelated to describe the system in the critical region. The following is a general approach for handling the experimental data and for finding the critical point.

We may begin with a series of acid solutions of known mole per cent of sulfur trioxide,

$$X_1 \; , \; X_2 \; , \; X_3 \; \cdots \cdots \; X_n \; .$$

With each known solution we may fill a given sample tube volume with liquid solution and measure the fraction filling. For each solution

we will have a series of fraction fillings,

$$f_1 \ , \ f_2 \ , \ f_3 \ \ldots \ldots \ f_n \ .$$

From this data we can calculate the concentration of each individual

sample tube. For all fraction fillings of solution number one we will

have $\quad c_{11} \ , \ c_{12} \ , \ c_{13} \ \ldots \ldots \ c_{1n} \quad$ and for all

fraction fillings of solution number two we will have

$$c_{21} \ , \ c_{22} \ , \ c_{23} \ \ldots \ldots \ c_{2n} \ .$$

Finally the nth. solution will have concentrations of

$$c_{n'1} \ , \ c_{n'2} \ , \ c_{n'3} \ \ldots \ldots \ c_{n'n} \quad .$$

These sample tubes can be heated and the temperature observed

at which the meniscus vanishes. Each solution, that is, X_1, X_2, etc.,

will have a series of temperature and fraction fillings as indicated in

the graphs and data in Chapter II. There are, therefore, the following

series of temperatures corresponding to each of the above concentrations.

$$T_{11} \ , \ T_{12} \ , \ T_{13} \ \ldots \ldots \ T_{1n}$$
$$T_{21} \ , \ T_{22} \ , \ T_{23} \ \ldots \ldots \ T_{2n}$$
$$\cdot$$
$$\cdot$$
$$\cdot$$
$$\cdot$$
$$T_{n'1} \ , \ T_{n'2} \ , \ T_{n'3} \ \ldots \ldots \ T_{n'n}$$

We have now related the temperature at which the meniscus vanishes to the

mole fraction of one component and to the fraction filling of the tube.

It should be pointed out that the graph in Figure XX of

critical temperature as a function of mole fraction of sulfur trioxide

is an arbitrary curve and is drawn only to determine the general shape of

such a curve. In Chapter I we defined critical temperature as that

temperature at which the meniscus vanishes at the center of the tube.
This is entirely arbitrary as it does not follow a priori, from its
correctness in one-component systems, that this is the case for which
the two phases become identical in intrinsic properties in two-component
systems.

We may now relate pressure to our other variables in the
following way. A given solution, say X_1 , fills our pressure vessel to
a given fraction filling, f_1 . A series of temperature and pressure
measurements are made and the process repeated for each fraction filling
and then for each solution. We then have a series of pressure and temper-
ature measurements for each of the following samples.

$$X_1 f_1 \quad , \quad X_1 f_2 \quad , \quad X_1 f_3 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad X_1 f_n$$

$$X_2 f_1 \quad , \quad X_2 f_2 \quad , \quad X_2 f_3 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad X_2 f_n$$

$$\cdot$$
$$\cdot$$
$$\cdot$$
$$\cdot$$

$$X_{n'} f_1 \quad , \quad X_{n'} f_2 \quad , \quad X_{n'} f_3 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad X_{n'} f_n$$

The data may now be related in numerous ways.

If we construct a pressure vs. concentration diagram for a
constant temperature, we may draw tie lines at any selected pressure in
the two-phase area. We can then write equations representing the total
mass of one component for each of two sample tubes whose concentrations
are different but which lie on the same tie line in the two-phase area.

$$V_{(liq)} \, C_{x(liq)} \quad + \quad V_{(gas)} \, C_{x(gas)} \quad = \quad M_x$$

$$V'_{(liq)} \, C_{x(liq)} \quad + \quad V'_{(gas)} \, C_{x(gas)} \quad = \quad M'_x$$

These equations may be solved for the concentration of component 'x' in each phase. By interpolation of data obtained in the critical region we can find the point at which the two phases become identical.

This report has presented a general introduction to the phenomena in the critical region and a specific introduction to the phenomena in the critical region of the binary aqueous system sulfur trioxide - water. Experimental data relating temperature, composition, and fraction filling were collected by using a semi-micro phase study apparatus. Equipment for relating pressure and temperature to the composition and fraction filling was designed, developed, and tested. The method of relating pressure, volume, temperature, and composition data to obtain the critical point of the binary aqueous system was presented. The test of the practical applicability of the method must await the accumulation of adequate data.

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