PRESSURE, VOLUME, TEMPERATURE, AND DENSITY RELATIONS IN THE CRITICAL REGION

A Thesis

by

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FOREWORD

The laboratory work described in this thesis was carried out during one University year. Shortly after the beginning of the second year it was interrupted by the advent of war. The researches carried out since that time, although credited by the Faculty towards the degree, because of their confidential nature, cannot be reported on here.

CONTENTS

INTRODUCTION

For over one hundred years experiments and observations have been made on the so called 'critical' change of a liquid to a gas. No adequate explanation of all the phenomena has yet appeared. Some investigators cling to the classical picture of this transition. They believe that a liquid differs from a gas by degree only, and hold that when the critical change occurs the two phases are physically identical. Anomalous behaviour, which has been observed, would be attributed to impurities, gravitational effects, and other extraneous factors. On the other hand, an increasing amount of evidence has been, and is being presented, in favour of a structural concept of the liquid state. Many suggestions as to the nature of the liquid have been presented but most agree that it differs from the gaseous state in kind as well as degree. Studies of the critical temperature - critical pressure region, where the two phases interchange, have been most fruitful in obtaining data on the nature of the differences between them. It will be seen from the review, presented below, of the data so far obtained on the physical properties of critical systems, that the older 'Continuity of State' hypothesis is no longer tenable, at least, in its simple form. Dynamic structure hypotheses have been satisfactory in explaining many of the critical phenomena. Among the most satisfactory of these is the theory of Regional Orientation developed by Maass and his co-workers. In the light of the known experimental facts, the author adopts accepts this hypothesis. The experiments described in this thesis give further support to this picture of the liquid state and have led the author to suggest a mechanism for the phase transformations in the critical region.

The critical phenomenon of a liquid changing into a gas, as seen by the disappearance of a meniscus, was first reported by de la Tour in 1822 (1). He observed the phenomenon by heating a liquid, in equilibrium with its vapour, in a closed tube. The meniscus disappeared only if the amount of material in the tube was between certain limits, otherwise either all the liquid evaporated or the liquid expanded and filled the tube. The temperature at which the visible demarcation disappeared has been called the critical temperature.

Two explanations of this phenomenon were forthcoming. Since the density difference between liquid and vapour was known to decrease with rise in temperature, it was postulated by Ramsay (2) and Jamin (3) that it became zero at the critical temperature. The two phases would then become mutually miscible at that temperature. Since the surface tension of a liquid decreases with the rise in temperature, it was suggested that at the critical temperature the surface tension became equal to zero. Since there was no surface tension there was no surface and the liquid and gas became indistinguishable. It must be pointed out that it does not follow, from either of these explanations, that the two phases are physically identical at the critical temperature.

Andrews (4) compressed carbon dioxide at constant temperature in a sealed tube. He found that at temperatures below 30.9°C the liquid phase could be formed by compression, while at higher temperatures the material always remained as a gas. This limiting temperature of spontaneous condensation he considered to be the same critical temperature as was observed by de la Tour and others by the stationary heating method.

Andrews further observed that the isothermals below and above the critical temperature were exactly contiguous throughout that region. Because of this, it should be possible to obtain one equation connecting the pressure, temperature, and volume for both the liquid and gaseous states. Such an equation was developed by Van der Waals (5), by taking into account the space occupied by the molecules and their attractive forces on one another. The agreement between Van der Waals' equation and the experimental data is good. The critical point is determined from the equation as the point of inflection on the family of curves.

It was further evident from Andrews' work, that, by correctly choosing the temperature and pressure changes, ~~that~~ it was possible to pass from a wholly liquid system to one wholly gaseous, without any discontinuity of physical properties. This is usually referred to as the 'Continuity of State'. This fact, together with the single equation for both states, gave rise to the view that a similar structure, or rather lack of structure, existed for both gases and liquids.

A liquid was considered to differ from a gas only because its molecules ~~were~~ are so close that their mutual attraction is greater than their thermal kinetic force. The critical point was explained as the temperature where the kinetic forces of motion finally overcome the attractive forces, no matter how closely the molecules are compressed.

According to the theory outlined above, the critical phenomenon should take place at only one point. De la Tour had already observed that the meniscus was seen to disappear over a range of mean densities, and Hein (56) has reported that with carbon dioxide the critical phenomenon occurs when the mean density varies from 0.241 gms./c.c. to 0.589 gms./c.c. This, and other objections, soon arose against the simple "Continuity of State" explanation of the nature of liquids and gases, the outcome of which has been to assign a structure to the liquid state in contrast to the pure randomness of gases.

As an explanation for the occurrence of the critical phenomenon over a density range, Ramsay and Jamin (2,3) postulated that the liquid state existed above the critical temperature. They concluded that there is a difference between liquid molecules and gas molecules. This difference was not wholly destroyed at the critical temperature, and above that temperature the system might contain various proportions of liquid and gas molecules. Ramsay suggested that the two types of molecules differed in their number of atomic constituents, thus the difference between the two states was chemical as well as physical. Their method of measuring density was based on the determination of the position of the disappearing meniscus in the tube, a method which at best is very inaccurate.

Cailletet (6) reported experiments in general agreement with those of Ramsay and Jamin, and concluded that at the critical temperature the liquid and vapour became miscible. Young (7), by observing the position of the disappearing meniscus, inferred that the density of both phases became equal at the critical temperature. In all of the above experiments, no density determination could be made ~~any closer than~~ within one half of a degree ~~to~~ of the critical temperature. The broadening of the meniscus made accurate determination of its position very difficult. The density temperature curves obtained were extrapolated in the form of the classical parabola, a procedure which is not justified in this region.

A new concept of the critical phenomenon began to develop subsequent to more accurate density determinations in the critical region. The critical phenomenon of methyl ether was investigated by Galitzine (8). A density ? difference as great as 20% between the region below where the meniscus vanished and that above was found to persist indefinitely. He also found evidence of a density heterogeneity as much as 7°C above the critical temperature. Because these results were not in agreement with the theory of equal densities for both phases, Galitzine concluded that the persistence effect was produced by impurities. He also reported that the temperature of a reappearance of the meniscus, on cooling, was lower than that of its disappearance on heating. Young (9) repeated Galitzine's experiments, using highly purified ether and failed to observe the same effects. He therefore agreed with Galitzine in attributing the density persistence to volatile impurities. Young further found that by adding traces of a foreign gas he could retard the rate of equilibrium establishment and the formation of critical opalescence.

Hein (10) studied the systems carbon tetrachloride, sulphur dioxide, and carbon dioxide, and found a density heterogeneity persisting above the critical temperature. He could destroy the heterogeneity by mechanical stirring and concluded, in agreement with Young, that the persistence was caused by impurities.

Guoy (11) suggested, as an explanation of the phenomenon of persistence, that a density gradient could be established by the gravitational field. Because of the high compressibility in the critical region, this idea seemed plausible. He found however, that the experimental differences were much greater than could be explained by any method of calculation.

Teichner (12) and Traube (13) measured the density of a medium in the critical region by means of small glass floats of various densities. By observing the positions taken by the floats along the length of the tube, a measure of the density gradient was obtained. The results of their experiments supported the theory of discontinuity, and were in agreement with the results of Galitzine. Traube postulated that there are two types of molecules, those of the liquid, "liquidons", and those of the gas, "gasons". He made no suggestion as to what were the differences between these two types. He considered that the two species existed in equilibrium, and that heating the system increased the concentration of "gasons" and decreased the concentration of "liquidons". At the classical critical temperature there were still some "liquidons" present. However, their concentration became zero at some temperature slightly above this.

De Heen (14) extended the hypothesis of Traube by requiring that the concentration of "liquidons" is a function of the mass - volume ratio of the system, as well as of the temperature. Onnes (15) disagreed with these ideas, and again attributed the whole phenomenon of persistence to the presence of impurities and to poor experimental methods. He also agreed with Guoy that an apparent density difference might be due to a gravitational effect caused by the medium compressing itself.

The careful work of Callendar (16) on water is of great importance. He found, that by using carefully purified water, it was possible to obtain accurately reproducible density measurements. The water was sealed in a quartz tube, and he found that the density of the liquid and vapour did not become equal at the critical temperature. A density difference existed as much as 6°C above the critical temperature. Traces of air made reproducible determinations impossible. To confirm these results by measuring some other quantity that could be determined accurately for both liquid and vapour, Callendar measured the total heat. With pure water he obtained reproducable data giving the same effect as his density measurements. When the meniscus vanished the total heats of liquid and vapour were not equal but became equal 6° above that temperature.

Extensive measurements of the densities of various substances in the critical region have recently been carried out in ? this laboratory. Accurate studies have been made by Tapp, St~~a~~ecie and Maass (17), Winkler and Maass (18), Geddes and Maass (19), and McIntosh and Maass (20).

The experimental method, originally developed by Tapp and Maass, made possible the measurement of density in various parts of the medium to an accuracy of 0.05%. The density was measured by means of a McBain-Bakr balance (21) and float. Accurate temperature control was achieved so that either a uniform temperature or a temperature gradient could be maintained along the length of the bomb. This apparatus permitted the verification of many former results and led to the discovery of new phenomena occuring in the critical region.

It was found that the density difference above the critical temperature did not occur as a gradual gradient but as a sudden discontinuity near the point where the meniscus was last seen. The magnitude of the density difference depended on the overall mass-volume ratio, the greater the ratio, the greater the difference. A difference as great as 5% was observed for propylene 1.5°C above the critical temperature. Subsequent to a temperature change, an equilibrium value of the density was reached after thirty minutes, after which no further change could be observed. Mechanical stirring was found to leave the value unchanged after stirring for as long as six hours. It was found that the density difference decreased with increasing temperature, and reached zero at some point above the critical temperature. The temperature of equalization of density was different for different substances, being 10°C above the critical for methyl ether, 8°C for propylene, and 1.5°C for ethylene. Once the density difference was destroyed, a subsequent cooling of the system resulted in the persistence of a uniform density throughout the tube until condensation occurred at some point slightly below the temperature where the meniscus disappeared. Thus a density hysteresis was found in taking a system through a heating and cooling cycle in the critical region. It was found that expanding the system, at some temperature slightly above the critical, destroyed the heterogenity and that subsequent compression failed to reproduce it. The density difference could also be destroyed by cooling the top of the bomb, thus causing condensation in the upper region of the system, and violent stirring. This process has been called 'molecular stirring'. No way of re-establishing the density difference, once it had been destroyed, was found, other than by cooling below the critical temperature.

The gravitational effect due to the weight of the medium itself, as a cause of the density difference, has been considered by Winkler and Maass. This does not account for the magnitude of the effect ~~of the magnitude~~ observed, nor does it explain the discontinuity in the density gradient at the point where the meniscus disappears.

The work of Geddes and Maass is of great importance. An apparatus was used whereby density, temperature, pressure, and volume could be measured and varied as desired. Density and pressure isochores were determined with high accuracy. Of paramount interest in this work was the investigation of the time lags involved in the establishment of equilibrium of density subsequent to changes of temperature, pressure, or volume. The much greater time lag in passing from vapour to liquid than from liquid to vapour were interpreted as indicating a greater degree of orientation in the liquid state. McIntosh and Maass continued the work of Geddes and Maass. More accurate density hysteresis curves were obtained. The effect of small quantities of air mixed with the ethylene was investigated. Such an air-ethylene system could be heated to many degrees above the critical temperature without becoming homogeneous.

As well as from direct density measurements, the measurement of other physical properties has led to the conclusion that the liquid state exists above the critical temperature.

Determinations of the solubility of dyes and solids in liquids, through the critical temperature region, have been made. The observations of Hannay and Hogarth (22) on the system potassium iodide-alcohol are the first reported. They found that the solute was precipitated when the liquid was evaporated just below the critical temperature, but that it remained in solution after the meniscus had disappeared at temperatures slightly above the critical. These results were considered as indicating that the liquid existed above the critical temperature. Results in agreement with this were obtained by Cailletet and Hautefeuille (23), using the system iodine-carbon dioxide. The blue colour, due to the iodine, was seen to remain in the space occupied by the liquid, even several degrees above the critical temperature. However, Cailletet and Collerdeau (24) found that the oil of galbanum separated from carbon dioxide at the critical temperature. Picet (25) presented more evidence in support of liquid persistence in his observations of borneal- and alizarin-alcohol systems. Neither of these precipitated from the solution at a temperature slightly above the critical, yet both are insoluble in gaseous alcohol. Wilip (26) has reported similar results for borneal-ether systems, and Bertrand and Lecarme (27) for the systems potassium chromate-water and alizarin-alcohol. In general the results of solubility measurements are indicative of the persistence of the liquid state above the critical temperature.

The existence of critical opalescence has been reported by many observers and has been the subject of much discussion. The opalescence will occur on heating the system up to the critical temperature. The effect is, at first, limited to the phase boundary region and has its greatest intensity in the liquid phase. If the system is kept at one temperature long enough, or is stirred, or shaken, the opalescence will finally occupy the whole volume. On heating well above the critical temperature the opalescence disappears but reappears on subsequent cooling. It appears most intense just before condensation and in the boundary region. A brown colour is observed with some compounds which are otherwise colourless. The most generally accepted explanation for this phenomenon is that advanced by Smoluchowski (28) and based on the Einstein theory of density fluctuations. Kuster (29), with essentially the same concept, attributed the effect to local concentrations of density due to distribution of the energy among the molecules. On the other hand, Altschul (30), Donnan (31) and Trevers and Usher (32), regard the opalescence as due to droplets of liquid floating in the vapour. A similar opinion was held by Schroer (33) and Cardoso (34). They believe that the surface tension of the small drops of liquid did not become equal to zero at the critical temperature and thus the critical temperature for a system of small droplets is higher than that for the mass of the liquid. They define the true critical temperature as that of the disappearance of the opalescence. All of the attempts to explain opalescence stress the inhomogeneity of the system until the opalescence has disappeared. The whole question of opalescence has been investigated recently by Mason, Naldret and Maass (35), who found support for the opinion that the opalescence is due to liquid groups.

The study of the X-ray diffraction patterns of liquids by many investigators has yielded definite evidence of a structure in liquids. This structure is thought to be some type of molecular aggregation of ordinary gas molecules. Stewart (36) uses the term "cybotactic" groups in reference to these aggregates. The amount of grouping seems to be dependent on the temperature, while grouped and ungrouped molecules exist in equilibrium. X-ray studies of liquids in the critical region have been undertaken by Stewart, Noll (37), and Spangler (38), who have obtained definite indication that "cybotactic" groups exist at temperatures higher than the critical. Stewart found that the degree of liquid persistence depended to a greater extent on the specific volume than on the temperature and pressure. No "cybotactic" groups were found at temperatures higher than the critical unless the specific volume was higher than the critical volume. A decrease in the volume greatly increased the number of groups while increasing temperature only slightly decreased them. The grouping, it was concluded, is dependent largely on the distance between the molecules.

Conductivity measurements have yielded further evidence in favour of the discontinuity of state. Eversheim (39) measured the temperature coefficient of various ammonia solutions through the critical range. The conductivity did not equal zero at the critical temperature but rapidly approached it at a slightly higher temperature. Kraus and Franklin (40) obtained similar results with the system sulphur-ammonia, finding conductivity

$6.5^{o}C$ above the critical temperature. Walden and Centnerszer (41) found similar persistence of conductivity in binary mixtures.

Eversheim also measured the dielectric constants of a liquid and its vapour in the critical region (42). The dielectric constants of the two phases were not equal at the critical temperature but became so at a slightly higher one. More recently, Marsden and Maass (43) have found similar results with methyl ether and propylene. In the case of the former, the dielectric constants of the two phases became equal $8^{o}C$ above the critical temperature.

Winkler and Maass (44) have measured the surface tensions of methyl ether and propylene as they approach the critical temperature. They found that the surface tension-temperature curve does not become asymptotic to the temperature axis at the critical temperature. They conclude that the surface energy does not become equal to zero, which is interpreted as being indicative of a discontinuity of state still remaining at the critical point.

Further evidence in support of the theory of persistence was obtained from the work of Morris and Maass (46) on the adsorption of propylene on alumina. They found that a discontinuity in the adsorption processes accompanied a change from liquid to gas. Edwards and Maass (47) found similar effects with the adsorption of dimethyl ether on alumina. They interpreted these results as indicating an essential difference between liquid and compressed vapour.

The specific heat of the system ethylene was found by

Braughton, Pall and Maass (48) to depend on the thermal history of the system. Different specific heats were found for the heterogeneous and homogeneous systems depending on whether the substance was previously heated to above the critical temperature or not.

The reactivity of the hydrogen chloride-propylene system has been extensively studied by Maass and his co-workers. The unsaturated hydrocarbons and the hydrogen halides react homogeneously and in a reproducible manner when the reaction occurs wholly in the liquid state. No reaction whatever occurs in the gas state. A catylitic factor is involved which is peculiar to the liquid state. Sutherland and Maass (49) found that propylene and hydrogen chloride would not react when brought together as gases, heated above the critical temperature, and then compressed to a system denser than the liquid. Thus, the reaction does not depend on concentration alone. In a liquid mixture the reaction rate varies with temperature in the usual manner up to the critical temperature. Slightly above this temperature the rate drops to zero. Marsden and Maass (43) found that the presence of even an inert liquid, carbon tetrachloride, made the reaction possible between the two gases, thus supporting the catylitic hypothesis. These experiments clearly show a difference between liquid and vapour other than concentration. Holder and Maass (50) have repeated the work of Sutherland, Marsden and Maass with a refined experimental method. Holder found that in the critical region the "critical concentration" has a larger effect on the reactivity than the temperature. Here again the importance of specific volume on the persistence of structure is evident.

Viscosity determinations on the system ethylene in the critical region have been made by Mason and Maass (51), using a very sensitive oscillating disk method. They found, in agreement with Clarke (52), that there is a hysteresis in viscosity on heating and cooling. The temperature of disappearance of the liquid phase, as indicated by a minimum in the viscosity-temperature curve, is in good agreement with that presented in this thesis as determined from measured pressure isothermals.

From the above review of the information obtained so far on the critical state, it is clear that all the phenomena cannot be explained on the basis of the classical theory of the Continuity of State. It is evident that there must be some difference between the liquid and gaseous states, other than concentration. The concept of regional orientation, advanced by Maass, satisfies all the requirements. A quotation from O. Maass will give the best expression of what is meant by regional orientation:

> "The distinction between regional orientation and a small crystal is that all the atoms in a small crystal may be looked upon as belonging to the same molecule, whereas in a region where orientation has taken place the molecules retain their identity and have translatory and rotational energy possessing only an average orientation for a time. The regions in a liquid are not sharply defined, but pass gradually and without any discontinuity into one another.

These regions may be momentarily represented by arrows giving the direction of orientation. Contour lines around these arrows would represent the gradual diminution of orientation and blending with the direction of a neighbouring region. These contour lines would be continuously shifting, orientation arrows disappearing and new ones appearing in fresh places." (53)

The work described in this thesis is the continuation of that of Geddes and Maass and McIntosh and Maass. Two lines of investigation were undertaken.

As pointed out above, it has been shown that above the critical temperature as defined by the temperature of the disappearance of the meniscus, a heterogeneity in one component system persisted. By "molecular stirring", by heating the medium considerably above this temperature and then reproducing the original temperature, or by isothermal expansion, this heterogeneity disappeared and a homogeneous system was obtained which persisted indefinitely. heretofore Up till now it has been impossible to produce a heterogeneous system once the critical temperature, as defined above, has been passed. It was considered of importance to attempt to achieve this. An experimental method, described below, was developed whereby this is made possible.

It was considered important to accurately determine the isothermals in the critical region. Geddes had calculated the isothermals from the experimentally determined isobars but the accuracy was insufficient, particularly as a test for the prediction of Mayer and Harrison, referred to below. Mayer and Harrison predicted the existence of a region above the critical temperature where $\left[\frac{\partial p}{\partial V}\right]_T = 0$ would be equal to zero. With the hope of testing this prediction, and of obtaining further information about the nature of the liquid to gas transformation, a careful measurement of the isothermals throughout the critical region was undertaken. The results of these experiments have led the author to a picture of the liquid gas system which, in his opinion, adequately explains all of the experimental data. The experimental methods and results leading to this hypothesis are outlined below.

APPARATUS AND TECHNIQUE

In the course of the main investigations described below, two types of apparatus were used; hereafter they will be referred to as apparatus no.1 and no.2. Both designs had been used by former investigators but several new methods and devices have been added (19,20).

Apparatus No.1

This apparatus was designed for the study of the effect of compression, produced thermally, on the density of the liquid phase of the system ethylene in the critical region. The variables to be measured were density and temperature.

The ethylene was contained in a "Pyrex" glass bomb supported on a brass rod. The bomb was made from a tube by rounding one end and drawing the other down and sealing it to a capillary tube. The dimensions of the bomb were approximately 10 m.m. inside diameter, 3 m.m. wall thickness, and 350 m.m. length.

The bomb contained a McBain-Bakr balance and float (21) for the determination of density. The quartz spiral was suspended from a steel spring which clung to the sides of the bomb. When not buoyed up, the float rested on a support made from a small ring of glass wound with cotton. When thus resting, the spiral was extended to a point lower than where any readings were required. The volume of the float was .7614 c.c. and was measured by means of a picnometer. It had a diameter of .6 c.m. and a length of 2.5 c.m. It was made from "Pyrex" glass and was tested to a pressure of seventy-five atmospheres before calibration.

A method of manufacturing quartz spirals is described by Tapp (17). The spiral used in this case had approximately one hundred turns and a normal length of 4.075 c.m. Its diameter was approximately .5 c.m. The sensitivity of the spiral was determined by measuring its extension under various loads in the range of extensions where it was to be used and at a temperature within ten degrees of the critical temperature of ethylene. The lengths were measured by means of a cathetometer to an accuracy of .05 m.m. The spiral sensitivity was .00511 gms./m.m.

The density of the medium in which the float was suspended was calculated from the formula:-

$$d = \frac{W - (X-N)S}{V}\text{, where}$$

d = density of medium

W = weight of float

S = sensitivity of spiral

V = volume of float

N = normal length of spiral

X = extended length of spiral

With this apparatus relative density measurements can be reproduced with an accuracy of 0.1% when the extension of the spiral is measured with an accuracy of 0.05 m.m. The absolute density value depends on the volume of the float which is known to an accuracy of .3 to .4%.

A glass condenser jacket was made to fit over the upper portion of the bomb. The purpose of this, was to make it possible to warm or cool the upper end independently of the rest of the bomb. This jacket was attached to the bomb by means of a watertight rubber gasket, in a manner which permitted easy removal or replacement. The jacket was equipped with intake and output leads to allow a circulation of water through it. Two streams of water, from the hot and cold water taps, were passed into a mixing chamber, and thence through the jacket. The temperature of the jacket was taken to be the average of the temperatures of the in-going and out-going streams. This was sufficiently accurate, as the control of this temperature was not required to be precise.

The temperature of the bomb was controlled by placing it in a water thermostat, which is described below. After the bomb was filled and the water jacket fixed in position, the whole was immersed in the thermostat. When no water was passed through the jacket, the temperature of the whole length of the bomb was that of the thermostat. When water was circulated, the upper end was either heated or cooled and a temperature gradient thus maintained along the length of the bomb. The heating and cooling controls of the thermostat could easily be adjusted to compensate for the effect of the circulating water on the thermostat temperature.

It was important to be sure that the temperature of the water in the jacket returned to the temperature of the thermostat, after circulation ceased. Since the outside room was at a higher temperature than the thermostat, it was possible that heat might be conducted along the water leads. Small copper coils were placed in the bath in series with the leads, thus removing any possibility of heating from conduction. The importance of this precaution will be seen in the discussion of the experimental results.

A diagram of this apparatus is given in Figure 1.

Apparatus No.2

This apparatus was designed for the determination of the isothermals of ethylene in the critical region. The design used was adapted from the apparatus originated by Geddes and Maass (19), and uses the method of measuring an unknown pressure by balancing against a known pressure produced by carbon dioxide at a known temperature.

The apparatus consisted of two heavy walled "Pyrex" glass bombs connected by a capillary U-tube as shown in Figure 2. The U-tube was made in the particular shape shown, since it was necessary to raise a thermostat bath around each bomb independently and also to be able to freeze the connecting U-tube when the apparatus was not in use. The bombs were 35 m.m. long with internal diameter of 5 m.m. and wall thickness of 3 m.m. Since no spiral was needed it was possible to use a tube of smaller diameter than with apparatus no.1, thus greatly increasing the

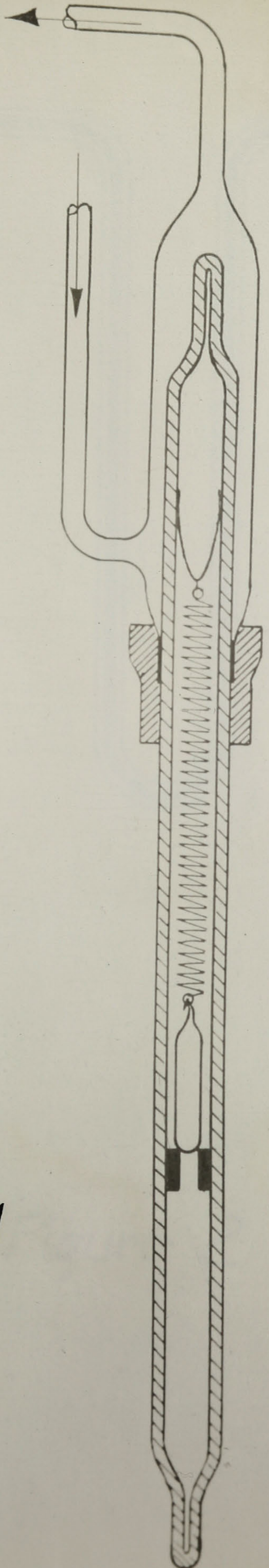

Figure 1

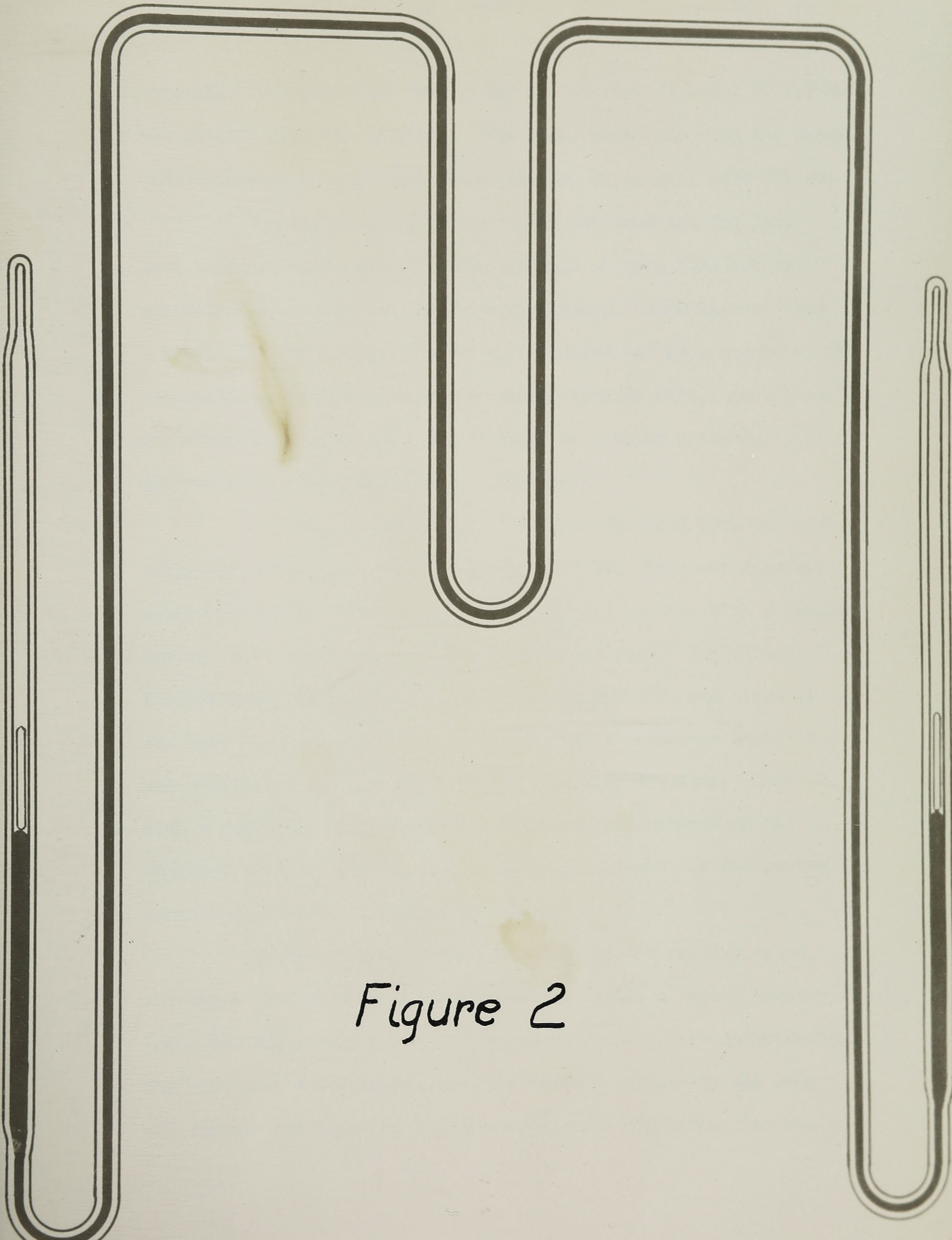

Figure 2

strength. The capillary tubing had an internal diameter of 2.5 m.m. and outside diameter of 8 m.m. The bombs were made with the upper ends connected to capillary tubes through which they were filled.

The right hand bomb contained ethylene and the left hand bomb carbon dioxide. The lower half of each bomb and the connecting capillary was filled with mercury. This mercury acts a piston in the manipulation of the ethylene and as a manometer in transmitting the pressure to the carbon dioxide side. Each bomb contained a small, glass encased, iron nail which acted as a stirrer when activated by an electro magnet.

The length volume ratio of the right hand bomb had been carefully determined before it was assembled. This was done by means of observing the position of a mercury surface with a cathetometer, and adding weighed quantities of mercury. The carbon dioxide bomb required no such accurate calibration and since it was made from the same piece of tubing as the ethylene bomb, it was considered to have approximately the same diameter. Thus with a change of mercury levels, the measured movement of the ethylene side was accompanied by an equal movement of the carbon dioxide side in the opposite direction.

After the bombs were assembled and the mercury added, and while the pressure in both sides was equal, a normal mercury level for the ethylene side was taken by means of the cathetometer. The volume of the ethylene from the mercury surface to the draw-off for all positions of the mercury surface was known from the calibration. The volume of the draw-off was computed by geometric estimation with sufficient accuracy since its value was very small. The volume of the stirrer was determined by means of a picnometer. From these data a graph of the mercury surface height, plotted against volume available for the ethylene, was constructed. These measurements were checked by repeating a point and a known isobar and gave excellent agreement.

The necessary pressure correction caused by the difference in level of the two mercury surfaces, in all but the normal position, was also plotted against the values of mercury height of the ethylene side. Thus, a reading of mercury height immediately gave the volume of the ethylene and the pressure correction. The true pressure was found by applying this correction to the vapour pressure of carbon dioxide at the temperature of the left hand bomb.

Before the construction of the apparatus, all glass tubing was carefully washed with distilled water. It was believed that harsher cleaning agents damaged the surface of the glass, weakening the tube and causing explosions. After it was in position the whole assembly was baked out at 200°C and under high vacuum for at least a half hour.

The mercury was distilled directly into the assembly, thus insuring that it was perfectly clean and dry. When the assembly was in position (see Fig. 3), two tubes with stop-cocks led from the upper ends of bombs to the pumps and gas storage volume. A side tube was fastened into the carbon dioxide lead. To this side tube was connected a small water condenser and boiling flask containing pure mercury. After evacuating the system, sufficient mercury to fill the entire U-tube and the lower half of the bombs was distilled in. This was done in the following manner. Sufficient mercury to fill the U-tube was first distilled into the carbon dioxide bomb, then, by closing the stop-cock on the ethylene side and carefully admitting air into the carbon dioxide side, the mercury was pushed over and filled the U-tube. By repeating this procedure sufficient mercury was added to bring the surfaces to the desired level.

The Thermostats

The thermostats used were essentially the same as those originally constructed by Geddes (19). Water was conveniently used as the thermostatic liquid since the temperatures desired were between 9.5 and 15°C. The general arrangement is illustrated in Figure 3.

Each thermostat consisted of a cylindrical container eighteen inches high and ten inches in diameter. The left hand container was a "Pyrex" glass jar, while the ethylene thermostat was made of sheet copper. These containers were supported on wooden cradles and were well insulated with sheep's wool. The right hand container was equipped with two windows so placed that the ethylene bomb could be clearly seen. The bomb was illuminated from behind by two 200 Watt frosted lamps, equipped with reflectors

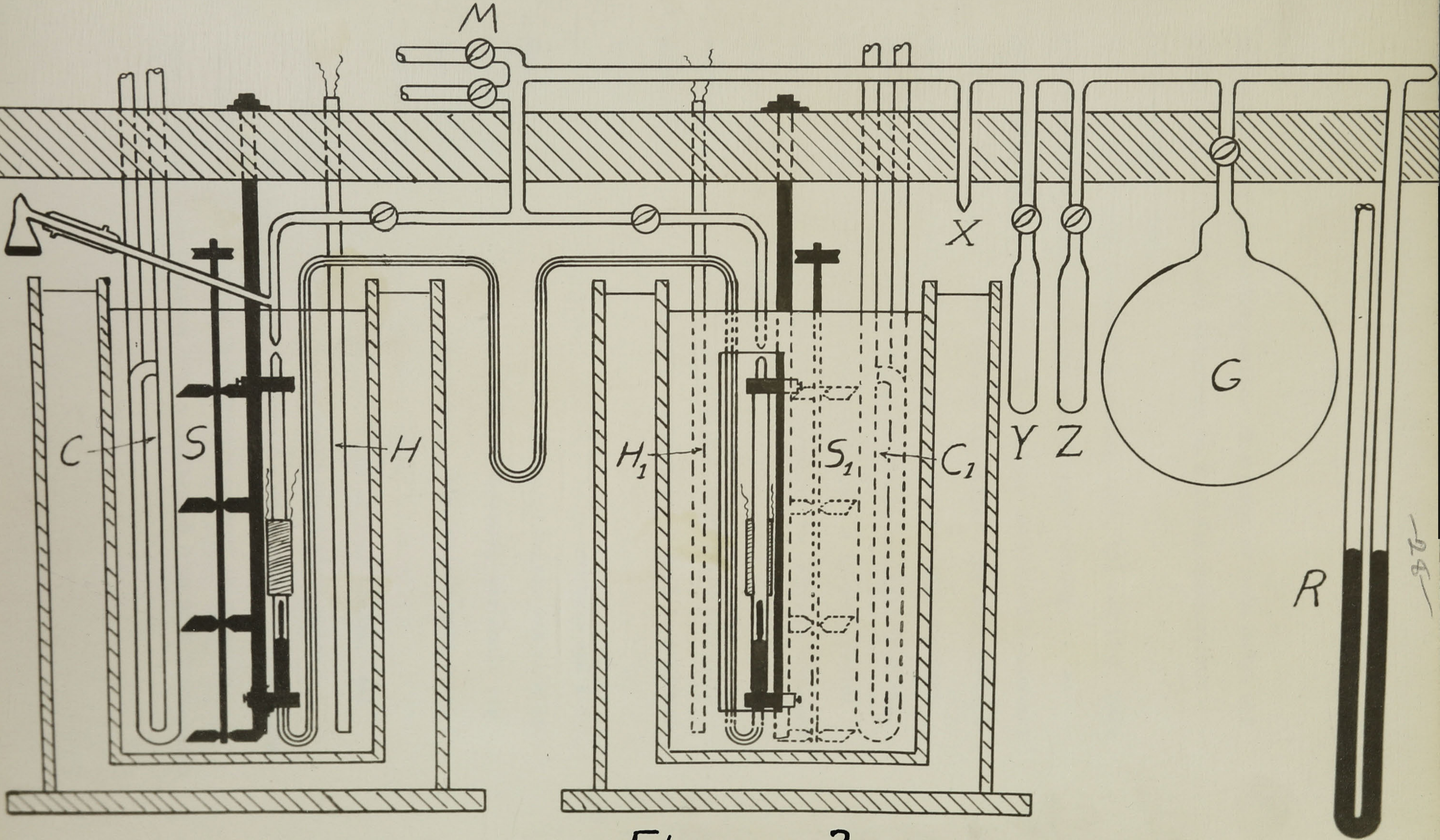

Figure 3

and cooled with circulating water. The front of both baths was illuminated from in front and above so that the thermometers could be easily seen.

Each bath contained a cooling coil, (C) and (C_1), made from six feet of half inch thin walled copper tubing. A two gallon water tank supported on the ceiling maintained a constant pressure for a steady flow through the coils. The rate of flow was adjusted by means of large taps. A smaller supplementary flow system was added and was used in the determination of the pressure volume isothermals reported below. A by-pass system of water flow was used. The flow necessary to maintain constant temperature was adjusted with a screw pinch-cock while a brief rapid flow, necessary when changing the temperature slightly, was achieved by briefly opening a spring pinch-cock in a different lead.

Each bath was equipped with a large 500 Watt and a small 100 Watt heater (H and H_1). The large heater was used in bringing the bath up to the desired temperature, the small one for maintaining constant temperature. Both heaters were controlled manually by means of rheostats.

Each bath had two stirrers (S) of four blades. All stirrers were belt driven by a variable speed shunt motor.

Temperatures were determined with Beckmann thermometers, calibrated with a standard Reichanstalt mercury thermometer. Each bath was also provided with a calibrated 0 to 50°C thermometer graduated in tenths. Thus alsolute temperature readings could be determined to at least 0.02°C and relative readings to 0.002°C.

All the apparatus, thermostats, heaters, cooling coils, thermometers, etc., were supported by the beam K. Since, when not under observation, it was necessary to cool the bombs with dry ice contained in Dewar flasks, the thermostats had to be easily removable. This was done by supporting the thermostat cradles with a system of ropes and pulleys, so that they could be raised and lowered at will.

Because of the high pressure, there was a constant possibility of explosion whenever the bombs were warmed up to the critical temperature. To protect the operator from the glass flying with such explosions, a double wall of heavy beaver-board was constructed in front of the apparatus. All observations were made through shatter proof plate glass windows, telescopes being used for temperature readings, etc. All controls, water flow, rheostats, ropes for moving the thermostats, etc., were operated from behind the protecting walls. The Dewar flasks which were placed around the bombs after each run were held in wooden frames. These frameworks could be raised and lowered from outside the wall by means of ropes and pulleys.

Purification of Gases and Filling

Great care was taken in the purification of the gases used in these experiments, since in former work on the critical phenomena much criticism was centered on this point.

The ethylene gas was supplied by the Ohio Chemical Company and was guaranteed to contain over 99% ethylene. This gas was distilled in a low temperature column of the Podbielniak type (54). This still was described in detail by D. Pall (45). Only a small middle fraction of constant boiling gas was used in the experiments.

The carbon dioxide used was obtained from clean powdered dry ice, and was purified by fractional distillation.

In filling the bombs the following procedure was followed:-

The sample of ethylene or carbon dioxide was first sealed into the apparatus' filling train at the point X in Figure 3. The apparatus was then completely pumped out through stop-cock (M) by means of a mercury diffusion pump backed by a "Hy-vac". M was then closed and the taps to Y and Z were also closed. Liquid air was removed from X and placed around Y or Z, while a bath of acetone-carbon dioxide mixture at -40°C was placed around X. The gas was then distilled from X to Y, the stop-cock M being occasionally opened to pump off any trace of non-condensable gas. When sufficient gas had been collected at Y, X was sealed off and the system evacuated completely. The liquid air was then replaced by acetone-carbon dioxide at Y, and about one third of the sample allowed to distill off. This was used to flush the calibrated storage volume (G), and the bomb to be filled. The remaining gas was then distilled into Z and the apparatus again evacuated. The stop-cock at Z was then opened and the storage volume flushed with a small amount of gas. The stop-cock was then closed and the apparatus evacuated. The stop-cock leading to the bomb was then closed and the storage volume allowed to fill. Z was then closed and left to stand in liquid air. The bomb was now carefully cooled, first with dry-ice-acetone and then with liquid air. By opening the stop-cock to the bomb, the necessary amount of gas, as measured by a drop in pressure on the manometer (R), was condensed into the bomb. The bomb was then sealed off at the capillary tip. The same procedure was followed for the carbon dioxide and ethylene.

In the case of the bomb containing a spiral and float the density was determined accurately from the spiral extension. Therefore it was not necessary to determine the amount of gas condensed with any particular care. However, with the apparatus which contained no spiral and float (#2), it was necessary to determine the amount of gas condensed with as great an accuracy as possible. The drop in pressure on the manometer was read to .1 m/m., which gave a total possible error of about .5 m/m. Since the overall drop was of the order of 10 c/m., this gives a possible error of .5%. The absolute density of the gas in the bomb at any time was therefore only known to .5%. However, the relative densities of different positions of the mercury level were limited only by the accuracy of the cathetometer and the original calibration of the bomb tube.

With the carbon dioxide, care had to be taken that the amount of gas condensed was such as would give a two phase system over the range of volumes and pressures necessary. This was done by calculation from the measured volume available for the carbon dioxide and the pressures to be expected as given by the data of earlier workers.

Experimental Procedure

Apparatus No.1.

With this apparatus only the right hand thermostat was used, since no pressures were measured.

After the bomb had been filled in the manner described above, it was packed in a Dewar flask filled with powdered carbon dioxide "snow". By repacking twice a day the bomb could be always kept at a low temperature.

In making a run, the thermostat was first cooled to a temperature below 9°C by adding ice. Cold acetone was then added to the "dry ice" in the Dewar, making a slush. The Dewar was then removed and the operator proceeded to his point of observation behind the protecting walls. After allowing several minutes for the bomb to warm, the thermostat was raised by means of the rope and pulleys, into its position around the bomb. With the apparatus in this position, the subsequent manipulation of temperature and reading of densities depended on the data required.

In the case of the compression experiments the following general order of experiment was followed with each bomb used. Without the cooling jacket in position, a complete density hysteresis curve for the critical region was first determined. This was done by slowly warming the bomb from a temperature well below the critical and taking density measurements at different temperatures, the float being in the liquid phase, until the density no longer changed with increasing temperature. The bomb was then cooled, and a similar series of density readings taken, until the temperature was again well below the critical. A curve of the type shown in Figure 4 was thus obtained. In taking any density measurement, the thermostat was brought slowly to the desired temperature and the spiral length measured by means of the cathetometer. The temperature was then held constant and spiral lengths measured until no change in length appeared for an interval of twenty minutes. The density corresponding to this length was then taken as the density of the liquid at that particular temperature. This normal hysteresis curve for any particular bomb was used as the reference curve to which the densities subsequent to various manipulations were related.

With the air-ethylene mixture similar preliminary measurements were made. The value of the mean density in this case, however, could not be obtained by heating the bomb to a few degrees above the critical temperature. It had already been shown by McIntosh and Maass (20) that the mean density for an air-ethylene mixture was best obtained by means of "molecular stirring". To do this the outer jacket was placed on the top of the bomb and cold water circulated through it. The jacket was maintained at about 5°C by tap water while the temperature of the bomb was raised to some value above the critical. Violent distillation occurred and after several such distillations of a few minutes duration, the density of the medium was found to be independent of the temperature at temperatures above 10.5°C. This density was taken to be the mean density. After having obtained this reference curve the compression experiments could be commenced.

To determine the effect of compression the bomb was first heated to 11.5°C and maintained at this temperature until the average density of the system was attained. In the case of the air-ethylene bomb, molecular stirring was used as described above. The thermostat was then cooled to the desired temperature. When temperature equilibrium had been reached the density value would now be represented by a point on curve B in Figure 4. Compression was then carried out by either of two methods.

By lowering the thermostat the upper portion of the bomb was allowed to project outside the bath; it was thus subjected to room temperature, which was some fifteen degrees higher than that of the bath. After the desired compression time, the thermostat was raised and a time-density curve taken. The second method of compression was by circulating warm water through the heating jacket as already described. The duration and extent of heating was varied as desired.

The heating jacket and its contained water had an insulating effect. Thus, during cooling from 11.5° to the desired temperature, when the jacket was used, the top of the bomb was always at a slightly higher temperature than the lower part, thus producing a slight compressional effect before the main compression was carried out. For the same reason, after the top of the bomb had been heated the rate of re-establishment of uniform temperature was slower than when no jacket was used.

It is important to note that at no time after heating to 11.5° was any part of the bomb at a temperature lower than that of the thermostat.

After having made a run, the closing down of the apparatus was the reverse of the commencing procedure. The thermostat was cooled as much as possible by means of the cooling coils, and lowered. The Dewar flask, attached to a stick and cords, was filled with "dry ice" and acetone mixture. This was raised slowly about the bomb. After the bomb cooled, the operator, entering in front of the walls, replaced the freezing mixture with carbon dioxide "snow".

Apparatus Number 2.

After each bomb was filled with its respective gas, it was packed in "dry ice". The mercury in the connecting U-tube was then frozen by a similar packing. Thus at the commencement of a run the two bombs and the connecting U-tube were all frozen.

The solid carbon dioxide in the Dewar flasks was first made into a soft slush by adding cold acetone. This was done so that the flasks could be easily removed without straining the glass tubing. The center U-tube was then submerged as much as possible into the freezing mixture. This was done in order to create as great as possible a contraction in the mercury in the U-tube, thus allowing for an expansion of the mercury in the bombs and their connecting capillary tubing when the thermostats were raised. Some expansion occurred in the capillary tubing before all the mercury had melted in the bottom of the bombs. The above precaution prevented the possible cracking of the capillary due to this expansion. The thermostats were then cooled and the Dewars removed from around the bombs. In raising the baths, care was taken to submerge all the mercury in as short a time as possible. If this were not done the mercury in the lower part of the bomb and capillary which was submerged first, would melt, and, since there was mercury above it which had not yet melted, the tube would be cracked due to the expansion.

The temperatures of the thermostats were then adjusted so as to give approximately the same pressure in each bomb. The Dewar flask was then lowered from around the connecting U-tube. The correct temperatures were taken from the vapour-pressure curve of carbon dioxide and ethylene as determined by former workers.

An isothermal run was made by keeping the ethylene bomb at constant temperature and changing the pressure by changing the temperature of the carbon dioxide bomb. The volume of the ethylene was determined from the height of the mercury surface as described above.

In closing the apparatus down, care was taken that the tip of the U-tube only was frozen at first to allow for the maximum contraction when starting the next run; otherwise the procedure was the same as for apparatus number 1.

A Note on Explosions and Their Causes.

The bombs used in these experiments had to stand a pressure of from fifty to fifty-one atmospheres. Because of this only specially selected glass was used and was treated with great care. In cleaning the glass, care was taken not to damage the inside surface, either by the use of harsh cleaning agents, or by scratches. In working the glass the seals were always annealed slowly with a hand torch. Despite all care to prevent explosions no satisfactory technique of construction was found. During the course of the investigation, fifteen complete bomb assemblies were constructed. Of these only three were sufficiently strong to be of use.

The bombs were always tested to seventy-five atmospheres pressure on a Caillete pump before being assembled. It was not practical to test them for more than a half hour, yet bombs which stood this test often exploded after several hours under fifty atmospheres pressure. Two types of explosion were observed. The first was a violent and complete collapse of the bomb wall. The second was a breaking of the capillary U-tube.

The first type of explosion was attributed to a weakness of the wall of the tube itself, perhaps caused by strains produced in the working of the glass and by the nature of the inside surface. In an attempt to overcome this, the effect of annealing the glass was studied. A series of small bombs, made of the same tubing, were tested for their bursting pressures, some being annealed and others un-annealed. The annealing was carried out by placing them in an oven and heating to above 550°C for two hours and then cooling over a period of twelve hours. No reproducible or uniform effect could be observed from these experiments.

The breaks in the U-tube were sometimes caused by a careless manipulation of the freezing and melting of the mercury necessary in using the apparatus. The precautions adopted to avoid this are outlined above. This type of break usually caused a lengthways split of the capillary. More often, the U-tube would shear off at the curved parts. This appeared to be due to a Burdon effect on the bends, when they were heated and cooled through a temperature range of approximately 90°. This was an inherent fault in the apparatus and nothing could be done to prevent it.

THE EXPERIMENTAL RESULTS

The experimental results can be conveniently divided into two sections. The effects produced by thermal compression on the ethylene and air-ethylene systems naturally belong together. The second division contains the data of the pressure isothermals and various calculations arising from them. As well as the main results, both of which give us new information about the general problem of critical phenomena, the experiments necessitated the repeating of much earlier work. This independent check on former results is not unimportant, and in general corroborates and extends them.

The Compression experiments.

Compression experiments were carried out on three different systems. The first two were with pure ethylene of average density, 0.1944 gms./c.c. and 0.2166 gms./cc. The third was with an air ethylene system of average density, 0.2108 gms./c.c. All of these measurements were made with the same bomb assembly. It was first filled to a density of .1944 gms./c.c., then emptied and re-filled to 0.2166 gms./c.c. The air ethylene sample was obtained by freezing the second filling with liquid air, opening the tip of the bomb, and re-sealing. Some ethylene was lost in the procedure giving the somewhat lower mean density of 0.2108 gms./c.c. The air admitted was the ordinary air of the room and was calculated to be 1.5% of the contained gas by weight. This bomb unfortunately exploded before all of the data desired of the air ethylene sample could be obtained.

The Density Isochores of the Systems.

As pointed out above, it was necessary to obtain complete density isochores of each filling before measuring the effect of compression. Tables I and II give these data for the pure ethylene samples. Figures 4 and 5 show the density curves. The solid white circles are the experimental points. The upper curve (A) is the heating curve and the lower (B) the cooling curve. Geddes and Maass have reported two isochores of this type for ethylene (19). McIntosh and Maass have also reported the complete density hysteresis curve for ethylene (20). The results of the present measurements are in complete agreement with McIntosh and Maass and differ from those of Geddes and Maass in that the mean density is reached at approximately one degree above the critical temperature, rather than four or five degrees. This difference has already been discussed by McIntosh and is attributed by him to the probable contamination of Geddes' sample of ethylene (19). However, the results are in general agreement with all others reported for ethylene, and are in accord with similar experiments on propylene and methyl ether obtained in this laboratory (17,18).

The density isochore for the air ethylene system differs from that for pure ethylene. It has already been reported by McIntosh and Maass that for an air ethylene mixture the mean

TABLE I

Density Temperature Curve

Mean Density .1994 gms./c.c.

Temperature °C	Density gms./c.c.
8.00	.2658
8.50	.2554
9.00	.2385
9.17	.2263
9.37	.2158
9.57	.2085
9.87	.2036
10.47	.2010
10.97	.1994
11.27	.1994
9.95	.1994
9.50	.1994
9.40	.1997
9.10	.2007
9.00	.2200
8.50	.2543

TABLE II

Density Temperature Curve

Mean Density 0.2166 gms./c.c.

Temperature °C	Density gms./c.c.
8.00	.2665
8.60	.2554
8.80	.2495
9.00	.2445
9.10	.2416
9.30	.2327
9.50	.2277
10.00	.2206
11.50	.2166
9.50	.2166
9.40	.2169
9.30	.2200
9.10	.2331
9.00	.2395
8.80	.2476

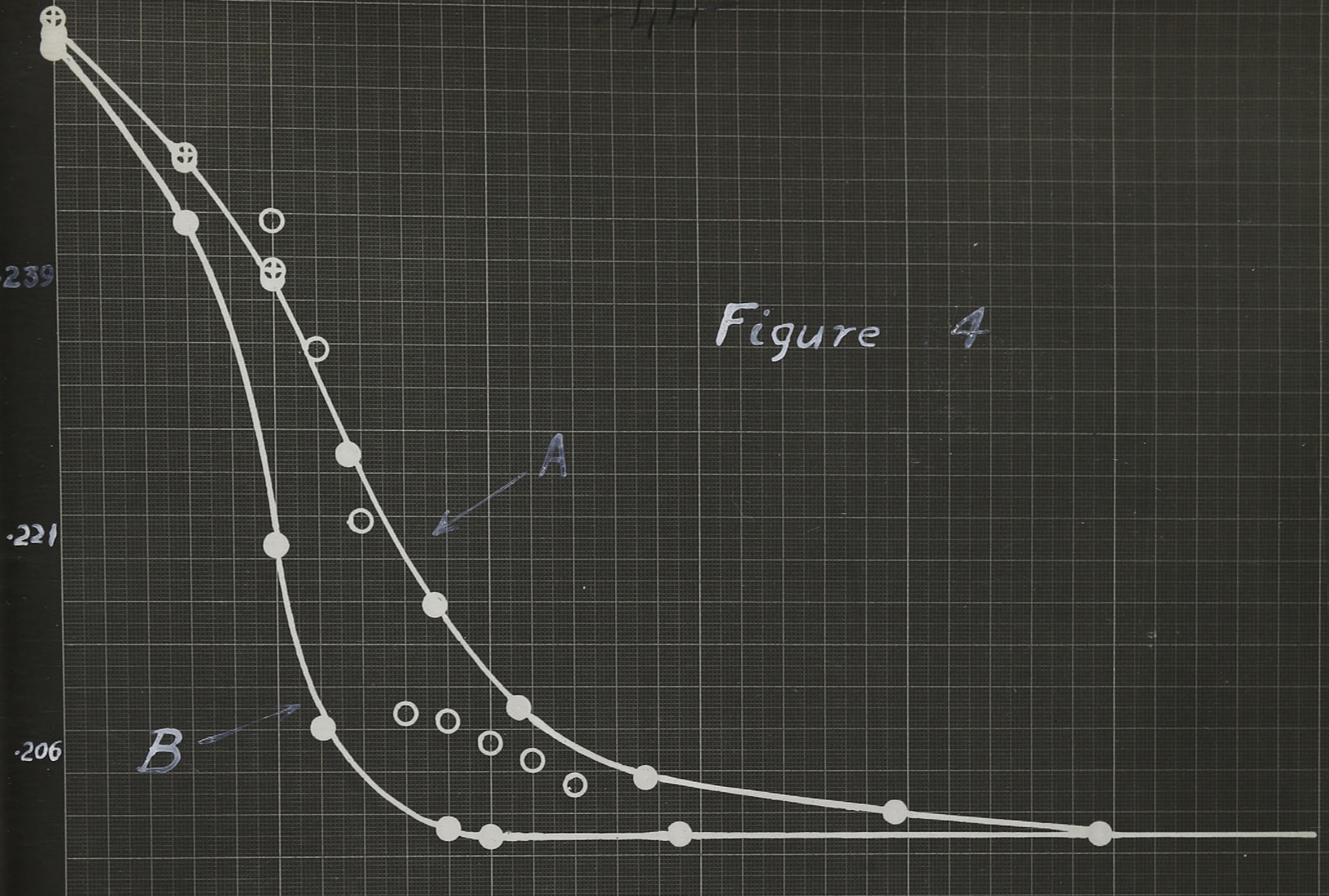

Figure 4

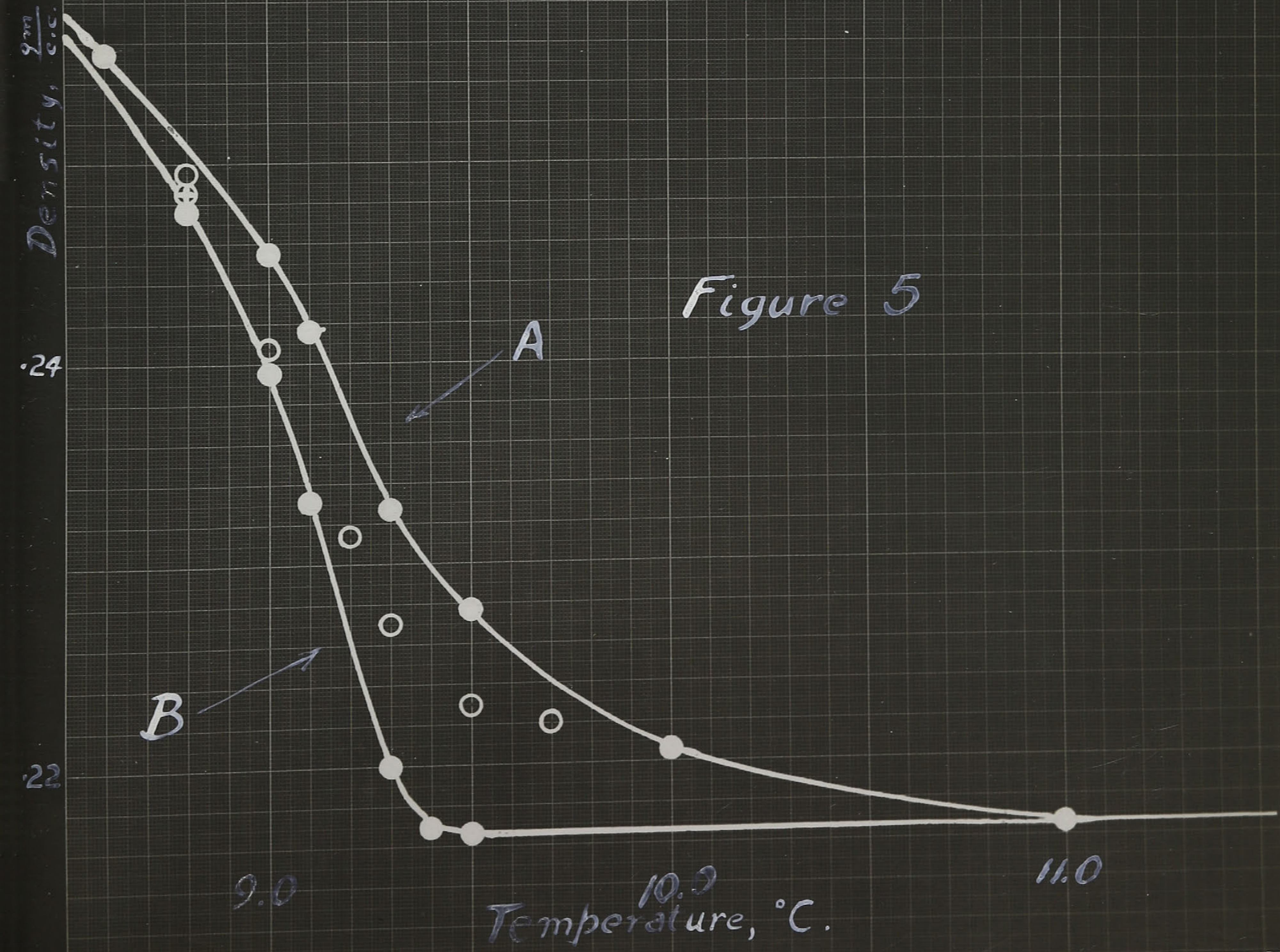

Figure 5

density is not reached at temperatures well above the critical, and that the cooling curves for such systems fall only slightly below the heating curves making only slight hystereses. In both these respects air ethylene systems differ greatly from pure ethylene systems (20). The density isochores for the system reported here are given in tables III and IV and are shown graphically in figures 6 and 7. The behaviour observed is exactly as described by McIntosh. Two complete curves were taken. In the latter case the system was heated to 34.5°C. This is, much higher than any formerly reported and it is of interest to note that even 25° above the critical temperature the system is not yet homogeneous but shows a density difference of 7%. The mean density was obtained by "molecular stirring" as described above, and after such treatment the density was found to be independent of the temperature at temperatures above the critical temperature.

It will be seen that the data of table IV do not agree with those of table III, yet both were measured in the same way on the same apparatus with the same filling. The figures of table IV were obtained immediately after the air was added. The ethylene was melted and the density measurements taken as soon as the system had reached the necessary temperature. These values could not be repeated at any later time. The data of table III were obtained after the bomb had been heated up and subsequently cooled. The figures were checked several times later and no disagreement was found. It is considered likely

TABLE III

Air Ethylene Mixture

Density temperature relations after standing at -78°C for at least 12 hours or longer

Temperature °C	Density gms./c.c.
8.60	.2703
9.00	.2678
9.50	.2644
10.00	.2604
11.00	.2543
12.00	.2492
14.00	.2405
17.00	.2338
20.00	.2294
17.00	.2324
15.00	.2365
12.50	.2442
11.00	.2530
9.50	.2629
8.60	.2695
8.00	.2767

TABLE IV

Air Ethylene Mixture

Density Temperature Relations immediately after adding air to the solid ethylene

Temperature °C	Density gms./c.c.
8.60	.2740
8.90	.2722
9.20	.2715
9.50	.2699
9.80	.2688
10.30	.2659
12.30	.2546
13.80	.2486
15.30	.2432
16.80	.2391
18.30	.2355
19.80	.2334
21.30	.2314
24.30	.2280
27.30	.2260
30.30	.2247
34.50	.2230
28.00	.2251
22.00	.2283
16.50	.2352
12.00	.2530
10.00	.2621
9.00	.2695

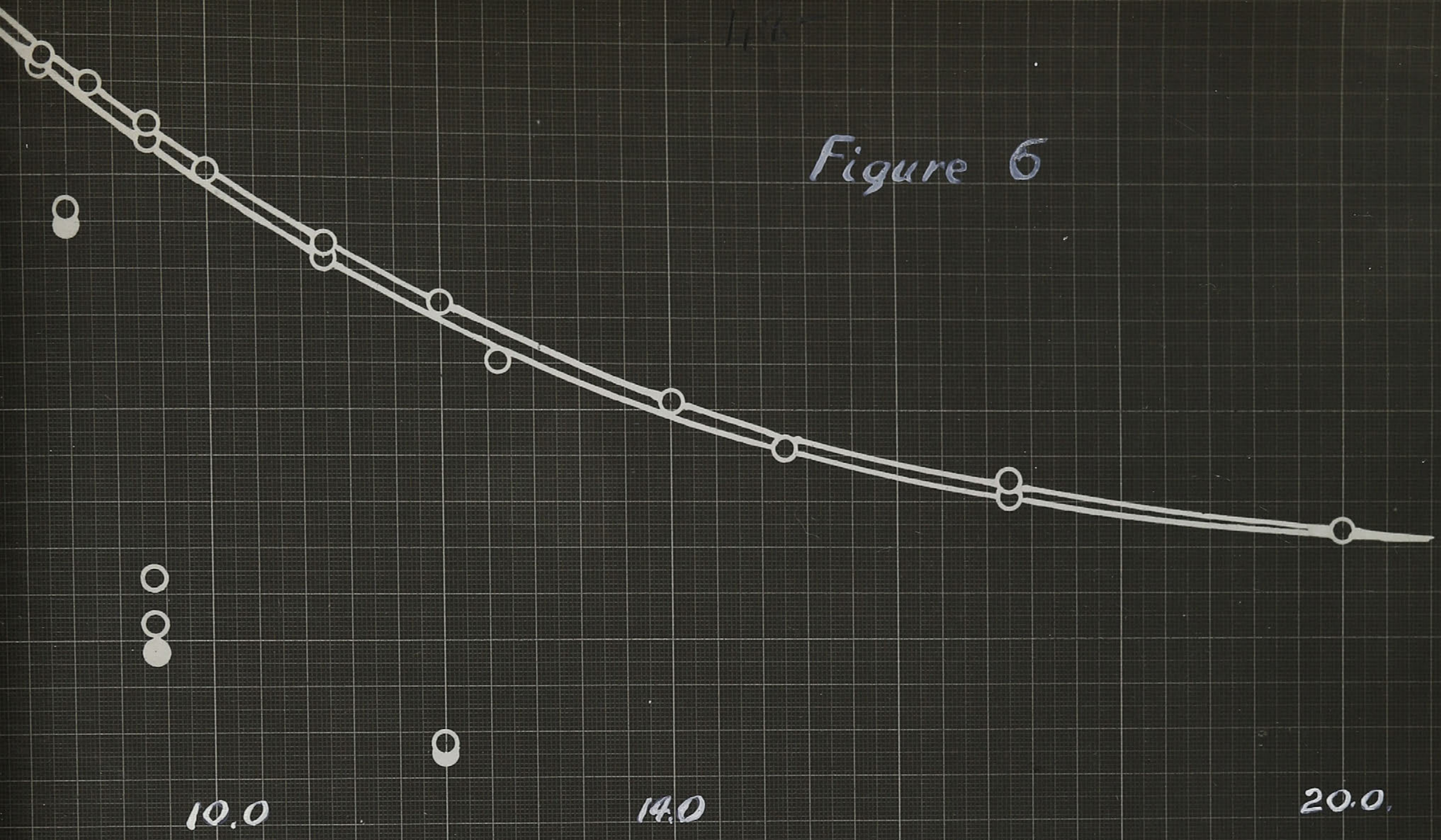
Figure 6

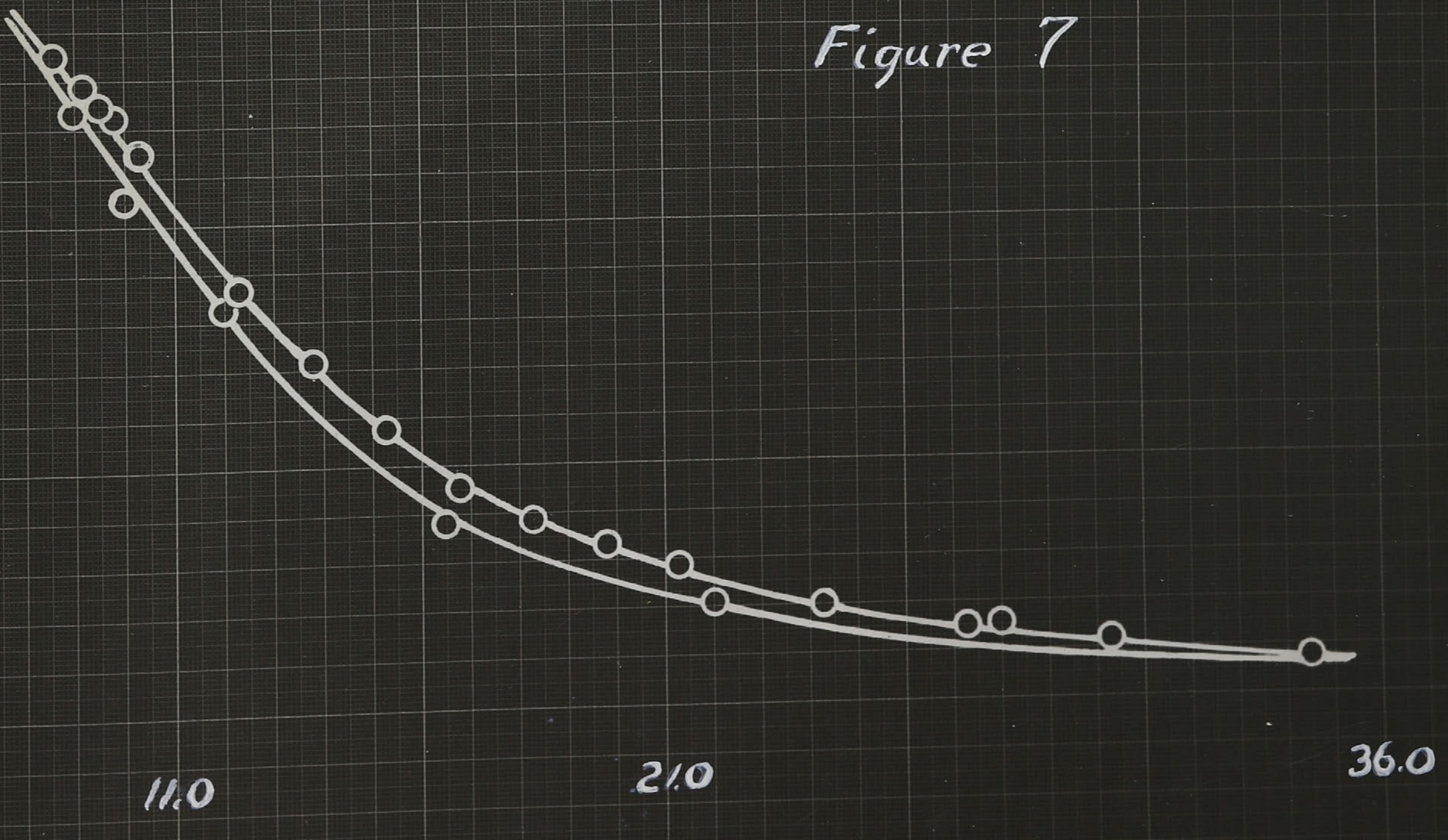
Figure 7

that the first measurements made differ from all subsequent ones because the air had not yet dissolved in the liquid phase. This process apparently takes place very slowly and is probably greatly aided by heating and cooling the system. These observations were not repeated because this necessitated opening and re-filling the bomb.

The critical temperature is defined as that temperature above which there is no visible demarcation between the phases, as the system is heated in a stationary bomb. With pure ethylene this phenomenon can be easily observed, and an agreement to .01°C is found between many observations by different people. The author records 9.50°C which is the accepted critical temperature for ethylene. As has been pointed out by Geddes (19), this temperature is reproducable only if the system is cooled well below the critical temperature and then heated up to that temperature. The temperature of reappearance of the meniscus on cooling the system from above the critical temperature is .3°C lower than the critical. With pure ethylene, this phenomenon too takes place over a very narrow temperature region, and all observations are in agreement. On the other hand, with air-ethylene systems, both the phenomenon of disappearance and re-appearance of the meniscus take place gradually over a wide temperature range, and in such a manner that the observer cannot be sure when the demarcation disappears. However, at 9.50°C a noticeable difference occurs with the complete disappearance of a surface and the formation of a widening region of changing refractivity. This phenomenon can be considered as indicating the critical temperature. With the air-ethylene mixture the meniscus reappears by the contraction of such a region rather than by the formation of a fog of droplets, as is the case with pure ethylene. In both cases noticeable brown colour appears in the surface region.

The Effects of Compression.

The results of the compression experiments on ethylene are listed in tables below. The data have been presented in three sections. The first deals with the results obtained when the substance was maintained at a higher temperature than the classical critical of 9.50°C; the second, with those results obtained between 9.50°C and 9.20°C; and the third group with those of temperatures of 9.17° and lower. The reason for this classification is that at 9.17°C spontaneous condensation occurs, and a liquid phase is formed which possesses a density, as measured in this manner, different from that of the original liquid of the same temperature. There is thus seen to be three broad divisions of the system, the first being at temperatures above the last visual heterogeneity; the second at temperatures lower than this, but above the temperature of spontaneous condensation, without compression; and the third at temperatures below that at which the meniscus normally reappears.

Table V contains the compressional data obtained with both samples above the critical temperature. The measurements designated "T" refer to compression with the jacket in position. The other measurements were made by exposing the upper part of the bomb to the air of the room. Times of compression are also recorded in the table.

Table VI gives the data for the temperatures between 9.20°C and 9.50°C. The observations marked "C" indicate that the meniscus re-formed subsequent to compression.

The results below 9.17°C are given in table VII. The symbol "T" has the same significance as before.

Table VIII gives the density relations and meniscus positions of the various two phase systems both before and after compression.

These results are represented graphically in Figures 4 and 5. The open circles are obtained with the heating jacket in position, the closed circles when no jacket was used.

The technique of the experiments has been described above. It is important to note that all compressional data were obtained upon systems which were originally in a state represented by curve B in the diagrams. At no time after compression was any part of the system at a temperature lower than that of the thermostat. Much of the data was checked satisfactorily by repeating the experiments. The three divisions made above for the presentation of the data are maintained for their interpretation.

TABLE V

Summary of the Results of Compression above the Critical Temperature

Temperature °C	Density gms./c.c.	Duration, Mins.	
Part I	Average Density 0.1994 gms./c.c.		
9.50	.2060	-	T
9.50	.2060	30	T
9.50	.2060	5	T
9.50	.1994	30	-
9.60	.2048	5	T
9.60	.2048	5	T
9.70	.2030	-	T
9.70	.1994	10	-
Part II	Average Density 0.2166 gms./c.c.		
9.70	.2220	7	T
9.50	.2230	7	T

TABLE VI

Summary of the Results of Compression below the Critical Temperature and above the Temperature of Reappearance of the Meniscus

Temperature °C		Density gms./c.c.	Duration, Mins.	
Part I Average Density 0.1994 gms./c.c.				
9.40		.2074	10	T
9.30		.2081	10	T
9.20	C	.2217	10	T
Part II Average Density 0.2166 gms./c.c.				
9.30		.2270	10	T
9.20	C	.2314	10	T

TABLE VII

Summary of the Results of Compression below the Temperature of Meniscus Reappearance

Temperature °C	Density gms./c.c.	Duration, Mins.	
Part I	Average Density 0.1944 gms./c.c.		
9.10	.2335	5	T
9.10	.2335	-	T
9.00	.2426	-	T
9.00	.2391	-	-
8.80	.2472	-	-
8.50	.2564	-	-
Part II	Average Density 0.2166 gms./c.c.		
9.00	.2406	-	T
8.80	.2492	-	T
8.80	.2486	-	-

TABLE VIII

Compressional Experiments. Density Relations and Meniscus Heights.

Temperature °C	Density after Compression	Density Curve A	Density Curve B	Meniscus Curve A	Meniscus Curve B	Meniscus after Compression
			Mean Density 0.1994 gms./c.c.			
8.50	.2564	.2554	.2543	20.8	20.3	20.8
8.80	.2472	.2466	-	21.1	19.7	20.8
9.00	.2426	.2385	-	21.3	18.9	20.7
9.10	.2335	.2330	-	21.4	18.0	20.7
			Mean Density 0.2166 gms./c.c.			
8.80	.2486	.2495	.2476	-	26.3	27.0

(1) Above the critical temperature it is clear that thermal compression of a homogeneous system re-creates heterogeneity.

It has been found by many earlier workers that a heterogeneity of density persists above the critical temperature as defined as that temperature at which the meniscus disappears. This heterogeneity was found to be destroyed by heating to a temperature well above the critical, by expansion and compression to the proper density values, by temperature fluctuations, and by "molecular stirring". No method had been found to reverse this phenomenon, that is, to create a heterogeneous system from a homogeneous one, except by cooling below the point of condensation. Thermal compression as described above is such a method. Its main significance is that since the system is not cooled below the temperature of condensation, the density heterogeneity cannot be explained as the effect of an extremely slow density change with rising temperature, as has been suggested by some workers.

Another hypothesis is suggested below.

The amount of heterogeneity which is reformed by the compression is independent of the magnitude and duration of the temperature gradient. This can only be claimed within the ranges of time and temperature difference observed in these experiments. It is not unlikely that very brief time or slight temperature difference would not re-create the same density difference.

The heterogeneity re-formed does, however, depend on the rate of re-establishment of uniform temperature along the length of the bomb, that is, on the rate of removal of compression. In this region, above the critical temperature, heterogeneity only persists after a slow removal of compression. This is seen from the fact that compression by means of the water jacket does cause persistence while compression by means of exposing the top of the bomb to the temperature of the room does not. The insulating effect of the water jacket has already been commented on. This difference must be due to the rate of temperature return since particular care was taken to see that, after compression, the temperature of the thermostat was reached in both cases.

Density readings taken subsequent to compression always became constant in less than thirty minutes. Experiments were made to show that the constancy did not tend to disappear and was as persistent as that observed when heating the system from below the critical temperature. Density readings were made as long as a hundred minutes after constant density had been observed. No further change could be detected.

(2) At temperatures below the critical temperature and above the temperature of reappearance of the meniscus the effect of compression was similar to that above the critical temperature. An important difference, however, was that at a temperature slightly greater than the temperature of reappearance of the meniscus compression caused a persistent condensation of a liquid phase. At such a temperature the rate of removal of compression had only a slight effect, for once the liquid phase separated, its density

was only slightly less after a rapid removal of temperature gradient than when the heating jacket was used. The liquid which condensed at 9.20°C was of a different density than that of the original heating curve at 9.20°C. An explanation of this difference is offered in the next paragraph.

(3) Below the temperature of reappearance of the meniscus there is always a liquid phase present. Thermal compression of such a system, in the state represented by curve B, in the diagrams, results in the increase of the density and the amount of the liquid present. The rate of removal of compression and the extent and duration of compression have little effect within the range investigated. The increase in density of the liquid is such as to re-create the original density of the heating curve. In the case of the first sample (mean density 0.1994 gms./c.c.), the liquid formed by compression at 9.00°C was slightly denser than that of the original heating curve. Since this occurred only with the sample of lower density, it is thought to be due to the following fact:

The branching of the density-temperature curves from a common density curve at lower temperatures, for various mass volume ratios, occurs at some temperature below 9.00°C for mean densities less than 0.200 gms./c.c. For this reason it is possible to have a stable liquid at 9.00°C of higher density than the heating curve of a system of mean density .1994 gms./c.c. Such a liquid is formed by compression. Tables VII and VIII give the effect of compression on the density and amount of liquid. Two concepts of what constitute the liquid phase have been suggested which give explanations of the existence of different densities for the same liquid at the same temperature. Geddes has applied the theory of orientation, while Bradley, Browne, and Hale (55) have followed Traube in making a distinction between the molecules of a "real" liquid and a "real" gas. This subject will be referred to in a later section.

The data for the air-ethylene system is given in Table IX and appear graphically in figure 6. Heterogeneity was recreated by compression in the same manner as with the pure ethylene system. One difference is to be noted - the duration of compression determined the degree of heterogeneity produced, the density difference becoming greater the longer the compression. No such effect was observed with pure ethylene. An air-ethylene system, above the temperature of condensation, which has been subjected to "molecular stirring", has the air distributed evenly throughout. The system is therefore similar to pure ethylene on curve B, with air dissolved in it. The effect of the air may be to slow down the formation of the heterogeneity; in this way increased duration produces greater density difference.

Pressure-Volume Isothermals of the System Ethylene.

By means of apparatus number 2, already described, the pressure-volume isothermals of the system ethylene were obtained between 8.92°C and 10.00°C. The data is presented in Table X and

TABLE IX

Compression of the Air-Ethylene Mixture

Mean Density 0.2108 gms./c.c.

Temperature °C	Density before Compression	Density after Compression	Duration
9.50	.2189	.2214	10 mins.
8.80	.2557	.2570	10 mins.
9.50	.2189	.2254	60 mins.
12.00	.2108	.2121	10 mins.

TABLE X

Pressure-Volume-Temperature Relations of Ethylene

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 8.92°C		
2.532	0.716	3.563	49.92
2.587	0.716	3.613	49.73
2.672	0.716	3.731	49.54
2.893	0.716	4.040	49.45
3.271	0.716	4.568	49.45
3.681	0.716	5.141	49.46
4.303	0.716	6.009	49.38
4.317	0.716	6.029	49.34
	Isothermal at 9.22°C		
2.590	0.716	3.617	50.18
2.613	0.716	3.649	50.06
2.665	0.716	3.708	49.96
2.715	0.716	3.791	49.87

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.22°C (continued)		
2.794	0.716	3.902	49.83
2.830	0.716	3.952	49.80
2.970	0.716	4.148	49.75
3.284	0.716	4.586	49.75
3.666	0.716	5.120	49.73
3.876	0.716	5.410	49.72
4.006	0.716	5.594	49.68
4.174	0.716	5.831	49.65
	Isothermal at 9.42°C		
2.710	0.716	3.770	50.26
2.735	0.716	3.819	50.15
2.838	0.716	3.963	50.06
2.950	0.716	4.120	50.02
3.176	0.716	4.437	49.99
3.300	0.716	4.609	49.99

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.42°C (continued)		
3.550	0.716	4.958	49.97
3.723	0.716	5.199	49.94
3.910	0.716	5.446	49.90
4.104	0.716	5.731	49.85
	Isothermal at 9.50°C		
2.705	0.716	3.777	50.44
2.722	0.716	3.801	50.34
2.762	0.716	3.857	50.24
2.789	0.716	3.895	50.21
2.829	0.716	3.951	50.19
2.908	0.716	4.047	50.14
2.970	0.716	4.148	50.12
3.235	0.716	4.519	50.08
3.455	0.716	4.826	50.07
3.624	0.716	5.061	50.05
3.857	0.716	5.386	49.98
4.197	0.716	5.861	49.92

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.60°C		
2.695	0.716	3.763	50.52
2.713	0.716	3.775	50.45
2.756	0.716	3.849	50.34
2.854	0.716	3.986	50.27
3.135	0.716	4.378	50.18
3.360	0.716	4.692	50.17
3.512	0.716	4.891	50.15
3.607	0.716	5.037	50.14
3.710	0.716	5.181	50.13
3.859	0.716	5.389	50.09
4.020	0.716	5.614	50.05
	Isothermal at 9.70°C		
2.823	0.722	3.909	50.42
2.884	0.722	3.994	50.35
2.953	0.722	4.090	50.30
3.109	0.722	4.306	50.28

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.70°C (continued)		
3.187	0.722	4.414	50.28
3.318	0.722	4.605	50.27
3.414	0.722	4.729	50.25
3.640	0.722	5.041	50.22
3.885	0.722	5.381	50.18
4.004	0.722	5.546	50.17
	Isothermal at 9.80°C		
2.761	0.722	3.824	50.65
2.776	0.722	3.844	50.61
2.808	0.722	3.889	50.56
2.863	0.722	3.965	50.50
2.902	0.722	4.019	50.47
2.954	0.722	4.091	50.44
3.025	0.722	4.189	50.42
3.066	0.722	4.246	50.40

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.80°C (continued)		
3.108	0.722	4.304	50.39
3.197	0.722	4.429	50.39
3.262	0.722	4.518	50.38
3.328	0.722	4.609	50.37
3.464	0.722	4.792	50.34
3.635	0.722	5.030	50.32
	Isothermal at 9.90°C		
2.770	0.722	3.837	50.74
2.807	0.722	3.890	50.69
2.854	0.722	3.953	50.65
2.923	0.722	4.048	50.60
2.961	0.722	4.101	50.57
3.030	0.722	4.197	50.54
3.072	0.722	4.255	50.52
3.132	0.722	4.338	50.51

TABLE X (cont'd)

Experimental Volume in c.c.	Amount of Ethylene in gms.	Specific Volume in c.c.	Pressure in Atmospheres
	Isothermal at 9.90°C (continued)		
3.224	0.722	4.466	50.50
3.302	0.722	4.574	50.48
3.512	0.722	4.864	50.45
3.737	0.722	5.178	50.42
	Isothermal at 10.00°C		
2.820	0.722	3.905	50.79
2.913	0.722	4.034	50.72
3.005	0.722	4.162	50.67
3.045	0.722	4.217	50.66
3.083	0.722	4.270	50.64
3.155	0.722	4.370	50.63
3.236	0.722	4.482	50.61
3.396	0.722	4.703	50.57
3.750	0.722	5.194	50.51

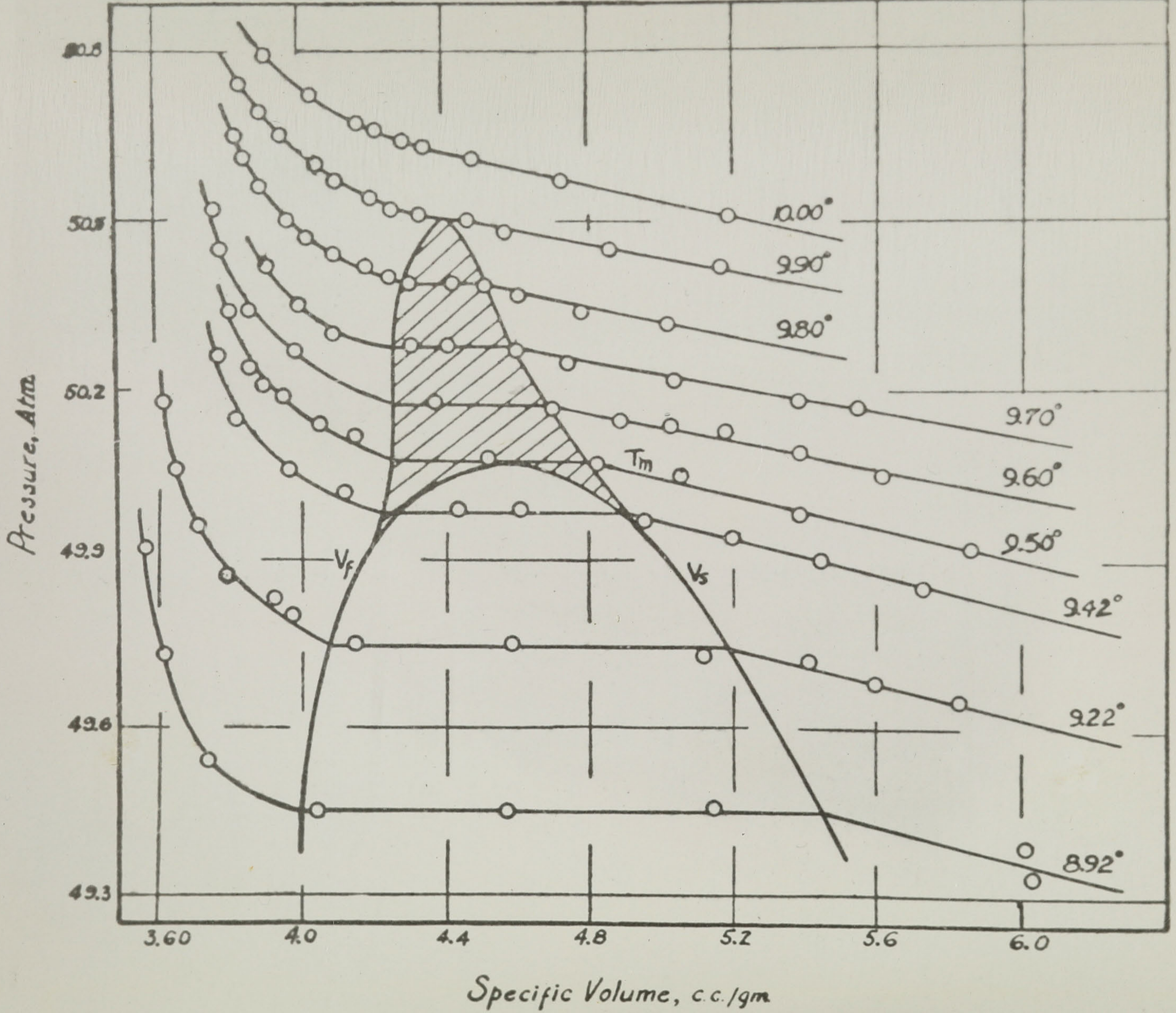
50.8
50.5
50.2
49.9
49.6
49.3
Pressure, Atm.
3.60
4.0
4.4
4.8
5.2
5.6
6.0
Specific Volume, c.c./gm
10.00°
9.90°
9.80°
9.70°
9.60°
9.50°
9.42°
9.22°
8.92°
Tm
Vf
Vs

Figure 8

appear graphically in figure 8. The method of measurement is already described.

It was found that both above and below the critical temperature, the isothermals showed regions of density where $\left[\frac{\partial p}{\partial V}\right]_T = 0$. Such a region could no longer be observed on the isothermal at 10.00°C. The complete envelope of this region was determined and appears in the diagram. The lower curve shows the manner in which this envelope would be drawn, rounding off at the critical temperature, on the basis of the classical theory. The upper curve, experimentally determined, includes a shaded region wherein $\left[\frac{\partial p}{\partial V}\right]_T = 0$ above the critical temperature. The envelope of this region should represent the true density-temperature curve, and anywhere within it the system behaves like a truly two phase system, although in part above the critical temperature. An objection arises in that a one phase system of very great compressibility would behave like a two phase system, in that would apparently equal zero. In an attempt to clear this point, the direction of measurement along the isothermal at 9.60°C was reversed, that is, the substance was first expanded to a point beyond the flat region of the isothermal and the pressure then increased. After temperature equilibrium had been reached, the pressure was maintained constant for ten minutes. A series of measurements with increasing pressures were made in this manner, and the upper curve of figure 9 was obtained. The data appear in table XI. This shows that the compressibility of the system is

TABLE XI

Isothermal at 9.60°C

Expansion from Liquid and Compression from Vapour

Experimental Volume in c.c.	Pressure in Atmospheres
Expansion	
2.695	50.52
2.713	50.45
2.756	50.34
2.854	50.27
3.135	50.18
3.360	50.17
3.512	50.15
3.607	50.14
3.710	50.13
3.859	50.09
4.024	50.05
Compression	
4.000	50.10
3.958	50.16
3.903	50.20
3.782	50.23
3.586	50.29
3.148	50.34
2.858	50.36
2.753	50.42

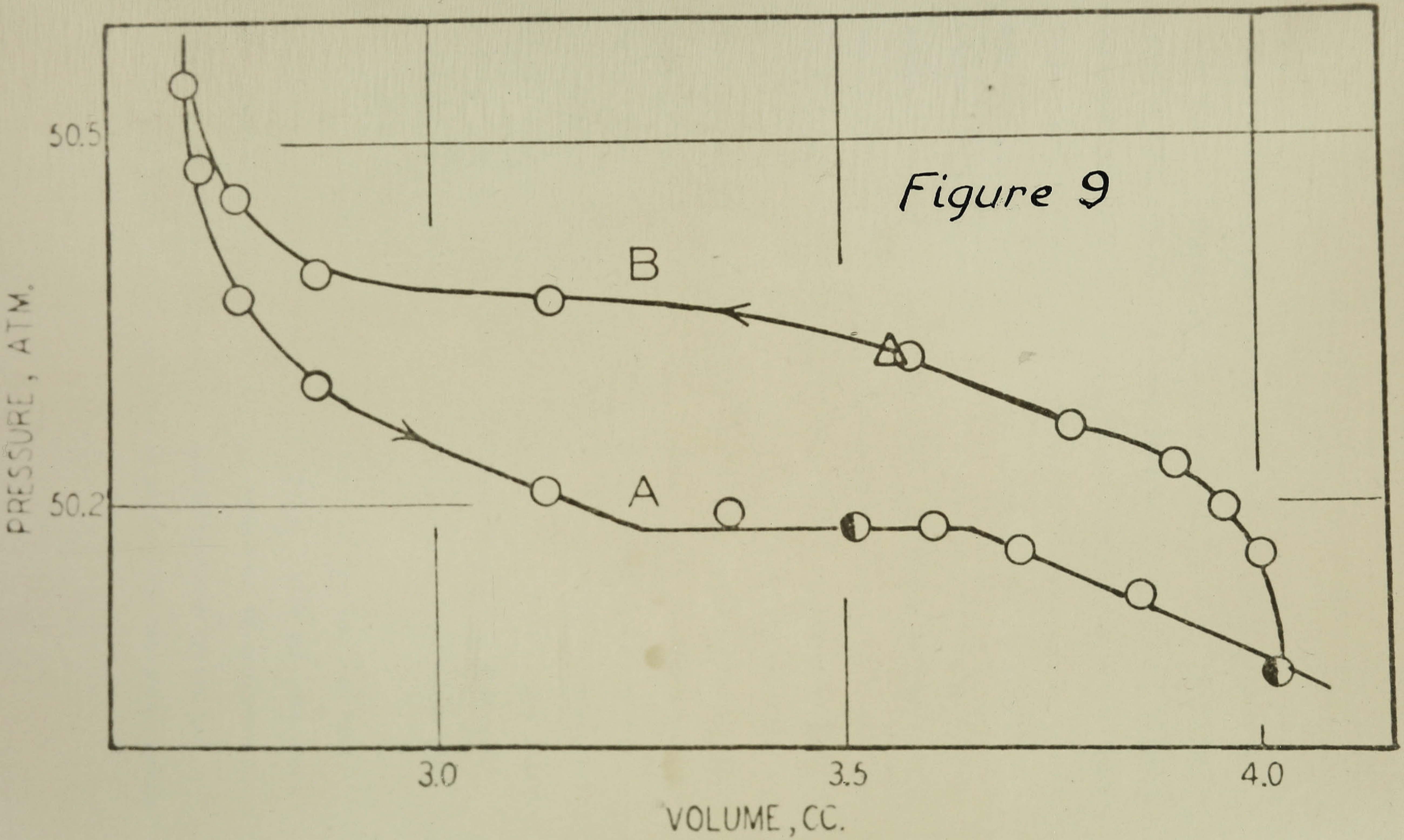

Figure 9

dependent on its former history. That the points on the lower curve are not dependent on the previous condition of the system, provided that expansion into the "gaseous" region had not occurred, was shown by repeating a point upon the flat portion several days later. This was done simply by adjusting the pressure to the desired value, whereupon the system expanded directly to the correct point from a system of higher density. No change was subsequently observed. The last "vapour" point shown on the diagram was similarly reproduced and no tendency to change was found. The repeated points are shown in the diagram as darkened circles.

The question of the stability of the upper curve was then investigated. After expansion into the "gaseous" region the system was adjusted to give the triangular point on the upper curve. The volume was then maintained constant and the change of pressure with time taken. It was found that the pressure fell to the original isothermal where it remained constant. The figures are given in table XII. That this behaviour involves a time of the order of an hour makes it clear that we are not dealing with a highly compressible gas.

A magnetic stirrer was included in the ethylene side of this apparatus, as was already described. This was done since the question of mechanical mixing was emphasized in criticism of the work done in this laboratory. A heterogeneous system was obtained at 9.51°C. This was done by heating the two phase system

TABLE XII

Experimental Volume c.c.	Temperature °C	Pressure in Atmospheres	Time in Minutes
3.59	9.60	50.28	0
3.55	9.60	50.27	7
3.55	9.60	50.24	13
3.55	9.60	50.22	20
3.57	9.60	50.20	26
3.57	9.60	50.18	34
4.57	9.60	50.18	40

Note: Zero time was taken at about twelve minutes after the original pressure adjustment.

up to 9.51° in the stationary bomb. The pressure was carefully recorded. The system was then violently stirred for a period of twenty seconds and the pressure again taken. This procedure was repeated several times, during and after which no change in pressure could be detected. Although no movement of material could be seen during the stirring, it was of sufficient violence to cause visible transfer of the liquid into the vapour phase at temperatures below the critical. It may be noted here that the phenomena observed in this apparatus, without a quartz spiral, were similar to those reported by previous workers. This observation refutes the suggestion of Ruedy (57) that the presence of a spiral, acting as a deterrent to the diffusion of the system, is the reason for the anomalous behaviour observed in the critical region.

Pressure of the Heterogeneous and Homogeneous Systems at 9.51°C

Considerable interest has centered around the question of whether the heating or cooling curve of a typical density isochore (see figure 4) might not be the more stable. This question of stability should be settled by a measurement of the pressure of both curves at the same temperature.

The procedure was as follows:

The volume of the system was fixed, by freezing the mercury in the central U-tube, at a value known to produce a heterogeneous system. The temperature of the mercury was brought up to 9.51°C thus producing such a system (Curve A). The mercury was melted and the pressure of the system determined. The mercury was again frozen. The system was then heated to above 11.5°C and twenty minutes allowed for equilibrium to be reached. After cooling to 9.51° again, a system of homogeneous density was obtained (Curve B). The mercury in the U-tube was then melted and the pressure again determined.

Throughout the range of densities studied, the pressure of the A and B curves are the same and are independent of the mass-volume ratio of the system. The data appear in table XIII. These pressures agree with the flat portion of the isothermal at 9.51°C. A calculation checking this appears beneath the table. Furthermore, the density range covered by the flat portion of the isothermal at 9.50°C is from 0.231 gms./c.c. to 0.198 gms./c.c. approximately, which agrees with the range of densities found for 9.51°C.

Since the pressures of the cooling and heating curves are the same, it must be concluded that the homogeneous and heterogeneous systems are equally stable. Within the loop formed by the density hysteresis curve, any point is just as stable as those above and below it. Since the pressures of a system along a cooling curve are independent of the mass-volume ratio over the range of densities represented by the flat portion of an isothermal, although of homogeneous density, it does not behave as a true gas.

Further measurements of this type were made using a new experimental assembly. Pressure-temperature curves at constant

TABLE XIII

Pressure of the Homogeneous and Heterogeneous Systems

Average Density in gms./c.c.	Pressure A in atmos.	Pressure B in atmos.	Temperature in °C
.1990	50.08	50.08	9.51
.2040	50.08	50.08	9.51
.2090	50.08	50.08	9.51
.2173	50.08	50.08	9.51
.2287	50.08	50.08	9.51

Pressure of the flat portion of the Homogeneous Isothermal at 9.50°C is 50.07 atmospheres. $\frac{dP}{dT}$ for horizontal regions is,

$$\frac{50.51 - 50.07}{9.90 - 9.50}$$

$$\frac{.44}{.40} = 1.1 \text{ atm./c.c.}$$

volume were determined for three different mean densities, both on heating and cooling. These data appear in table XIV.

Comparing the data of table XIV with the isothermals of figure 8, it is clear that as long as the system has a mean density represented by a point within the envelope, its pressure is independent of the mass-volume ratio. This pressure corresponds to the pressure of the flat region of the isothermal of the same temperature and is the same whether an A or a B isochore. All the systems therefore, must be equally stable, and, since the isothermals have already been shown to be in equilibrium, the other systems must be equilibrium systems.

Once outside the shaded region, the pressure is seen from the data to be dependent on the volume, the system behaving as a one phase system.

The pressure temperature curves are reversible, which again shows that along the cooling curve of an isochore the system behaves like a two phase system, even above the temperature of condensation.

TABLE XIV

Pressure Measurements of Heterogeneous Systems

Temperature in Degrees C	Pressure, Atm. Density - .2046 gms./c.c.	Pressure, Atm. Density - .2109 gms./c.c.	Pressure, Atm. Density - .2270 gms./c.c.	Pressure of Isothermals
		Heating		
9.00	49.50	49.51	49.50	
9.20	49.74	49.75	49.74	49.74
9.50	50.06	50.07	50.06	50.07
9.80	50.38	50.39	50.40	50.39
10.50	51.13	51.15	51.22	Limit of flat portion of isothermal corresponding to limit of at 10.00°C
11.00	51.66	51.69	51.84	
		Cooling		
10.50	51.12	51.15	51.22	
9.80		50.39	50.40	
9.50	50.06	50.07	50.06	
9.20	49.74	49.75	49.74	
9.00	49.50	49.51	49.50	

The Vapour Pressure of Ethylene between 8.92° and 9.90°C.

The vapour pressure curve of ethylene in the critical region was determined from the isothermals given above. The values are given in table XV and graphically represented in figure 10. The pressure for any temperature was taken as the average of the pressures of the region where $\left[\frac{\partial p}{\partial V}\right]_T = 0$. The accuracy of measurement was 0.01 atmospheres; however, because these are average values an extra figure is included although of doubtful significance. As would be expected, over this narrow range of temperature, the vapour pressure is seen to be a straight line function of the temperature.

TABLE XV

The Vapour Pressure of Ethylene

Temperature	Vapour Pressure
8.92	49.453
9.22	49.743
9.42	49.983
9.50	50.066
9.60	50.166
9.70	50.276
9.80	50.386
9.90	50.510

From Figure 10: $\frac{dP}{dT} = \frac{50.600 - 49.450}{9.975 - 8.960}$ atm./^{o}C

$$= \frac{1.150}{1.015} \text{ atm./}^{o}\text{C}$$

$$= 1.133 \text{ atm./}^{o}\text{C}$$

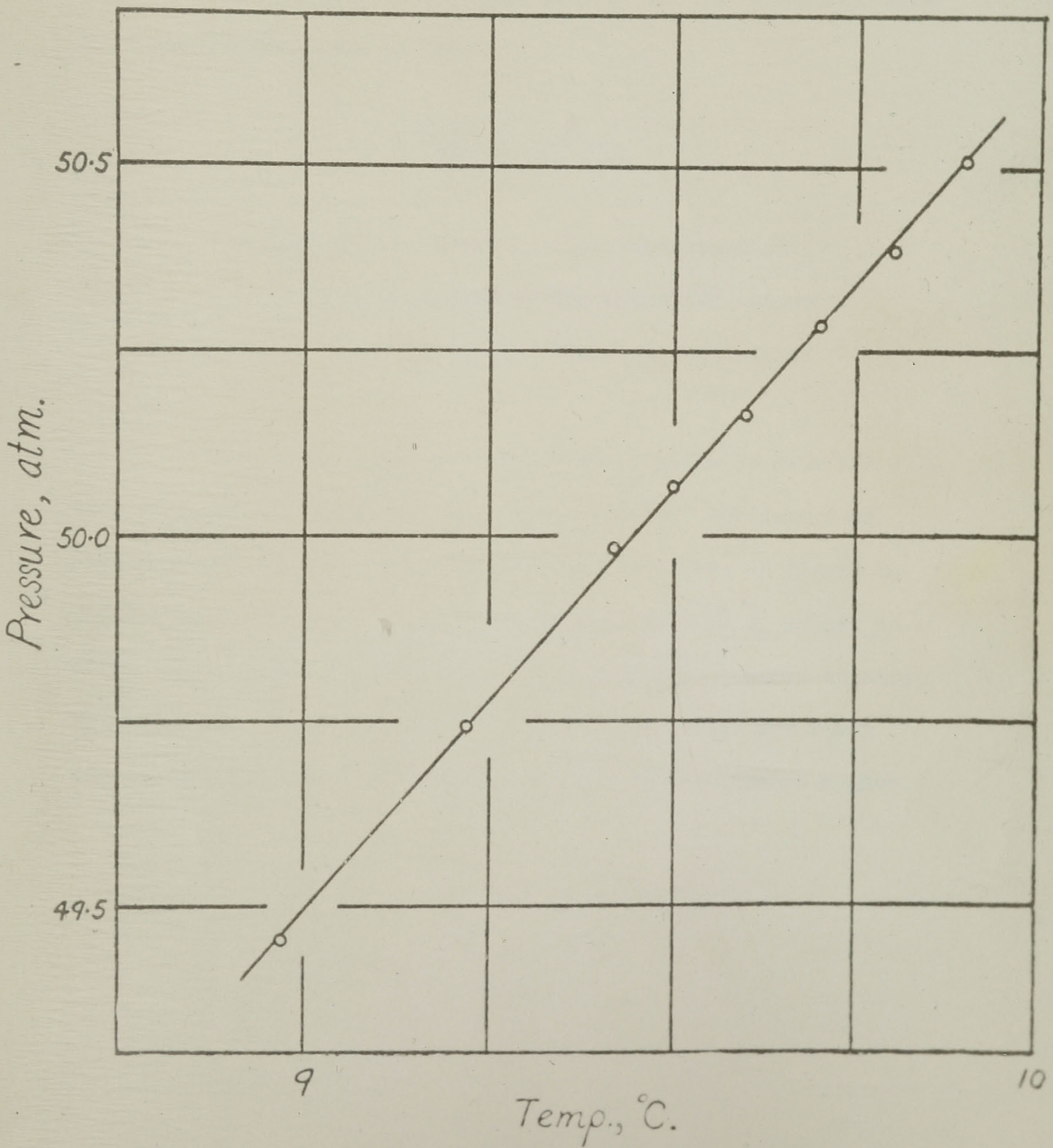

Figure 10

The Heat of Vapourization of Ethylene in the Critical Region.

The latent heat of vapourization may be calculated from the Clausius-Clapeyron equation

$$\frac{T\,dP}{dT} = \frac{\lambda}{v_2 - v_3}$$

where λ = latent heat of vapourization

v_2 = volume of the saturated vapour

v_3 = volume of the saturated liquid

The value of $\frac{dP}{dT}$ was determined graphically from the figures of table XV, while the specific volumes of the saturated liquid and vapour were evaluated from the envelope of figure 8. These values together with the calculated value of λ appear in table XVI. A graph of the latent heat-temperature curve appears in figure 11. It is seen that the latent heat does not reach zero at the critical temperature but at a point somewhat higher.

TABLE XVI

Latent Heat of Vapourization of Ethylene in the Critical Region

V_2	V_1	T	$\frac{dP}{dT}$	λ cal./gm.	$V_2 - V_1$
5.448	4.000	282.1	1.133	11.19	1.448
5.176	4.072	282.4	1.133	8.53	1.104
4.896	4.224	282.6	1.133	5.20	.672
4.800	4.256	282.7	1.133	4.21	.544
4.688	4.256	282.8	1.133	3.34	.432
4.596	4.256	282.9	1.133	2.63	.340
4.520	4.280	283.0	1.133	1.86	.240
4.400	4.400	283.1	1.133	0	0

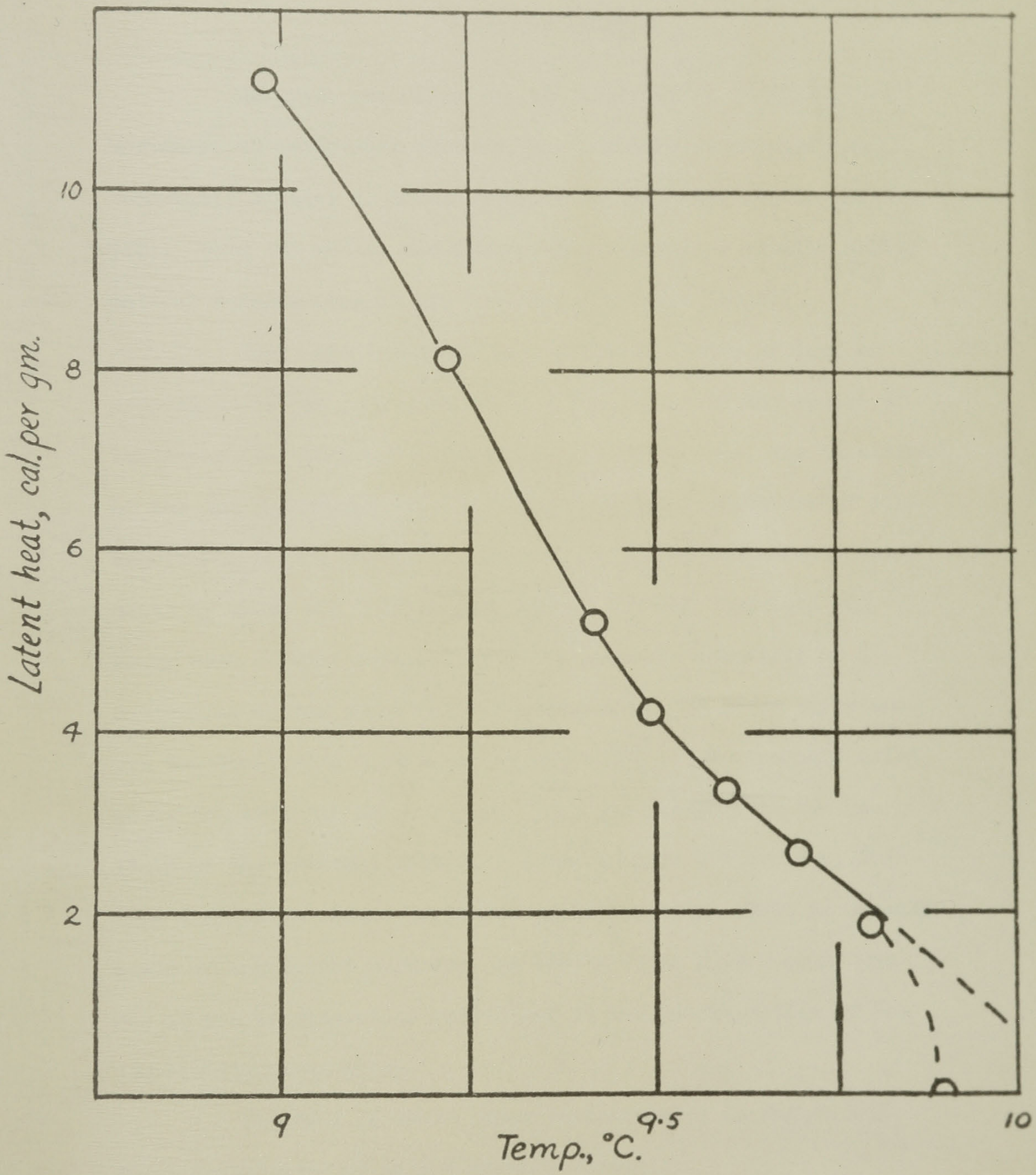

Figure 11

The Predictions of Harrison and Mayer and their Comparison with Experiment.

Harrison and Mayer, by the application of Statistical Mechanics to condensing systems, have arrived at conclusions remarkably similar to those observed by Maass and his co-workers (58). Born and Fuchs, and Frenkel have presented similar mathematical examinations of the critical phenomena (59,60).

They have predicted that discontinuities of various properties of the condensed phase should occur in the region of the classical critical temperature. In particular, the densities of the two phases should not be equal at the temperature of disappearance of the meniscus. These conclusions had already been shown by Maass and others to be true. However, Harrison and Mayer went further and predicted the probable behaviour of a condensing system under various conditions. Of major importance was the conclusion that a region where $\left[\frac{\partial p}{\partial V}\right]_T = 0$ should exist above the critical temperature. This was contrary to the accepted ideas of the critical change. It was important therefore, that this conclusion should be tested experimentally. That no measurements of sufficient accuracy had been made in this region, was one of the considerations which led to the determination of the isothermals given above.

Figure I of their paper is reproduced in Figure XII. Their description of this diagram follows:

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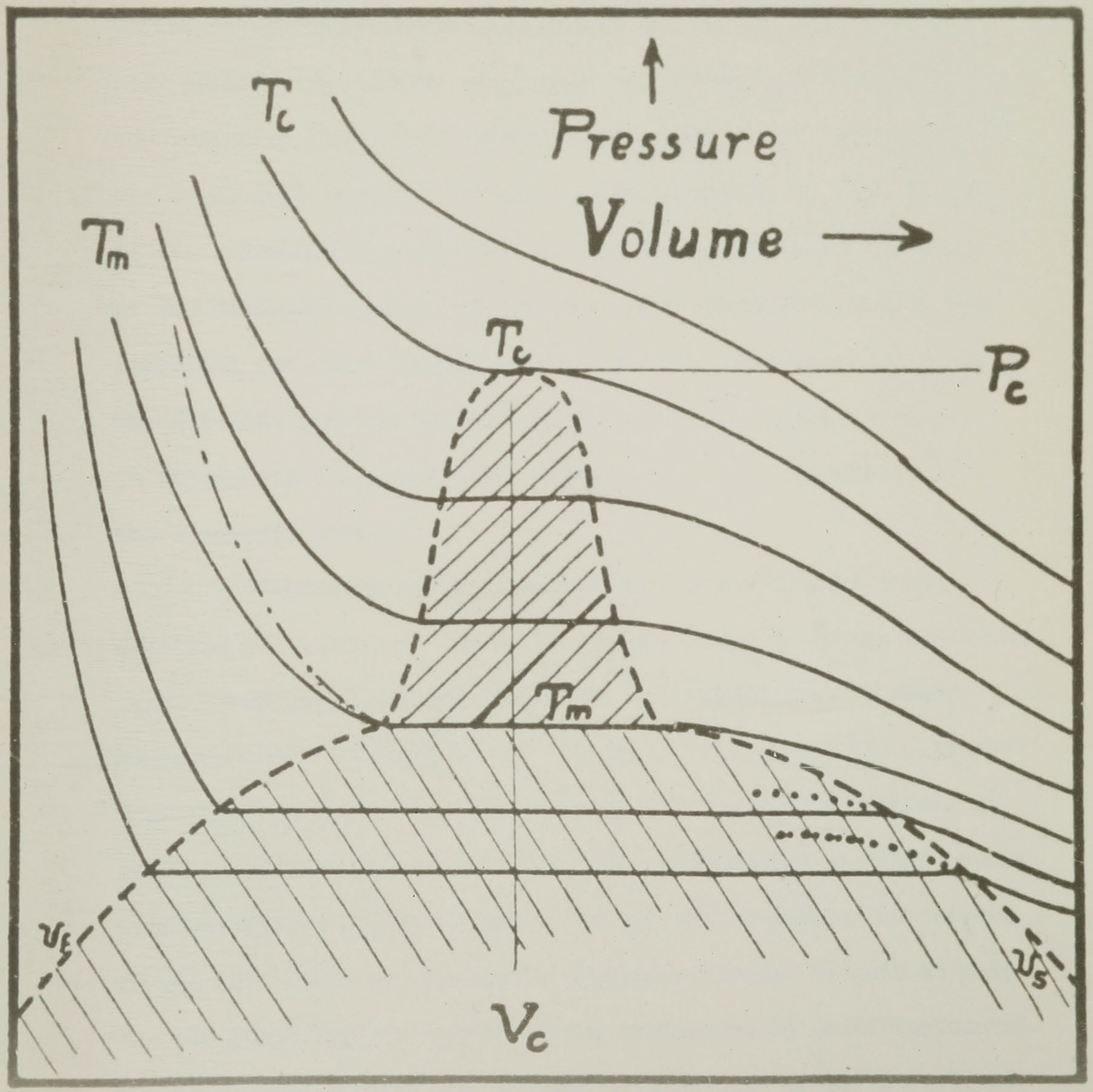

Figure 12

"In this figure pressure is plotted as a function of volume, at various temperatures: the heavy solid lines. The curves at two characteristic temperatures Tm and Tc are especially marked. The shaded area enveloped by the dashed line is the region in which the lines are horizontal, that is where the right hand boundary of this region is called vs, the volume of the saturated vapour, the left hand boundary vf is the volume of the condensed phase. The dotted lines inside the shaded area represent the extrapolated pressure of the supersaturated vapour. The dot-dash line on the left hand side of the shaded area at Tm represents a discontinuous transition in the properties of the condensed phase.

"Below Tm the isothermals show discontinuous changes of slope at vs and vf. At Tm the surface tension of the condensed phase disappears, and above Tm there will be no visible sharp meniscus between condensed and dispersed phase. The discontinuous transition in the condensed phase shows no heat of transition at least at the vapour Pm .... The isothermals go continuously with continuous change of slope through the shaded region between Tm and Tc. At Tc the isothermal has a horizontal tangent at only the one point vc, Pc. Above Tc the isothermal is never horizontal.

"The part of the diagram to the right of Vc, and all of it above Tc, is deduced strictly from the equations of the previous article. The portion to the left of vc and below Tc represents a logical guess from the nature of the kinetic picture deduced from these equations. The authors, however, are less certain of the details of this portion of the diagram.

"Below Tm and above Tc the diagram corresponds to the usual conception of the diagram below and above the critical point respectively. Between Tm and Tc a system in the shaded area will be expected to have certain unusual properties."

A comparison of this figure with figure XII will show a striking similarity as to general form. The symmetry they suggest is lacking, the experimental isothermals showing a more nearly perpendicular boundary for Vf. However, this is not surprising since the left hand of their curve is admittedly not certain. The important prediction of a region above the classical critical temperature where $\left[\frac{\partial p}{\partial v}\right]_T = 0$ has been verified by experiment.

A difference in the behaviour of the system on compression from that predicted must be noted. To quote:

"Below Tm compression of the system through a volume region between vs and vf will be accompanied by the separation of two distinct phases of densities 1/vf and 1/vf. The miscroscopic density corresponding to a volume between vs and vf is unstable. This is indicated on the diagram by the dotted lines showing the higher pressure of the supersaturated vapour. As is well known this phenomenon is associated with the fact that the surface tension increases the vapour pressure of very small droplets of liquid.

"Between Tm and Tc, however, the denser phase has no surface tension, and corresponding to this, the isothermals pass smoothly through the condensing region, allowing no extrapolation to higher pressure for the supersaturated vapour."

The experimental data do not agree with this picture. Reversal of the measurement along the isothermal at 9.60°C resulted in a pronounced hysteresis. That is, compression of a system between Tm and Tc does not result in a smooth passage of the isothermals into the shaded region. Some of this effect is probably due to a temperature lag. Compression will heat the vapour causing the curve to rise above the normal isothermal. However, since times of the order of one hour were necessary for final equilibrium to be reached, it is felt that there must be at least another factor. Such a time lag points strongly to the existence of a structure in the condensed phase. This structure would require time to be built up, thus accounting for the slowness of equilibrium establishment.

Harrison and Mayer make several other predictions which have not yet been tested experimentally. It will be of interest to observe how far the theory agrees with fact.

DISCUSSION

In this discussion there will first be presented the picture of the liquid - vapour transformation as it appeared to the writer when the experiments described above were commenced. This view was formed from the results of previous workers and the difficulties and uncertainty in it led to the experiments referred to. There shall then follow the changes necessitated from them and the explanation of the critical phenomena which appears most reasonable.

There was no doubt that the simple classical explanation of the critical phenomena was inadequate. The whole hypothesis was based on the belief that at the critical temperature the two phases became identical. Extensive and convincing evidence had been presented to show that this was not the case. This evidence has been summarized in the Introduction. In particular, measurements of density, on various systems by many investigators, had shown that the density of the two phases differ considerably at the critical temperature. It is surprising that this fact was neglected by earlier workers in the formation of a general theory. In the original work of de la Tour (1) the observation that the critical phenomenon occurs over a range of mass - volume ratios, rather than at one discrete density, had been recorded. This fact alone can hardly be explained except by admitting that the densities of both phases are not alike at the critical temperature. The possibility of this was suggested by several investigators during the last generation but it was not until comparatively recent years that it has met with general acceptance.

The density difference had been found to persist indefinitely at any one temperature, and could be detected several degrees above the critical temperature. A natural explanation was forthcoming, by postulating the continued existence of the liquid above the temperature where the surface disappeared. However, this region of denser material did not behave as a true liquid. It could be destroyed by "molecular stirring", by expansion, or by heating the medium to a sufficiently high temperature. Once the heterogeneity had been destroyed, on subsequent cooling to the same temperature, or on compression to the original volume, it failed to re-form. In this respect it did not behave as a true liquid. Because of this, the well known density hysteresis occurred on heating and cooling. That is, on heating the system the density difference persisted above the critical temperature and finally disappeared at a higher temperature. On cooling, no heterogeneity was formed until the liquid finally condensed. The picture was further complicated by the fact that the liquid that condensed out on cooling was different in both amount and density to that at the same temperature on the heating curve. The density of the condensed liquid did not agree with that of the original liquid until one or two degrees below the critical temperature. Of great importance was the discovery that the time necessary for the establishment of equilibrium subsequent to a change of conditions was much greater when the change was from gas to liquid, than when vice versa. This was the case with both temperature and volume changes.

The most reasonable explanation that was offered for these phenomena was based on the concept of regional orientation of the molecules of the liquid phase. It is well known that the molecules of a substance can become oriented with respect to one another. In a solid crystal this orientation is perfect. The phenomenon of the mesomorphic state has shown that considerable orientation can exist above the melting point. In the gaseous state, on the other hand, the molecules are in a random distribution. This would be true of all matter at sufficiently high temperatures, where the kinetic energy overcomes all attractive forces. It is not unreasonable to suppose that the liquid state is intermediate between the solid and gaseous. It is therefore believed that a dynamic orientation exists in the liquid. This is not sufficient to restrict all rotation of the molecules and is limited to small regions. The molecules of any one region are oriented to one another while many regions of this type exist throughout the liquid. Constant changes occur, the life of any one region being limited by the kinetic motion of the molecules. New regions are constantly being formed and old ones disappear. Evidence for such a picture was found in the time lag measurements mentioned above, and in the X-ray diffraction studies of Stewart and his co-workers (36).

Applying this concept to the liquid state, it was possible to explain most of the phenomena of the critical change that had been observed. Maass and Geddes have made use of such an hypothesis (19). Below the critical temperature, the liquid is an oriented homogeneous medium, the vapour is a random distribution of molecules. On heating the system, the forces tending to destroy orientation are increased. At the same time the density and pressure of the vapour increase. Eventually the critical region is reached. Here a rapid destruction of structure takes place. However the surface disappears before all the structure is destroyed, the remaining structure being concentrated in the bottom of a stationary tube. This surfaceless region resembles a liquid phase. Although there is no true surface there is a narrow boundary of steep density gradient. The density will remain unchanged for an indefinite time. Expansion or heating will destroy the denser region as they would destroy a true liquid phase. However it differs from the true liquid in that subsequent compression or cooling does not recreate a denser region. This was explained by the assumption that once the structure was destroyed it could not be re-formed until condensation had occurred. Hence the heating curve of a density isochore represents a pseudo two phase system above the the critical temperature, while the cooling curve is a one phase vapour system until condensation takes place. The liquid which separates out is less dense than the corresponding liquid on the upper curve. This was explained by saying that the upper curve represents a maximum amount of orientation for any temperature, since we are passing from a system of high density to one of lower, while the cooling curve represents the minimum amount of orientation possible. Thus the two liquids are said to differ in their degree of orientation. This briefly is a description of the probable course of events in the light of the known facts at the time the work of this thesis was commenced.

Several difficulties were evident. It was not clear whether the heating or cooling curve of the isochores represented the stable condition. Experiments on temperature fluctuations had shown that the system would move from the upper to the lower curve but never in the opposite direction. It would appear, therefore, that the lower curve is the more stable; however this behaviour could also be explained on the basis of time lags. Pressure measurements which had been made on both curves had been insufficiently accurate to indicate any conclusion. It was therefore possible to say that the upper curve was due to a super-heating effect while the lower was the really stable condition. This opinion was further supported by the fact that the condition represented by the upper curve could never be reached except by approach from lower temperatures.

To explain the existence of different liquids at the same temperature was difficult. The differences in density were attributed to different degrees of orientation. However, it was not clear what was meant by degrees of orientation nor how this was possible.

Turning now to the isothermals of figure 8, it is at first apparent that a region where $\left[\frac{\partial p}{\partial V}\right]_T = 0$ exists above the critical temperature. In this region the system behaves as a two phase system; furthermore, it corresponds to the temperature range where a density heterogeneity persists above the critical temperature on the heating curve of an isochore. This, therefore, agrees with the conclusion that the density persistence is due to the presence of a liquid structure. To call such a region a phase is not in accord with the general definition of a phase, which demands the existence of a surface, without stretching the meaning of the word "surface" from that of a region of molecular dimensions to one of appreciable width. However, for the lack of another word, we will still refer to it as the liquid "Phase".

In expanding the system, the volume values were directly reached. In compression, from gaseous to liquid, a time lag was found, however. The flat portion of the isothermal was the ultimate equilibrium value. This lag may be partly due to the heating effect of compression, but it is thought also to be due to the slow building up of structure. It is therefore further evidence for the orientation hypothesis of liquids. Since the flat portion of the isothermals are equilibrium curves from either direction, it follows that a homogeneous system which has been formed by the expansion and compression of a heterogeneous system, is just as much a two phase system as when the density difference is present. The only reasonable conclusion is that the "liquid phase" is uniformly dispersed in the homogeneous system and not detectable by means of the spiral and float. Therefore, within the shaded region above the critical temperature, a two "phase" system exists, either homogeneous and dispersed, or heterogeneous with the liquid "phase" concentrated in the lower region. This is not unreasonable when we consider that the "phase" has no surface. This fact, together with its dynamic nature and only slight density difference from the surrounding vapour, makes its tendency to settle very slight. At the same time, if it is formed by heating the liquid at constant volume, and is concentrated in the bottom of the bomb, its tendency to disperse would also be very slight.

Evidence from the pressure measurements at constant volume lead to similar conclusions. It is evident that the pressure of the heating and cooling curves are both alike, and both correspond to the flat region of the isothermal at the same temperature. Hence we must conclude that the heating and cooling curves of a density isochore have the same Gibbs' free energy and are equally stable. Furthermore they both represent equilibrium systems since the flat regions of the isothermals have been shown to be equilibrium systems. The only conclusion is that the cooling curve is not of a vapour system but of a two "phase" system, with the liquid "phase" dispersed. It is true that thermodynamically both the dispersed and stratified systems are equally stable, yet one would expect, due to the gravitational gradient that a density difference would be set up over a very long period of time in the homogeneous system.

If the surface tension did not disappear before the phase densities became equal, the system would behave in the classical manner. The critical constants would be given by the upper limit of the region wherein $\left[\frac{\partial p}{\partial v}\right]_T = 0$ (i.e. 50.50 atm., 9.90°C, and 4.40 c.c.). However, since the surface tension disappears at 9.50°C, an anomalous region exists where the "phases" can be separated or dispersed, depending on the history of the system.

It is interesting to note that the critical temperature has been variously defined as the temperature of disappearance of the meniscus, the temperature of equal phase densities, the temperature of the isothermal which exhibits the point of inflection, etc. For historic reasons we still mean by the critical temperature that of surface disappearance, although the inflection point might be the more logical.

The envelope of the region wherein $\left[\frac{\partial p}{\partial v}\right]_T = 0$ should give the true phase densities. It remains therefore to explain how liquids of different density can exist at the same temperature, depending on whether we are on a heating or cooling curve or on the overall mass - volume ratios of the systems. This is admittedly difficult. However, if we allow the possibility of the vapour being dispersed or dissolved in the liquid phase an explanation can be offered. When we measure the density of a liquid condensing on the cooling curve of an isochore, we are not measuring the true phase density but that of a liquid containing dissolved vapour. At the same time the vapour in equilibrium contains dispersed liquid. At lower temperatures such solution becomes very slight and the density depends only on the temperature.

The boundary of the shaded region above the critical temperature gives the densities of the liquid "phase" and of the vapour in equilibrium with it. Expansion of this system, that is, moving from left to right across a flat isochore, decreases the amount but not the degree of heterogeneity. In other words, the number of oriented regions is decreased but the forces holding the molecules together in any one region remain the same. To look at at in another way, because of the increased average distance between the molecules, the chance of building up a region of structure is reduced, thus shifting the equilibrium towards the gaseous state. On the other hand, heating decreases the degree and amount of heterogeneity. The forces destroying structure are increased causing a less closely packed formation. At the same time, the increased number of molecules of greater velocity causes a greater proportion to exist as true vapour, i.e., the vapour pressure of the "phase" increases. For this reason, different values of density can exist at the same temperature in systems of different mass-volume ratios. Remembering that the tendency for the "phases" to separate is very slight, and that the density measured is the macroscopic density, this explains the existence of "liquids" of various densities above the critical temperature. Extension of this idea to systems slightly below the critical temperature, would permit the existence of true liquids, bounded by a surface, of different densities to exist at the same temperature. However this is difficult to visualise and far from satisfactory. The point is worthy of further investigation.

The experiments on compression can now be easily explained. Their main significance lies in the fact that since a system of stable density heterogeneity can be established without cooling, the phenomenon of density persistence can no longer be attributed to a superheating effect. Here again we find evidence in favour of the dispersion hypothesis. Ordinary mechanical compression of a system represented by a point on the cooling curve of a density isochore above the critical temperature, would result in the increase of the amount of heterogeneity. However this would not be detectable by a spiral and float. Compression brought about by heating the top of the bomb destroys the structure in the upper region while increasing it in the lower. Slow removal of the temperature gradient leaves the lower region with a higher density which is detectable. The amount of structure is the same as before compression but it is now no longer dispersed.

As the temperature is lowered below 9.50°C, conditions suitable to the spontaneous stratification of liquid are more nearly approached. At 9.20°C, conditions are such that compression can cause a large enough number of liquid molecules to group themselves together for settling out to be possible, and condensation occurs.

In compressing the two phase system, the density and amount of the liquid is changed. The change is assumed to be caused in the following manner. The dispersion of vapour in liquid, which has been brought about by heating and then cooling, is altered on compression. The compression largely changes the vapour groups in the liquid to liquid groups. In addition, liquid that is still dispersed in the vapour drains out, and both the density and the amount of the liquid is increased.

Moreover, the lower density of the liquid phase at 9.00°C, on the heating curve of the system of mean density 0.1994 gms./c.c., compared to the constancy of liquid density at this temperature for systems of higher average density, is explained by the greater amount of vapour in the liquid phase. Compression of the reformed liquid at this low average density at 9.00° on curve B causes an increase in density above that of the original heating curve, but never in excess of the density of 0.245 gms./c.c., which is characteristic for fillings of higher mean density. This can be explained on the assumption that, at the lower mean density under discussion, the mechanism of compression does not permit as great an artificial density to be developed, and some of the vapour is left unchanged in the liquid, with a consequent lower liquid density even after compression.

Although a mechanism for the behaviour of pure ethylene, when compressed as described above, has been offered, it does not seem feasible in the present state of our knowledge of multi-component systems to extend the same explanation to an air-ethylene mixture. The real interest in the study of such systems has been with respect to the hypotheses of earlier workers who have attempted to explain the anomalous behaviour in the critical region by the presence of minute quantities of impurities.

It has already been pointed out that small quantities of air contained in an ethylene sample increased the amount of heterogeneity and the temperature range above the classical critical temperature throughout which the liquid "phase" may persist. In the present study it is apparent that the presence of air now retards the establishment of a heterogeneous system from a homogeneous one, and impurities of such a nature would therefore tend to obscure the phenomena caused by compression. The reason for this behaviour cannot be discussed upon any firm basis until the effect of the impurity upon the interfacial tension has been established.

Briefly reviewing the conclusions, a liquid below the critical temperature consists of a dynamically oriented system of molecules bounded by a true surface; the vapour is in the form of a perfectly random distribution. On heating the system, the forces tending to destroy the structure in the liquid become greater, and the vapour density increases. A point is eventually reached where the surface can no longer exist due to the decrease of cohesive force. However at this temperature structure is still present, and in a stationary system is concentrated in the lower region. At any one temperature this structure may be more or less mixed with true gas, depending on the volume. At higher temperatures all structure is destroyed and we have a true gas. On subsequent cooling, structure reforms but is uniformly distributed and not detectable by density measurements. Since there is no surface tension no phase can be formed. However, on further cooling, a surface forms and a liquid phase appears. The vapour still contains some orientation while in the liquid there may be some vapour, giving a different density than before. On further cooling the original conditions are reached.

Much is yet unexplained, particularly with regard to the nature of the different types of liquid and the effects of small amounts of air. However, the above hypothesis should be useful as a guide to further investigation of the physical properties of critical systems.

APPENDIX

In continuation of the work described above, it was considered important to observe and measure the critical phenomena with a system whose molecules had an appreciable polar moment. Hitherto, compounds with zero or little moment had been used. It was felt that, if, as is believed, orientation plays an important part in the persistence of liquid structure throughout the critical region, a system of polar molecules should show some differences. With this in view, an investigation of methyl fluoride has been commenced. The work was carried out in collaboration with Mr. A. C. Topp.

Methyl fluoride was prepared by two methods. Potassium methyl sulphate reacts with potassium fluoride to give potassium sulphate and methyl fluoride (61). Potassium fluoride, C.P., was made anhydrous by heating. This was mixed with dry potassium methyl sulphate in the ratio of the molecular weights. The mixture was ground for several hours in a ball mill. On heating in a generator from 160° to 200°C, methyl fluoride was given off. The product was contaminated with methyl ether which was removed by bubbling the gas through a tower of concentrated sulphuric acid. It was then passed through a solution of potassium hydroxide, and two drying tubes containing soda lime. The gas was collected in a trap cooled with liquid air. This method gave a small yield and was only used for two preparations.

A more satisfactory method was by the reaction of dimethyl sulphate and potassium fluoride in a water solution. This is adapted from an established method of preparing methyl iodide (62). The apparatus used consisted of a two litre, three necked flask equipped with a dropping funnel, thermometer, and reflux condenser. The flask was heated on a water bath. The condenser was connected so that the gas passed through two wash bottles containing concentrated sulphuric acid and a solution of potassium hydroxide. It then passed through two drying tubes containing calcium chloride and soda lime, a trap cooled to -20°C, and was finally collected in a trap cooled with liquid air. The train was connected to a Hy-Vac and equipped with a manometer.

A mixture of 282 gms. of hydrous potassium fluoride, 36 gms. of calcium carbonate, and 75 c.c. of water was placed in the flask. The system was evacuated. After warming to 65-70°C dimethyl sulphate was added from the dropping funnel at such a rate that the gas was produced smoothly. 285 c.c. of dimethyl sulphate was used. The figures are for a typical run. The amount of water was varied, better results being found with less water.

The gas produced by this method was contaminated with carbon dioxide, which was, however, easily removed by the potassium hydroxide. The yields varied from 20% to 25%.

The methyl fluoride was purified by distillation in a Podbielnisk column (54). The constant boiling fraction was considered pure, the boiling point was -78°C at 750 m.m. pressure.

In a preliminary determination of the density where the critical phenomenon occurs with methyl fluoride, a series of small bombs were used. The bombs were made of Pyrex glass of 1 c.m. inside diameter and 3 m.m. wall thickness.

These bombs were filled to various densities by condensing a measured quantity of methyl fluoride into the evacuated bomb. On heating to the critical temperature of methyl fluoride (44.8°C), it was observed whether the meniscus dried up on the bottom or disappeared in the middle of the bomb.

The data obtained are listed below:

Bomb No.	Density	Observation
1	.22 gms./c.c.	No critical phenomena
2	.28 "	Meniscus disappears low in bomb
3	.31 "	Meniscus disappears in middle of bomb

The lower limit of the critical phenomena is a density somewhere near .28 gms./c.c., the upper limit is undetermined but is at least above .33 gms./c.c. This is in agreement with the results reported by Patterson and Carwood (63).

The apparatus used to study the density changes consisted of a Pyrex glass bomb 50 c.m. long, 1 c.m. inside diameter, and 3 m.m. wall thickness. The bomb contained a McBain-Bakr spiral and float and was of the type formerly used in this laboratory for density measurements.

Four of such bombs were used all of which exploded before any measurements could be made. This is attributed to the high critical pressure of methyl fluoride, 60 - 61 atmos., that is 11 to 12 atmos. higher than that of ethylene.

A new type of bomb has been constructed but not yet tested. This consists of a heavy Pyrex tube, 20 c.m. long, 1.4 c.m. inside diameter, and 1.5 c.m. wall thickness. The ends of the tube are ground square and capped with two lead disks. The tube is bolted between two steel plates. By tightening these two plates together a gas tight seal should be made between the lead gaskets and the ground surface of the glass. The bomb will be filled through a narrow brass tube which is soldered to the upper lead gasket, and which passes through a small hole in the upper steel plate. This tube can be soldered tight.

This work is incomplete and has been suspended to permit the investigation of problems arising with the present war.

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CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

Two new types of apparatus for the investigation of critical phenomena were developed.

The first was based on the principle of design due to Maass and Geddes. Pressures were measured by balancing the system against a two phase system of carbon dioxide at a known temperature. An accurate method of measuring the volume of the system and the mercury height, by means of a cathetometer was employed. An improved means of thermostating was developed by the use of a manually controlled water flow. An electromagnetic stirrer made possible the mechanical stirring of the system under investigation.

The second apparatus made possible the investigation of the effect of compression on the system. A water jacket was used to produce a temperature gradient along the bomb. Densities were measured in the usual manner, by means of a McBain-Bakr balance.

The following are the contributions to the knowledge of the critical state which have been made:

(1) Thermal compression, in the critical region, of a homogeneous system, both of pure ethylene, and of an air-ethylene mixture, re-creates a stable density heterogeneity.

(2) The pressure volume isothermals throughout the critical region.

(3) The true form of the density temperature curve throughout the critical region.

(4) The establishment of the region above the critical temperature where heterogeneous systems are stable, and wherein

$\left[\frac{\partial p}{\partial v}\right)_T = 0$

(5) The "true" critical constants for ethylene as determined by the pressure-volume-temperature relations.

(6) The vapour pressures for both the homogeneous and heterogeneous systems throughout the critical region, indicating their relative stability.

(7) Mechanical stirring has no effect on the pressure-volume relations of a heterogeneous system at constant temperature.

(8) Further evidence of molecular orientation from the pressure-volume time lags.

(9) The probable cause of the density hysteresis is disclosed from the new knowledge listed above.

SUMMARY

of the Thesis

PRESSURE, VOLUME, TEMPERATURE, AND DENSITY RELATIONS OF THE SYSTEM ETHYLENE IN THE CRITICAL REGION

by

J. R. DACEY.

The effect of thermal compression on the system ethylene in the critical region is reported. Such compression on the homogeneous system above the critical temperature produces a stable heterogeneity. Below the critical temperature and above the temperature of reappearance of the meniscus, a similar effect is produced; however, 0.3°C above the normal temperature of meniscus reappearance the liquid phase can be caused to condense. The liquid so formed is stable. Below the temperature of condensation, compression increases the liquid phase both in density and amount. Similar effects have been found with an air-ethylene mixture.

The pressure - volume isothermals of the system ethylene have been accurately determined between 8.90 and 10.00°C. A region above the classical critical temperature wherein $\left[\frac{\partial p}{\partial v}\right]_T = 0$ has been discovered. Mechanical stirring of the heterogeneous system has no effect on the pressure-volume relations. The identity of the pressures of the homogeneous and heterogeneous systems has been established, from which it follows that both the system of

heterogeneous density, formed on heating, and that of homogeneous density, formed on cooling, are equally stable. The heat of vapourization has been calculated from these data and is found not to equal zero at the classical critical temperature. Long time lags required for the establishment of equilibrium on compressing the gaseous system above the critical temperature have been found, and are interpreted as indicating a structure formation.

An hypothesis for the liquid vapour transfer in the critical region is presented. In the border region between liquid and gas a variety of systems of different phase densities are equally stable. Applying the concept of regional orientation, the amount of structure in any given system is a function of the temperature and volume. This structure may be concentrated in the lower region of the system or may be uniformly dispersed. If conditions are constant, tendency to change a dispersed to a stratified system, or vice versa, is extremely slight.