AN INVESTIGATION OF THE TRANSITION REGION OF LIQUID TO GAS IN THE SYSTEMS ETHYLENE AND ETHYLENE-AIR MIXTURES

A Thesis
by
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Submitted to the
Faculty of Graduate Studies
and Research
of
McGill University
in partial fulfilment of the
requirements for the degree
of
Doctor of Philosophy

McGill University,
Montreal,
Canada.

April, 1939.

The writer wishes to express his appreciation to Dr. O. Maass for the guidance and encouragement throughout the course of this investigation.

Acknowledgment is made to the National Research Council of Canada for a Bursary and Studentship held during this period.

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INTRODUCTION

One of the most interesting problems of the physical sciences has been the investigation of the changes of form and properties which occur when matter passes from one state of aggregation to another. Of these transitions, not the least fascinating is that from liquid to gas. For well over a hundred years, the nature and mechanism of the changes which a liquid undergoes as its temperature is raised, have been the subject of much experimentation and contemplation. Even now the problem is still a controversial one. There are two distinct schools of thought, both presenting good evidence in support of their opinions as to the nature of the changes. It is hoped that this thesis will be of value in showing that the various opinions which have been presented are not mutually exclusive, and that a combination of the ideas, championed so strongly by both sides, leads to a reasonable explanation of the quantitative measurements which have been made in this particular transition range upon ethylene.

The first recorded observations of the change from liquid to gaseous states were those of Cagniard de la Tour in 1822 (1). He found that when a pure liquid, in equilibrium with its vapour, is heated in a closed tube, the visible line of demarcation between the liquid and vapor, disappeared at some definite temperature. This temperature has been called the critical temperature, or the temperature of Cagniard-la Tour. Shortly afterwards, the classical experiments of Andrews (2), in which the pressure-volume relations of carbon dioxide were determined for various temperatures, revealed that the isothermal just below the critical temperature was contiguous to that just above the critical temperature. This fact was interpreted by Andrews to indicate a continuity of state at the critical temperature. A liquid and a gas were considered by him to be widely separated forms of the same condition of matter. To add to the strength of this theory, the famous equation of state due to Van der Waals (3), was found to give fair quantitative agreement for liquids as well as gases. The simplicity of his theory, and the wide utility of his equation in predictions of the behaviour of liquid systems, led to the widespread acceptance of the theory of continuity of state.

Almost immediately, however, experimental evidence began to be accumulated which pointed to the possibility of more complex changes taking place than the theories of Andrews and Van der Waals would indicate. For instance, on the disappearance of the meniscus at the critical temperature, it was thought that the properties of both phases, such as density, etc., had become identical, and that a homogeneous gas system had been created. If this were so, the critical phenomena should occur only for one specific density, and not as it is found to do, over a range of densities. Ramsay (4) and Jamin (5) were first to postulate that the liquid state exists above the critical temperature, as an explanation for the density range over which the critical phenomena were observable.

Their density measurements were made by calculations based upon the meniscus position, a method which ~~has~~ leaves? much to be desired. They concluded, however, that the densities of liquid and vapor became equal at the critical temperature, and the phases became mutually miscible in all proportions. Ramsay, for example, went so far as to suggest that liquid and gaseous molecules differed in their number of atomic constituents, and that even above the critical temperature matter might be wholly liquid at high density, or wholly vapor at low density, or a mixture of both at intermediate densities. The system was considered to be physically homogeneous and chemically heterogeneous. Cailletet (6) obtained results in agreement with those of Ramsay and Jamin, and defined the critical temperature as that at which the liquid and vapor become miscible in all proportions. Young (7) concluded from his density measurements that the liquid and vapor had identical densities at the critical temperature, and that in a qualitative way, the evidence favoured the theory of continuity of state.

With more accurate density determinations in the critical region, a distinct modification of this concept was introduced. Galitzine (8) found that in the case of methyl ether a density difference as great as twenty percent exists indefinitely above and below the position where the meniscus disappears, at a temperature just above the critical. Evidence of a heterogeneous system was reported by him until a temperature approximately 7°C above the critical temperature had been reached. These results were at variance, of course, with the theory of complete miscibility, and were attributed by him to the presence of air in his samples. Young (9) repeated the experiments of Galitzine with very carefully purified material, and could not reproduce the density heterogeneity. He therefore concurred with Galitzine in attributing the result to impurities. Guoy (10), moreover, had offered as an explanation of a density discontinuity the gravitational effect of the weight of the medium itself in establishing a density gradient throughout the system. The calculated magnitude of such an influence fell, however, far below the values which had been observed experimentally. The presence of an inert gas in the vapor phase, even in small concentration, could conceivably magnify this effect to the proper proportion, and immediately strong support for the theory of causation by impurities was voiced. The workers in the field then became protagonists of two different theories. Those who believed in the reality of density discontinuities devoted themselves to the development of experiments to support the theory of a persistence of the liquid state above the Cagniard-la Tour temperature. Their opponents claimed to disprove such experiments by showing the existence of temperature gradients, or impurities, or other errors in the experimental performance. Strange to say, some of these critics, having concluded that the theory of liquid persistence was invalid for one reason or another, continued themselves to study the opalescence which is exhibited in this region, and from these studies reach the conclusion that "non molecular aggregates" continue to exist above the critical temperature. For example, Travers and Usher (11) conclude that since the critical temperature is not dependent upon the mass volume ratio that any theory of an equilibrium between gas and liquid molecules, which should be dependent upon temperature, is vitiated. After studying the opalescence they conclude that "non molecular aggregates" persist above the critical temperature, by grace of a positive surface tension which is possible for droplets of very small radii, as suggested by Donnan (12). The localization of opalescence they find related to the mass volume ratio, due to the motion of the meniscus. This concept has been used to explain the relation of phase density to mass volume ratio as described in the body of this thesis.

Since the discussion of opalescence permeates all work on the critical region, a description of the type of opalescence and the theories advanced to explain it is essential. The existence of systems which are capable of scattering light is well established in the critical region.

? I dont see the meaning. I expect it means intensity differs in different parts of system'

The opalescence which occurs is limited in extent on raising the system to the critical temperature. It is greatest in intensity in the disappearing phase. If the system is kept at this temperature long enough, or is violently stirred, this opalescence gradually occupies the whole volume in which the substance is confined. On heating well above the critical temperature the opalescence gradually disappears, but reappears again on cooling, becoming very intense just before condensation. The theories developed to explain it are two-fold. The one, developed by Smoluchowski (13) from the Einstein theory of density fluctuations, and that of Kuster (14) which is essentially the same, attribute the effects to local concentrations and rarefactions of density due to the distributions of energy amongst the molecules. The other, supported by Altschul (15), Donnan and Travers and Usher, Schroer (16) and Cardoso (17), regards the opalescence as due to liquid groups floating in the vapor. According to F. B. Young, the slow decrease in intensity of the opalescence with rise of temperature favors the Kuster theory, unless the density temperature curve is peaked in form, rather than parabolic as generally accepted. As we shall see, the density temperature curve is actually peaked, at least for ethylene, and the theory of Travers and Usher et al must be supported by the author. This whole question of opalescence has been investigated by Mason (18) and further support for the opalescence as due to liquid groups has been obtained.

Did L.V. King not publish something on this also.

Returning to the work of those who directed their efforts toward the establishment of the reality of the density discontinuity, we find a new technique developed by Traube (19) and Teichner (20), and Hein (21) who determined densities by the use of small glass floats. These measurements were more accurate than any previously made, and in good agreement with those of Galitzine. As a result of his measurements, Traube became the chief proponent of a difference in character between liquid and gas. True liquid molecules were termed "liquidons" by him, and true gas molecules "gasons". These were assumed to exist in equilibrium with one another, and the ratio to be fixed by the temperature. This concept was extended by de Heen (22) to include the influence of specific-volume upon the concentration. This view has received much support from the studies of x-ray diffraction by Stewart (23) and his co-workers Noll (24) and Spangler (25). Onnes (26) again, however, could not duplicate de Heen's results, and attributed them to temperature gradients and to the gravitational effect as outlined by Guoy.

Further evidence for the existence of liquid above the critical temperature was found in solubility measurements. The first of these experiments was due to Hannay and Hogarth (27) on the potassium iodide - alcohol system. They found that the dissolved potassium iodide was precipitated if the liquid was allowed to evaporate, below the critical temperature, but that when the liquid was heated slightly above the critical temperature, the solute was not precipitated. This was not interpreted as pointing to a liquid persistence, however. The explanation was that gaseous alcohol under such conditions had the power of solution. And this in face of the fact, according to Bradley, Browne and Hale (28), that intense local heating caused precipitation in such regions as were subjected to it.

Cailletet and Hautefeuille (29) investigated the carbon dioxide - iodine system, and found it to yield the same sort of results as Hannay and Hogarth had discovered for the alcohol system. Contradictory evidence was also found by Cailletet and his co-worker Collardeau (30), who found blue oil of galbanum was precipitated from carbon dioxide at the critical temperature. More supporting evidence was put forward by Pictet (31) from his study of borneal and alizarin in alcohol solutions. Both these substances were insoluble in gaseous alcohol and soluble in liquid alcohol, but were not precipitated when the liquid was heated above the critical temperature. He predicted that such precipitation would occur if the temperature were raised high enough, although this prediction was not subjected to experimental verification.

Much other solubility data of a similar nature ~~has~~ have been obtained, some of ~~it~~ the data in connection with salts in water, ~~such as~~ for example that by Bertrand and Lecarme (32) with potassium chromate. An extrapolation of the temperature coefficient of the solubility of sodium carbonate in water to the critical region from a few degrees below it by Waldeck, Lynn and Hill (33) supports the opposite opinion of a discontinuity of solubility at the critical temperature. This work must carry less weight because of the extrapolation to a region where small temperature changes cause large changes in properties.

Still other properties were investigated in the critical region, such as conductivity. Eversheim's (34) measurements of ammonia solutions indicated a persistence of liquid. Franklin and Kraus (35) found distinct evidence of conductivity 6.5°C above the critical temperature.

Very strong support of this insistence on the persistence of liquid was provided by Callendar (36) in 1928 He found that on heating water in stationary quartz tubes, layers of different density were observable as high as 6°C above the critical temperature of 374°C He also measured the saturation curve through this region and found the result quantitatively corroborated by latent heat measurements. The latent heat did not become zero ~~until~~ below 380.5°C Moreover, the results were obtained with very carefully purified materials, and contrary to previous investigators, it was said by Callendar, that such phenomena had not been previously observed because of the presence of impurities, rather than that they are caused by impurities.

The whole subject was reopened by the discovery of Sutherland and Maass (37) that the reaction velocity of the hydrogen chloride-propylene system dropped to zero above the critical temperature,' in spite of the fact that the concentrations of the reactants were as great or greater than the concentrations in the liquid state. This startling result has led to the thorough investigation of many properties of ~~such substances as~~ ethylene, ethane, methyl ether and ~~so on~~ other substances. The properties investigated in these laboratories have been the density, dielectric constant, surface tension, specific heat, adsorption and so on. A brief survey of the methods and results obtained will serve to introduce the subject matter of this thesis in a clearer manner. The density measurements made by Tapp and Maass (38) were obtained by the use of a McBain-Bakr (39) spiral and a small glass float. This method gave a very great sensitivity in measurement, and proved conclusively that discontinuities of density do exist above the critical temperature. The spiral and float arrangement could be moved to various heights in the tube, and the discontinuity was thus shown to be a sharp one, and not a density gradient as the explanation of Guoy and later Ruedy (40) would require. By the same means mechanical stirring could be effected, and it was claimed found to be ineffectual in destroying the density difference. In the light of the present knowledge of the subject it appears that the mechanical stirring was not continued for long enough periods, or was not sufficiently violent. As will be apparent later, ~~such~~ sufficient stirring ~~should~~ does cause a condition of uniform density. This criticism does not, however, invalidate the conclusion reached by these authors, that the liquid state does persist above the critical temperature.

Winkler and Maass (41) measured the surface tension of propylene and methyl ether. The results indicated that the surface tension, but not the surface energy, became equal to zero at the critical temperature. According to Porter (42) this condition may be realised when the ratio of the molecular diameters of the species is equal to the ratio of the densities.

Marsden and Maass (43) found that the dielectric constant of a liquid and its vapor do not become identical at the critical temperature, but become equivalent at some higher temperature. They thus confirmed a similar discovery of Verain and Eversheim (44) by a more accurate method.

Morris and Maass (45) and Edwards and Maass (46) studied the adsorption of propylene and dimethyl ether upon alumina. They found no discontinuity in adsorption on passing from vapor to gas, but found a marked discontinuity in passing from liquid to gas.

a ?

Broughton, Pall and Maass (47) have observed an hysteresis in the specific heat curve when the specific heat is determined as the substance in a heterogeneous state is heated to temperatures above the critical temperature, and when the specific heat is determined on heating the homogeneous system through the same temperature range. The specific heat was thus seen to be dependent upon the thermal history of the substance.

Holder and Maass (48) have repeated and extended the work of Sutherland and Maass, and Marsden and Maass, upon the reactivity of the hydrogen chloride-propylene system. The refined experimental method has shown that the "critical concentration" or critical density has a larger effect upon the reactivity, which is believed related to the persistence of the liquid structure, than has temperature. This observation fits in well with the measurements of Stewart, Noll and Spangler, which have already been mentioned, and the theory of Warren and Gingrich (49). The importance of specific volume is again brought out in their work, the influence of pressure and temperature being of secondary importance with regard to liquid existence.

Mason (18) has investigated the viscosity of ethylene in this region by a very sensitive oscillating disc method. He has confirmed the very excellent work of Clark (50) in showing an hysteresis in viscosity on heating and cooling. He has extended it to show the probable temperature of disappearance of the liquid phase for critical fillings as indicated by the minimum of the viscosity temperature curve. The agreement with the new critical temperature as determined from the isothermals presented in this thesis is good.

The work of Geddes and Maass (51) has been of very great importance in the study of the critical region. These authors made a very thorough and excellent study of the density, pressure and temperature relations of ethylene throughout the critical range. Of paramount interest in this work was the investigation of the time lags involved in the establishment of equilibrium densities when the system was subjected to changing conditions of pressure, temperature and volume. The results show an extended time lag in passing from vapor to liquid densities which have been interpreted as indicative of molecular orientation.

In fact, the mass of data which has been accumulated in these laboratories has all been successfully explained upon this basis. That is, a structure has been assigned to the liquid state of aggregation. This structure has been conceived as a dynamic regional orientation, the extent or degree of orientation being dependent upon the temperature and density. This conception, due to Dr. O. Maass, is not vastly different from that of Stewart who speaks in terms of cybotactic groups, and Traube who speaks in terms of liquidons and gasons.

The mathematical treatment of such ideas has not been left neglected. Thus Mayer and Harrison (52) predicted from statistical mechanical treatments of condensing systems a behaviour remarkably similar to that observed by Maass. One prediction that had not previously been observed experimentally was the existence of a region above the critical temperature wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$. More rigorous and simpler treatments of condensing systems by Born and Fuchs (53) and Frenkel (54) respectively, have corroborated these mathematical calculations. Experimental verification of the previously unconfirmed prediction with regard to $\left(\frac{\partial P}{\partial V}\right)_T$ is presented in this thesis. From these pressure volume temperature relations, and from pressure temperature relations, a new conception of the liquid gas transformation has been forced upon the author. The transition picture now includes the influence of specific volume, temperature, and pressure, and explains quite plausibly the possibility of emulsified systems suggested by Donnan, Travers, Ostwald (55) and others. The experiments which led to this concept, which is again a "continuity of state" theory, are presented in the following sections.

EXPERIMENTAL

Three types of apparatus were used in the investigations described below. The first was copied exactly from the design developed by Geddes and Maass (51). It consisted in its essentials of two pyrex glass bombs, about 35 cm. in length, supported upon brass rods, and joined at the bottoms by pyrex capillary tubing, bent to form a u-tube. The dimensions of the bombs were approximately 11 mm. inside diameter, with walls of 3 mm. thickness. The capillary tubing had an inside diameter of about 3 mm. and an external diameter of approximately 8 mm.

The left-hand bomb contained a small nail enclosed in a glass sheath, and a small electro-magnet, which could be raised and lowered along the length of the bomb, was arranged outside the tube in order to stir the contents.

The right-hand bomb contained a McBain-Bakr balance and float for the determination of the densities. The quartz spirals had normal lengths varying from 3 cm. to 4 cm. and sensitivities ranging from .003 gm/mm. to .0045 gm/mm. The floats were made of pyrex glass, with diameters of about .5 cm , and volumes ranging between 7 cc. and .9 cc , while their weights varied between .3 gm. and .4 gm. Relative densities were determined by measuring the elongation of the spiral by means of a cathetometer to ± .05 mm. and could therefore be reproduced to within ± .1%. The densities were calculated from the equation

$$d = \frac{W - (E - N)S}{V}$$

where d is the density in gm/cc.

W is the weight of the float in gm.

E is the extended length of the spiral in mm.

N is the normal length of the spiral in mm., that is, the length when hanging under its own weight in air.

S is the sensitivity of the spiral in gm/mm.

V is the volume of the float in cc. + 1/2 volume of spiral.

A plot of spiral length against density gave a quick and convenient method of evaluating the densities.

Absolute values of the density were dependent upon ~~the determination of~~ the volume of the float, which was determined ~~carried~~ ~~out~~ by means of a picnometer. The values of the volume were found to be reproducible to three parts in eight hundred.

The spiral was suspended in the bomb from a glass collar, which rested upon a constriction blown in the glass wall of the tube. In order to remove a possible cause of explosions, this arrangement was later altered to that of a carefully bound steel spring, which pushed strongly against the glass walls, and was prevented from scratching the surfaces by a cotton covering. A cotton wound glass ring was inserted in the lower part of the tube in order to support the float and relieve the strain upon the spiral when the tube was empty. When these parts of the apparatus had been placed in position, the top of the tube was drawn down and joined to a capillary lead, which in turn was sealed to the purification train and filling system. The left-hand bomb was drawn down and joined to the filling system in the same way. The methods used for filling the bomb assembly with mercury and the gases employed in the investigations were common also to the second form of apparatus, and are described fully below. A scale was attached to the side of the right-hand bomb, by which the difference in mercury level between the two bombs was evaluated, and used to correct the pressure values. A diagram of this type of apparatus is given in Figure 1.

APPARATUS #2

The second type of apparatus was adapted from that described above. It consisted again of two pyrex glass bombs, joined at the bottoms as before. The diameters of the bombs were, however, greatly reduced. The internal diameters were now about .5 cm. with .3 cm. walls. The spiral and float of the previous design were not used. Instead, both sides of the apparatus were made exactly similar, a magnetic stirring arrangement being added to the right bomb in order to determine the effect of mechanical stirring upon the substance under investigation.

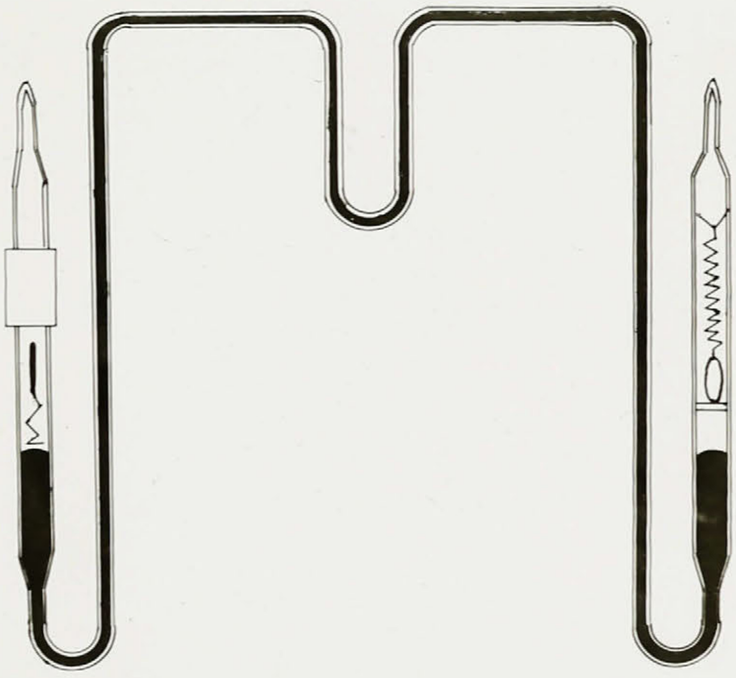

Figure 1

The apparatus was filled with pure mercury to about the half way position in each bomb. This mercury acts as a piston in the manipulation of the ethylene gas which is confined in the right-hand tube, and also transmits the pressure generated by the carbon dioxide of the left-hand bomb. The normal mercury level was determined by means of the cathetometer, and the volume of the ethylene bomb from the surface of the mercury to the draw-off was calculated from the diameter of the tube. This diameter was measured by means of the cathetometer, and was shown to be constant throughout its length by measuring the height of known amounts of mercury. The diameter of the carbon dioxide tube was determined and checked for constancy in the same manner. The volume of the draw-off was computed by geometric estimation. The total volume was then corrected for the presence of the stirrer, the volume of which had been determined by means of a picnometer. The volume was later checked by repeating a point upon a known isobar. The agreement was excellent. Volumes could then be computed for any mercury level, and a plot of mercury height against volume was used in the same manner as the plot of spiral length against density for apparatus #1. The necessary pressure correction was given immediately by the reading of the mercury height.

This design possessed two distinct advantages over the former assembly. The absence of the spiral and float permitted the use of much narrower tubing. The considerable risk of explosions, which was present in all the work, was much reduced. Moreover, mechanical stirring was now possible. It had, however, the inherent disadvantage that heterogeneous systems could not be detected. This was not a serious disadvantage in the investigations for which it was designed, because the conditions under which such systems were known to exist had been established from previous work, and the pressures of such systems were the point of interest, rather than the actual density differences themselves.

Insertion of Mercury

The simplest and most convenient method of inserting the desired amount of mercury into the bombs and the connecting u-tube, without trapping any air in the thread of mercury between the bombs, was that of distillation.

A small distilling flask was partially filled with pure mercury. The side-arm of the flask was fitted with a small condenser jacket, and then sealed to the lead of the carbon dioxide bomb. The system and the flask were then pumped out, and the mercury distilled into the carbon dioxide bomb. When sufficient mercury had been distilled to fill the capillary tubing and part of each bomb, the stop-cock in the lead to the ethylene bomb was closed, and air slowly allowed to enter the carbon dioxide bomb. The differential pressure forced the mercury through the u-tube and into the ethylene bomb. As soon as the mercury showed in the ethylene bomb, the stop-cock was opened and the pressures equalized in order to prevent the mercury from rising too high and damaging the float and spiral. This procedure was repeated until the desired mercury height was obtained in both bombs. The distilling flask was then disconnected, and the apparatus was ready to be filled with the gas samples.

A diagram of this type of bomb assembly is given in Figure 2.

APPARATUS #3

The third type of experimental unit was designed for the study of the effect of compression on the liquid phase. It consisted of a single bomb, with quartz spiral and float. A small glass condenser jacket was made to fit over the top portion of the bomb. This jacket was made water-tight against the bomb walls by means of a rubber gasket. Two leads were provided in the glass jacket itself, to allow a circulation of water through it. The temperature of the water to be passed through the jacket was controlled from outside the protecting screen. Two streams of water, one from a hot and the other from a cold water tap, were passed through a mixing chamber, and the temperature of the water issuing from this chamber was read upon a thermometer. This water could then be passed through the jacket upon the bomb, and the temperature of the return stream was read from a second thermometer, placed suitably in the return line outside the

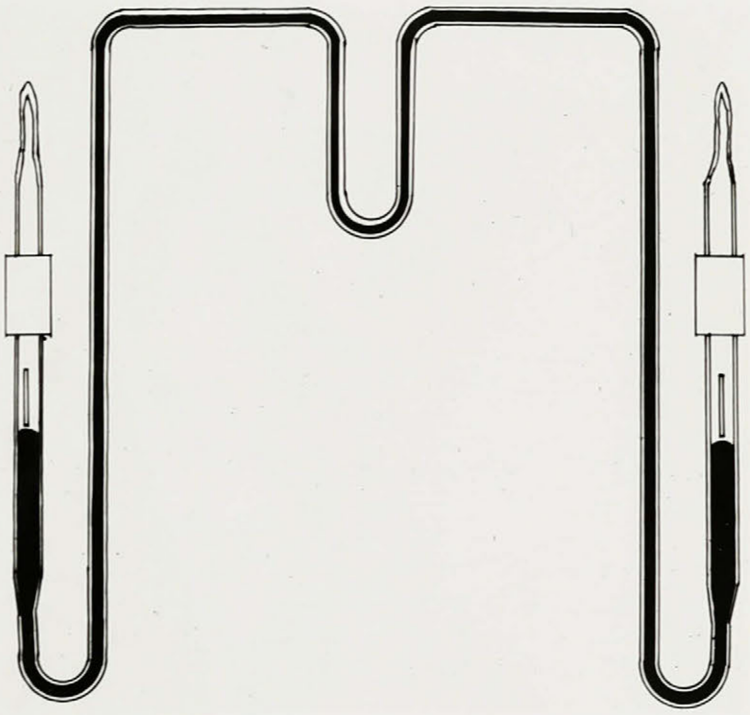

Figure 2

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protecting screen. As the control and production of temperature was not required to be precise, the temperature of the water passing through the water jacket was assumed to be the mean of the temperatures of the input and outlet streams.

After the bomb had been filled with ethylene and the top sealed off, the water jacket was affixed in proper position, the whole jacket and a large section of the leads were immersed in the thermostat water. Thus, when no passage of water was permitted through the jacket, the temperature of the whole length of the bomb was equal to the temperature of the thermostat water. When water was passed through the jacket, a temperature gradient could be maintained along the bomb It was necessary to ensure that the water of the jacket could return to the precise temperature of the thermostat. The only source of error was likely to be the heat which could be conducted through the leads of the water jacket, and which were exposed to the higher temperature of the air of the room. A calculation of the maximum temperature gradient which could be maintained in this way showed a possible value of .0008°C. This is less than the fluctuations of the thermostat itself, and should not be important. However, to preclude the possibility of such conduction, small copper coils were placed in the bath, in series with the jacket leads. The importance of this precaution is brought out more clearly in the subsequent discussion of the compressional experiments.

A slight alteration of this arrangement was used for "molecular stirring" experiments. The glass jacket was replaced by a small rubber coil. This substitution allowed more rapid establishment of thermal equilibrium, but could only be used to cool the top of the bomb, and was useless for compressional manipulation. The reason was this. It was hoped to re-establish liquid structure by means of local compression, in an originally homogeneous system. If any portion of the bomb top were not completely covered, the temperature of the exposed portion would be unknown, and might possibly be below the temperature of condensation. Thus the formation of liquid could not be attributed to compression, and the value of the experiment would have been nullified. It was, however, a very convenient method of bringing about "molecular stirring" of the air-ethylene mixtures which were studied. A diagram of the water jacket assembly is given in Figure 3. A drawing of the rubber coil assembly is not included, as the principle of construction was exactly the same.

Purification of Gases

The gases which were used in the present work were carbon dioxide, ethylene, and mixtures of ethylene and dry air. The purity of the gases was of the greatest importance, because much of the criticism of previous work done in the critical temperature region has been on the ground of lack of ~~directed at the~~ purity

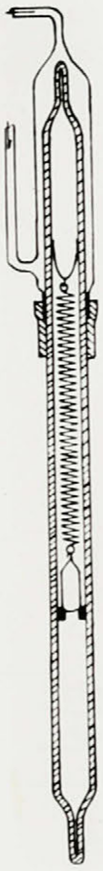
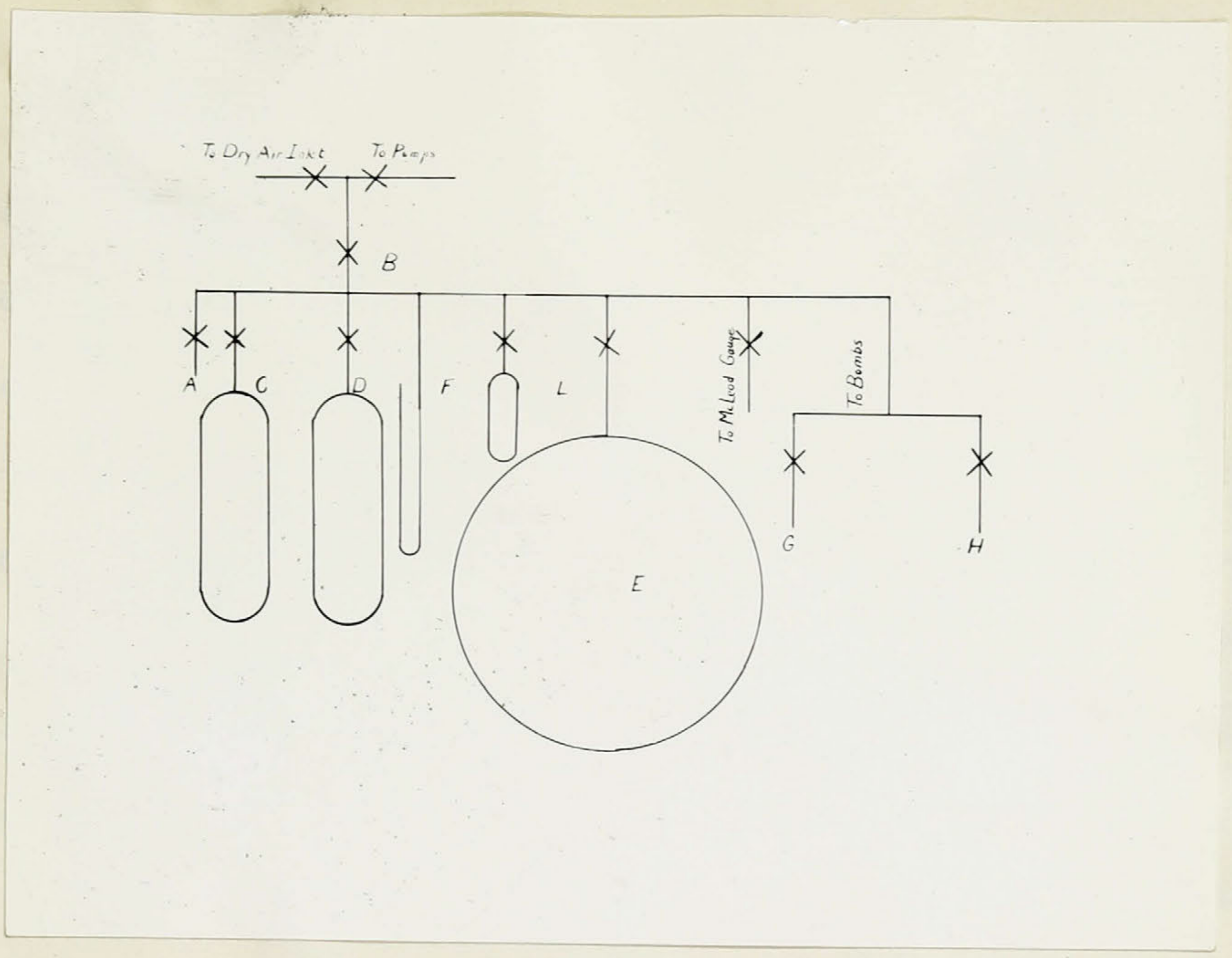


Figure 3

of the substances investigated. For this reason, great care was taken in the purification of the gases and in their introduction into the system.

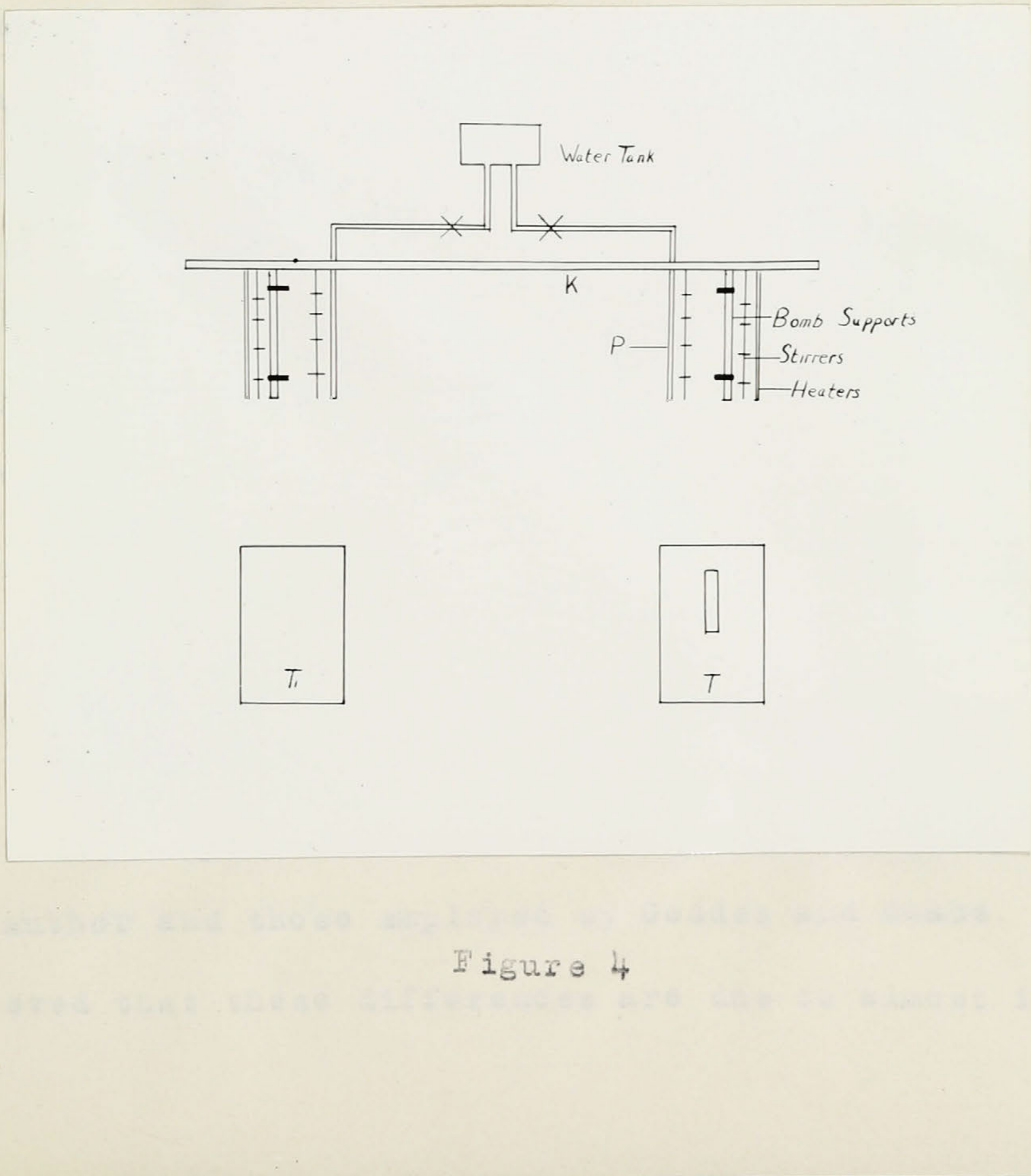
The purification was carried out by fractional distillation. The source of supply of the ethylene or carbon dioxide gas was first sealed to the purification train at the point A of Figure 4. The source of the ethylene gas was the tank material supplied by the Ohio Chemical Company. It had a guaranteed ethylene content of over 99%. The source of the carbon dioxide was clean powdered dry ice, which was placed in a glass container, and then sealed to the apparatus.

The apparatus was completely pumped down by opening the stop-cock at B. The stop-cocks in the distilling bulbs C and D were then closed, and liquid air placed around one of them. The gas was then distilled from A to D, the stop-cock B being opened at frequent intervals and a portion of the gas drawn off through the pumps. When sufficient gas had been collected in D, A was sealed off and the system thoroughly evacuated. The liquid air was then removed from D, and about one-third of the sample allowed to distil~~l~~ off. This fraction was used to flush the large calibrated volume E, and the appropriate bomb into which the gas would ultimately be distilled. The remaining gas was then distilled into C, and the apparatus again pumped down. The stop-cock in C was next opened, and the first third of the sample again used to flush the large volume and the bomb. The cock was then closed, and



A

Schematic representation of filling system



B

Schematic representation of bomb supports, water system and sliding thermostats

Figure 4

the apparatus again evacuated. The stop-cock to the bomb was then closed, and the large calibrated volume filled with the gas. The stop-cock in C was closed, and the bulb left standing ~~in~~ liquid air. The bomb assembly, which had previously been cooled by a dry-ice acetone mixture, was now surrounded by ? liquid air, and an amount of gas condensed in as desired, by opening the stop-cocks G or H, and measuring the change in pressure upon the manometer F.

An identical procedure was followed for the air-ethylene samples. In this case, however, before the bomb capillary was sealed off, the stop-cocks to the large volume and to the bomb were closed, the system again pumped down, and the stop-cock from the calibrated volume L, which contained dry air, was opened. The cock to the bomb was then slowly opened, and a measured amount of air allowed into the bomb. The bomb was then sealed off at the capillary tip.

At all times between runs the bombs must be kept immersed in a carbon dioxide acetone freezing mixture to reduce the pressure in the system and eliminate the danger of an explosion.

The purity of the gas samples obtained in this manner is believed to be very great. The behaviour of pure ethylene samples checked exactly with that of samples purified by careful distillation through a Podbielniak column. There are minute discrepancies in behaviour between the samples used by the author and those employed by Geddes and Maass. It is believed that these differences are due to almost immeasurably small quantities of air in the samples of the former workers, which were completely removed, or at least greatly reduced in amount by the particular care taken in preparing the samples used in these investigations. The amount of gas was calculated from the gas law, and the change in pressure of the large calibrated volumes. No account was taken of aberrations from the ideal law, because it was found to be unnecessary in the types of apparatus used. In the first design the average density was known directly from the spiral reading. In the second, an approximate drop of 10 cm. in pressure was all that was required to fill the smaller apparatus. The possible error from reading the manometer was 1%, which is of the same order of magnitude as the correction necessary for the ideal law at atmospheric pressure.

Care had to be taken to ensure that the proper amount of carbon dioxide was introduced into the system, so that under working conditions a two phase system was always maintained, despite the volume changes and temperature changes to which the carbon dioxide was subjected.

Treatment of Glass and Causes of Explosions

The experimental units used in these investigations were required to stand large internal pressures of 50 atmospheres or greater. For this reason the construction of the bombs required great care.

Despite all efforts which were made to remove causes of explosions, no surety of proper construction was ever achieved. The bomb assemblies were tested before being placed in position, by means of a Cailletet water pump, to well above the pressures generated in normal operation. In spite of this, frequent explosions occurred. The explosions were of two types The first was the complete collapse of the bomb walls themselves. The second was the cracking of the u-tube. The effect of annealing upon the glass was studied. The bombs were placed in an annealing oven at 550°C. for two hours, and were then slowly cooled over a period of twelve hours. This treatment had no apparent influence upon the bursting pressures as measured on the Cailletet water pump.

The breaks in the u-tube were traced to two possible causes. It was found that if the bombs were clamped very firmly in position, the u-tube frequently shattered. When the clamps upon the top of the carbon dioxide bomb were loosened, and a certain small play allowed in the bomb, the number of breaks in the u-tube was greatly reduced. The second cause appeared to be the Bourdon effect of the bends in the tube when cooled or heated through large temperature ranges. Nothing could be done to offset this inherent disadvantage of the design.

Cleaning of the Glass Surfaces

The glass was always carefully washed and then rinsed thoroughly with distilled water. When the bombs were in position they were thoroughly baked out under high vacuum at a temperature of about 200°C. for periods of well over half an hour.

Thermostats and Lighting

Since a temperature control of better than ±.01°C. was desired, it was necessary to construct thermostats in which the temperature could be very accurately regulated. Since the temperature of T was in the neighbourhood of 9.50°C., the critical temperature of ethylene, and that in T, in the vicinity of 15°C., the temperature at which carbon dioxide has a vapour pressure approximately equal to the critical pressure of ethylene, water baths served the purpose admirably. Each thermostat consisted of a cylindrical pyrex jar 18 inches high and 10 inches in diameter, well insulated with sheep's wool. A long narrow plate glass window was cemented in the jar T, so that when the latter was placed in position the measurements of the spiral extensions would not be influenced by imperfections in the glass wall of the jar. Since the temperatures were below room temperature, water sometimes condensed on the glass and prohibited clear vision. To eliminate this difficulty, a double window was placed in the front of the thermostat and a current of warm dry air passed between the windows. The ethylene bomb was illuminated from behind with 200 w. frosted lamps which were water cooled. The thermometers were illuminated by front lighting. Each bath contained a cooling coil P, made from six feet of half-inch thin-walled copper tubing. A two-gallon water tank supported at the ceiling, and which had a steady flow of cold water through it, served as a constant head source for the cooling coils. The rate of flow of water in the coils was adjusted by means of large taps. A smaller subsiduary flow system was added to this system in order to increase the sensitivity of control for the pressure volume isothermals reported below. Each bath was also supplied with a 500 w. and a 100 w. heater. All heaters were manually controlled by means of rheostats. Stirring was produced by means of two stirrers,with four blades each, for each thermostat. All four stirrers were operated by a D. C. shunt wound motor whose speed could be controlled. Temperatures were determined with Beckmann thermometers and standardized mercury thermometers divided into tenths. Thus absolute temperature readings could be made with an accuracy of ±.02°C. and relative readings with a higher accuracy.

All the apparatus contained in the thermostats was supported from above by the beam K. This allowed the thermostats to be moved up or down. By the use of a system of cords and pulleys, the baths could be raised for a run and lowered at its termination, to permit the Dewar flasks to be placed in position around the bombs, or removed therefrom.

The explosion hazard has already been mentioned. To protect the operator from flying glass in the event of an explosion, a double wall of beaver board was built in front of the apparatus. Observations were made through a shatterproof plate glass window, and all manipulation during a run was performed behind this screen. Thermometers were observed through telescopes, and the readings of the mercury height or spiral length were made by means of a cathetometer placed near the telescopes. After each run, the Dewar flasks were lifted around the bombs by means of string and pulley hoists, being guided into place by sticks which were attached to them and manipulated from behind the wall.

Experimental Procedure

The sequence of operations involved during an experiment was of great importance and must be followed rigidly if breaks of the u-tube and other causes of trouble are to be avoided.

The solid carbon dioxide in the flasks was first melted out with acetone so that the flasks could be removed without straining the glass assembly. Care was taken that some solid carbon dioxide was always present so that the temperature of the slush remained at -78°C. The level of the cooling mixture in the centre Dewar was maintained at the highest possible level. This was done in order to increase the contraction of the mercury in the u-tube to a maximum, and so increase the margin of safety for the expansion of the mercury in the bombs and capillary when the baths were hoisted into position. The bath water was next cooled by adding ice. The temperature of the ethylene thermostat must be below 8°C., since the behaviour of the system depends upon its thermal history if this temperature is much exceeded. The carbon dioxide thermostat was cooled to about 12°C. When this was done, and thermometers and lights properly arranged, the Dewars were removed from the ethylene and carbon dioxide bombs. These were allowed to warm up slightly in the air for several minutes and the baths then pulled up into place. The baths must be raised into position in such a manner that the frozen mercury is completely submerged in as short a time interval as possible. If this were not done, the mercury in that part of the capillary which is submerged would melt, and since the mercury above it in the bomb and in the capillary is not yet molten, there would be no room for its expansion, and the tubes would be shattered although no pressure had as yet been developed by the gases themselves. The temperatures of the thermostats were then adjusted to bring about an approximate balance of pressures between the two bombs. With ethylene these temperatures are well known, but for some substance whose vapor pressure curve has not been accurately determined, it is well to maintain a pressure in the carbon dioxide side which exceeds the probable critical pressure of the substance, and to keep the temperature of that substance slightly below the critical. In this manner the mercury will rise slowly when the frozen seal in the u-tube is allowed to melt, and will force the liquid up against the top of the bomb. This liquid is relatively incompressible, and more time is available for temperature adjustment than if the carbon dioxide were being compressed, because the carbon dioxide is present in such quantity as to guarantee a two-phase system throughout any volume change caused by the mercury movement.

Three types of experiment are now possible. These are constant pressure, constant volume and constant temperature runs. The first is performed by maintaining the carbon dioxide temperature constant, except for small changes to counteract the variance of mercury level, while the temperature of the ethylene or other substance is varied as desired.

Constant volume runs may be performed in either of two ways. On the one hand, the mercury in the centre u-tube may be kept frozen, while the change in density with temperature is followed. On the other hand, the volume may be kept constant by adjusting the carbon dioxide pressure to counteract for the volume change. Such experiments are the hardest to perform, and subject to the greatest error. With practice, however, the operator can maintain the volume constant to much less than 1/2% change.

Isothermal runs are made by making small changes in the temperature of the carbon dioxide thermostat. An increase in temperature, for instance, causes an increase in pressure upon the ethylene, which is given by the vapor pressure curve of carbon dioxide minus the increase in height of mercury caused by the volume change. Great importance has been attached to certain runs of this type which are described in the latter part of this thesis, and emphasis should be placed upon the care taken in their acquisition, and upon their reproducibility. Pressure changes could be made with certainty to .01 atmosphere, while temperatures of the ethylene were kept to ±.002°C. From day to day the estimation of the reading of the standard thermometers varied by about .02°C., but in any one run, pressures could be duplicated to ±.005 atmosphere or better. Two samples confined in different assemblies gave exactly similar results.

The closing down of the apparatus is essentially the reverse of the procedure outlined above. The mercury is brought to approximately the level position, and the tip of the centre u-tube is frozen. The thermostats are then cooled to about 8°C. and lowered away. The Dewar holders are attached to the sticks, and a freezing mixture slowly raised about the bombs. Care should be taken to see that the mercury is frozen at the three tips first. This ensures a maximum contraction and even spacing of the mercury. After the bombs have been thoroughly cooled, the operator may go behind the protection, and replace the freezing mixture by solid carbon dioxide.

RESULTS

The results which are presented in the following sections were obtained from investigations of one and two-phase systems of ethylene, and from studies of air-ethylene mixtures. Although a subdivision of the work into sections describing the results obtained from the one component system, and a second section describing those from the multi-component system would be quite natural, it is felt that the report will be somewhat more straightforward and offer better continuity if presented in a chronological sequence, because the early work in many cases led directly to the later, and the frequent changes of ideas in the interpretation of the results seem to lead quite naturally to the ideas now held by the writer. In particular it is interesting to note the rather distinct changes between the interpretations of Geddes and of the writer which developed rather rapidly as an increase in knowledge permitted the performance of more and more informative experiments. For this reason, a survey of the work done by Geddes is presented here somewhat more fully than in the introduction.

Geddes found that time lags in the establishment of equilibrium densities, subsequent to pressure, temperature or volume changes, were of an entirely different order than that required for thermal equilibrium. Measurements made at constant pressure showed that:

(1) the time required for the density change to reach half value, called the time to half value, is in general shorter with increasing temperature toward the critical temperature than with decreasing temperature toward the critical;

(2) the transition from "vapor" to "liquid" densities showed an extended time lag, as long in some cases as six hours;

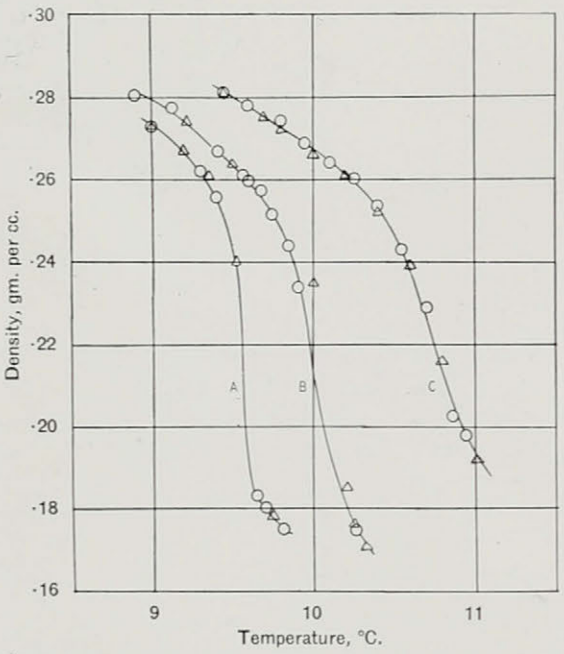
(3) the influence of pressure upon the time to half value is great, the time required falling off rapidly with increase in pressure;

(4) the time to half value is lessened the greater the difference between the initial and final densities, although the time to equilibrium is greater.

Measurements made at constant volume showed a persistence of a heterogeneous system until the temperature was approximately four degrees above the critical. Cooling from this temperature caused no increase in density until condensation occurred, when a liquid of a lower density than the original liquid appeared. Once the density difference had been destroyed, the homogeneous system was considered to be a true gas until the temperature of condensation was reached. Pressure measurements of the homogeneous and heterogeneous systems showed that the pressures were identical within experimental error for any given temperature.

Isothermal compression and expansion were found to destroy the heterogeneity and this was considered to mean that the two-phase character of the system had been destroyed. Temperature fluctuations and "molecular stirring" were found to have the same effect. These results were interpreted on the basis of a difference in structure of liquid and gas, with the concept of a dynamic structure or regional orientation ~~being characteristic of~~ for the true liquid. This interpretation has now been extensively altered to the concept of a simple two-phase system without specification as to the differential characteristics of the separate phases for the explanation of much of the phenomena reported below. It fails, however, to explain certain very pertinent experiments without some further elaboration as to the physical aggregation of the phases. Where the simpler explanation has been sufficient no mention is made of the hypothesis of regional orientation, but where this explanation has failed, the concept of a liquid which possesses some sort of structure of that nature has been used, and has been extremely useful.

The unusual nature and interest of the results of Geddes made the question of reproducibility an essential part of any subsequent work. Three typical isobars of samples of ethylene of satisfactory purity are given in Figure 5. The isobars are identical in shape to those obtained by Geddes, but show a difference of $.010_0$ gm/cc. in the absolute value of the density all along the curves. This is very clearly illustrated by the good agreement between the triangular points (which are the values obtained by Geddes minus a



Isobars of pure ethylene. A, 50.10; B, 50.54; C, 51.44 atm. Triangles denote Geddes' and Maass' values less 0.010_0 gm. per cc.

Figure 5

constant factor of .0100 gm/cc.) and the curves, which are observed values. The cause of the discrepancy can be suggested, and the present values are believed more nearly correct for several reasons. It is at once apparent that the carbon dioxide pressure cannot be the cause of the divergence, for the liquid density at 9.00°C., under the vapor pressure of ethylene alone, and obtained by keeping the centre u-tube frozen, is reported as .2567 gm/cc by Geddes, which differs by the same factor $.010_0$ gm/cc. from the observed values. The most likely source of error is therefore the calibration of the glass float. The volume constant in the present work was reproducible to 3 parts in 800, and the mean of a series ~~being~~ is, of course, still more accurate. Moreover, duplication with entirely new apparatus, including a new spiral and float, gave values agreeing with each other to 8 parts in 1000 on absolute values. Although two samples were used by Geddes, none of his work was repeated with a different experimental unit; in this investigation work was repeated with several units. Table I shows the reproducibility of the liquid phase density for different liquid vapor ratios, as well as checks obtained with different units. Consequently, it may be reasonable to assume that the absolute values of the data presented here are more nearly correct, and although no change is indicated in the relative density measurements of Geddes, ~~and~~ nor in the conclusions drawn therefrom, nevertheless, the values should be corrected.

TABLE I

Densities of Ethylene Liquid at 9.00°C. for Various Fillings and Experimental Units

Sample No	Average density	Density of liquid
1	0.2161	0.2455
	2334	2460
	2301	.2460
3	.2153	2450
	2210	.2450
	2253	2455
6	.2127	2443
9	2166	.2445

Densities of Sample 1 were measured by means of one experimental unit, of 6 and 9 by two other units. Samples 3 and 6 were distilled in a Podbielniak column (56)

Reproducibility of Time Lags

The degree of agreement of the time lags is all that may reasonably be expected from the experimental method. Very small differences in absolute temperatures cause large changes in density, especially at those positions of the isobars where time lags are most sensitive. Moreover, the correction that must be applied for the changing mercury level involves a personal error. This is due to the fact that the temperature of the carbon dioxide has to be adjusted continuously in such a way that the proper temperature change is achieved at the desired time interval. Since the effect of pressure upon time lags and density is marked, slight differences in pressure cause divergences in the time required for equilibrium. The correct order of magnitude is therefore all that should be expected along isobars, while much better agreement should be obtained in constant volume determinations where the u-tube is kept frozen. The results are given in Tables II and III. Following the practice initiated by Geddes, the results for isobars are expressed in terms of the time required for the density change to reach the half way mark, while the equilibrium times are recorded for isochore runs.

TABLE II

Time Lags Along Isobars

Maximum time lags observed on heating +0.20°C., pressures being kept constant

	Geddes	Observed		
Pressure, atm.	Pure ethylene t1/2, min.	Pure ethylene t1/2, min.	0.93% air t1/2, min.	o.55% air t1/2, min.
50.54	12	12	--	--
51.44	7.5	5	6.5	4

Time lags observed on cooling so as to produce specified density changes (in pure ethylene) pressures being kept constant at 50.54 atm.

Geddes		Observed	
Density change	t1/2, min.	Density change	t1/2, min.
0.262 to 0.245	2	0.265 to 0.254	2.8
0.240 to 0.205	8	0 245 to 0.210	7

Cooling Time Lags of Pure Ethylene

Isobar at 50.54 Atmospheres

Geddes		Observed	
Density change	t1/2, min.	Density change	t1/2, min.
.215 to .272	7.0	.214 to .272	10.0

Isobar at 51.44 Atmospheres

Geddes		Observed	
Density change	t1/2, min.	Density change	t1/2, min.
.190 to .215	34.5	.192 to .215	52

TABLE III

Time Lags of Isochores

	Pure ethylene		0.93% air	0.55% air
	Sample No. 3	Sample No. 6		
Temp. change, °C	9.20 to 9.50	9.30 to 9.50	9.30 to 9.55	9.30 to 9.55
Density change	0.2354 to 0.2256	0.2325 to 0.2241	0.2544 to 0.2517	0.2469 to 0.2386
Time to equilibrium, min.	23	23	3	3
Temp change, °C.	9.70 to 9.90	9.80 to 10.50	10.30 to 11.50	9.80 to 16.30
Density change	0.2094 to 0.2073	0.2175 to 0.2136	0.2175 to 0.2136	0.2346 to 0.2277
Time to equilibrium, min.	20	19	3	3

Geddes and Maass--approximately 20 min. in all cases.

Note--Cooling time lags of air-ethylene isochores are of same duration as the heating, i.e., 3 min.

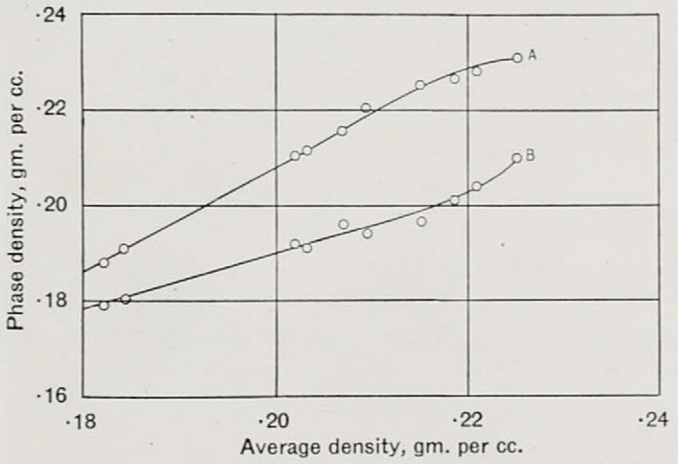
For purposes of a comparison to be made later, the time lags of ethylene-air mixtures are included in Tables II and III.

Although these determinations are by no means comprehensive, the reproducibility of the data of Geddes is well illustrated. The sharp increase in time to half value which occurs when densities are changed from the vapor region to the critical density, over that when changes are made from the critical density to the true liquid density is shown in the above figures.

The time lags of the isochores show excellent agreement, as was to be expected. It therefore appears that the time lag phenomenon, which was first discovered by Geddes, although not fully reinvestigated, is reproducible within the limits of experimental error.

Phase Densities of the One Component System at 9.50°C.

The dependence of the phase density at the temperature of meniscus disappearance upon the mass volume ratio was next investigated. In order to do this, the mercury level was adjusted so that the liquid or vapor phase, as the case might be, totally surrounded the float. The equilibrium density at 9.50°C. was then determined, and also the position of disappearance of the meniscus by means of a scale at the



Phase densities at 9.50° C. Upper curve, liquid. Lower curve, vapor.

Figure 6

side of the bomb. The total volume at this mercury level could be calculated from the average density of the medium, and the weight of ethylene. A plot of scale reading against volume gave the relative volumes of liquid and vapor from the position of disappearance of the meniscus. The amount and density of the phase not directly measured could then be calculated by difference. This procedure assumes the homogeneity of each phase, and is therefore not absolute, but such an assumption is the simplest and most obvious. The results are given in Table IV, and shown graphically in Figure 6.

It is interesting to note that the vapor phase at one average density may have a greater density than the liquid at a lower average density. According to the classical theory there should exist no difference, and, from the definition of equilibrium, the nature of the two phases should be independent of the relative amounts of each phase. One is therefore led to the conclusion that either the densities determined are not equilibrium values, a point that cannot be directly settled, since time is of infinite duration, or else some other factor besides the relative amounts of the phases is being altered as the mass volume ratio is changed. This factor may well be the regional orientation, in the nomenclature of Geddes and Maass (51), or the cybotactic groups of Benz and Stewart (23).

On the other hand, this anomaly may also be explained by a process of mixing of the two phases, which also

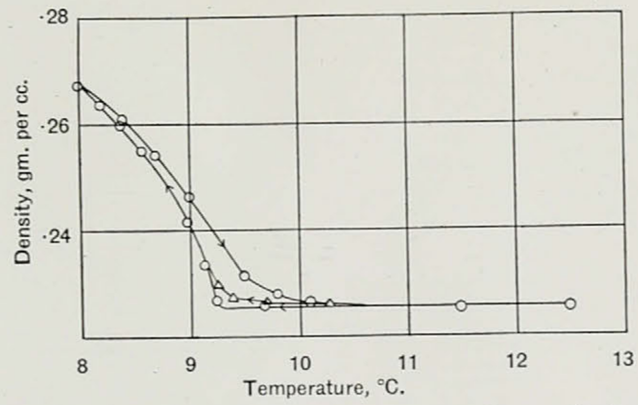
TABLE IV

Liquid-vapor Densities at 9.50°C.

Average density	Liquid density	Vapor density	Weight liquid gm.	Weight vapor gm.	Total volume cc.	Volume liquid cc.	Volume vapor cc.
0.1822*	0.188	0.1793	1.35	2.805	22.86	7.21	15.65
.1842*	.191	.1806	1.55	2.610	22.58	8.13	14.45
.2020	.2103	.192	3.654	2.77	31.78	17.38	14.40
.2032*	.2113	.191	2.498	1.66	20.52	11.82	8.70
.2070	.2154	.196	3.726	2.09	31.01	17.26	13.75
.2095	.2203	.194	3.965	2.46	30.64	17.99	12.65
.2153	.2255	.196	4.380	2.04	29.82	19.42	10.40
.2184	.2268	.201	4.490	1.93	29.40	19.80	9.60
.2210	.2283	.204	4.634	1.79	29.05	20.30	8.75
.2253	.2310	.210	4.670	1.73	28.50	20.25	8.25

* These values were obtained with an entirely new apparatus, and the ethylene was purified by means of a Podbielniak still.

explains the definite maximum difference of density between the phases at the classical critical density. For this reason the maximum divergence is to be expected at that density. At the critical density the movement of the meniscus should be a minimum, and therefore dilution of one phase by the other should also be minimum, and the greatest density difference should therefore be apparent under such conditions. The pressure volume isothermals which are discussed below lend support to this theory of mixing. They indicate that at least within the range of average density from .204 gm/cc to .232 gm/cc. the heterogeneous systems are truly equilibrium systems, and are one stable form which the system may possess. The other is an apparently homogeneous system, which, however, still retains a two-phase character, and which may apparently be obtained by an expansion from the true liquid state, a compression from the true vapor state, or a cooling from the true vapor state at some temperature exceeding 10.5°C., to some lower temperature greater than 9.20°C. Mason, Naldrett and Maass (57) have apparently obtained such systems by shaking above 9.20°C., when a system which resembles a dispersion of liquid in vapor is formed. These observations all lend strong support to the dilution theory outlined above, which was offered before the latter evidence had been obtained, as an alternative explanation of the relationship between phase density and mass volume ratio, and which makes no mention of the regional orientation or molecular structure theory.



Isochore of average density 0.2253. Triangular points denote cooling from 10.5° C.

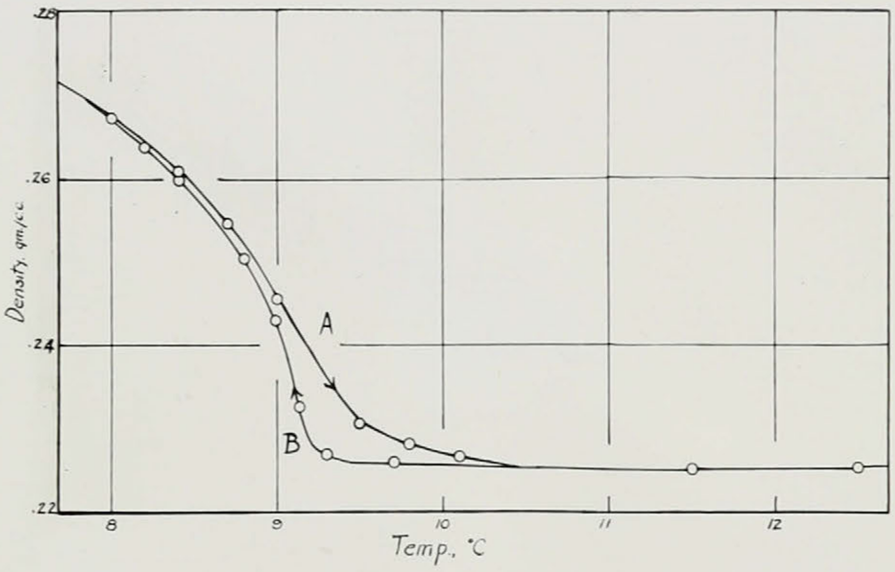


Figure 7

Complete Hysteresis Curve of Liquid Density at Constant Volume

The complete hysteresis curve of liquid ethylene, at temperatures both above and below the critical temperature ~~being included~~, was next determined. A typical isochore is shown in Figure 7 The first real discrepancy between the work of Geddes and the author is now revealed. Isochores determined by Geddes had a larger area of indeterminate densities than those observed by the present writer. In the first place, the temperature at which the average density is attained is lowered by approximately 3°, being 10.5°C. in the case of the present samples, and of about 14°C. in the case of the samples studied by Geddes. Moreover, the behaviour on cooling from temperatures above the critical temperature ~~and yet still~~ but below the temperature at which a homogeneous system is obtained is quite different. In the studies made by Geddes, the density always increased on cooling, and the lower the temperature the more nearly did the cooling curve follow the original heating curve, which is represented by the upper curve of Figure 7. This behaviour was interpreted as some sort of cumulative effect which the presence of liquid had upon the reforming of more liquid. It was not duplicated by this worker. In all cases in the present investigation, when cooling was performed from the critical temperature or temperatures higher than the critical yet below the temperature at which the system attains its average density, no increase in density was observed in the lower part of the tube until very close to the temperature of condensation. The triangular points in Figure 7 indicate the effect of cooling from 10.5°C. Further evidence is given in Table V. The probable reason for these divergent findings is now considered to be the presence of very small quantities of some inert impurity, such as air, in the samples used by Geddes. The amount of air must have been so minute, however, that the qualitative behaviour of Geddes' systems must be considered to be typical of pure ethylene, and the value of his work is very slightly changed. Delete (if at all). A clearer understanding of this explanation will be apparent as soon as the data upon air-ethylene mixtures has been presented.

TABLE V

Cooling from 9.60°C.

Temperature °C	Density gm/cc.
9.60	.2270
9.50	.2270
9.40	.2270
9.30	.2299

Constancy of Pressure with Changing Volume above the Critical Temperature

Mayer and Harrison (52), have recently made some interesting calculations based upon statistical mechanics as to what may be expected in the critical pressure - critical temperature region of a one component system. Specifically they predict that above the critical temperature as classically defined, the pressure volume isothermals shall exhibit a region in which $\left(\frac{\partial P}{\partial V}\right)_T = 0$. This region shall have an upper limit at which $\left(\frac{\partial P}{\partial V}\right)_T = 0$ for one point only. The isothermals of Geddes and Maass, which were with one exception, that at 9.80°C., evaluated from the isobars, showed no such region. However, the experimental points were not close enough together to settle this question definitely. The experimental isothermal at 9.80°C., which was determined in connection with the effect of expansion and compression upon the heterogeneous system, also showed no such region. It did, however, show clearly that the pressure of the heterogeneous system was the same as that of the system at the same temperature when homogeneous. If now the pressure of such a heterogeneous system could be shown to be independent of the mass volume ratio, the ~~results to be concordant~~ should show a region upon the homogeneous isothermals wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$. The evidence given in Table VI shows that the pressure is independent of the mass volume ratio within experimental error. Owing to the importance of the experiment the technique is fully described.

The mercury was adjusted so that the float would be completely immersed in liquid ethylene. The temperature of the carbon dioxide and ethylene was then carefully raised, care being taken to maintain the mercury at a constant level. The ethylene temperature was raised to 9.80°C., and the equilibrium density determined. This density measurement showed that the system had remained heterogeneous, for it was an equilibrium value, and differed from the average density at that volume. The carbon dioxide temperature was read, and the pressure corrected for the difference in mercury levels between the two bombs. The system was then changed to another volume by adjusting the carbon dioxide temperature, the centre u-tube frozen, the ethylene cooled to below 8°C., and reheated to 9.80°C. The mercury was then melted, and a density and pressure reading obtained at the new volume.

It therefore appeared that a major discrepancy between the work of Geddes and the author had been discovered. This could again be due to the presence of a small quantity of air in the samples used by the former, or also explicable on the assumption that the experimental points of his isotherm were taken at too wide intervals. The second form of apparatus described above was therefore contemplated, in which the correction for mercury level would be more precise, and this and other predictions of Mayer were planned as the subject for further investigation.

TABLE VI

Data Showing Constancy of Pressure with Changing Volume at 9.80°C.

Mercury level	Average density	Specific volume, cc.	Equilibrium density	Pressure
125	0.2178	4.591	0.2214	50.35
113	.2094	4.775	.2148	50 36
130	.2214	4.514	2247	50.36
108	2070	4.830	.2112	50.35

TABLE VII

Ethylene Temp. °C	Pressure	Observed Density
8.00	48.76	2688
8 00	49 06	2727
8.00	49.19	2772
8.00	49 25	2790
9.00	49.88	2484
9 00	50.08	.2574
9.00	50.23	2619
9.00	50.27	2640

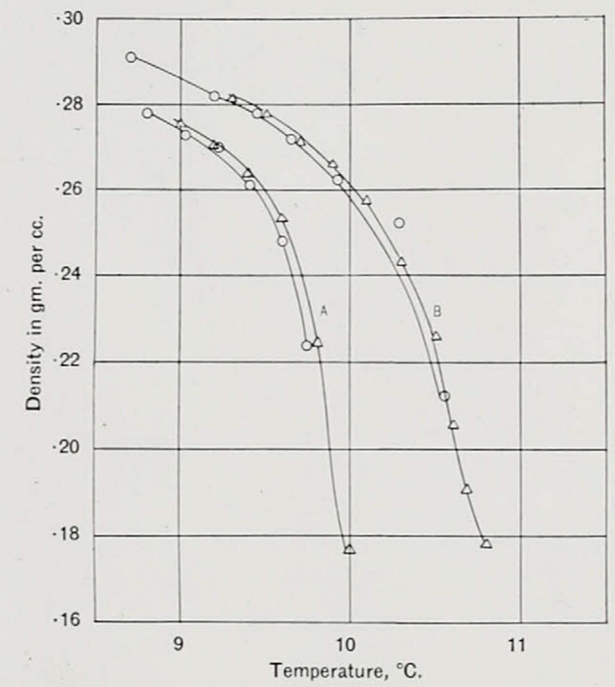
Air-Ethylene Mixtures

One sample of ethylene of supposedly very great purity gave anomalous results with respect to the hysteresis curve at constant volume. In order to trace the cause of this behaviour, isothermals at 8.00°C., and 9.00°C., at which temperatures the ethylene should follow the behaviour of a two-phase one component system, were determined. The results are given in Table VII, page 35, and indicate the presence of an inert gas.

Moreover, at a pressure of 50.23 atmosphere, which is well above the critical pressure of 49.98 atmosphere, reported by Geddes, two phases were still clearly visible. The most likely impurity being air, two systems of .55% and .93% air by weight were introduced into the bomb and studied.

Isobars of Air-Ethylene Mixtures

Two isobars of each sample are given in Figure 8 and the values tabulated in Table VIII. The time lags for both heating and cooling have already been recorded in Table II. The times to half value agree, within the sensitivity of the method, with the values obtained for pure ethylene. In addition, the shapes of the isobars are similar to those of the curves obtained with pure ethylene. These facts indicate that the inflections observed in isobar runs with pure



Isobars of air-ethylene mixtures. Circles, 0.93% air. Triangles, 0.55% air. A, 50.54; B, 51.44 atm.

Figure 8

ethylene are not noticeably affected by the presence of air in these concentrations. This is not the case with determinations at constant volume.

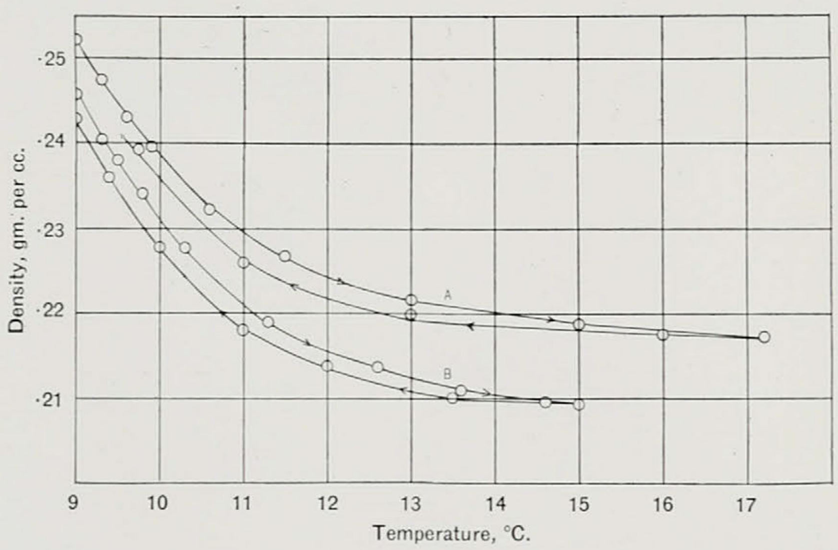
Another point of interest in these curves is the increase in density with decreasing air content The reason for this is that the isobar systems, although at pressures well above the critical in both cases, are now not homogeneous systems (they would be if ethylene alone were present) but consist of two phases. The air is apparently largely insoluble in the liquid ethylene. This causes an increase in pressure, a corresponding increase in total volume, and a consequent decrease in the density.

Isochores of Air-Ethylene Mixtures

These curves, of which typical examples are shown in Figure 9, and recorded in Table X, exhibit a behaviour vastly different from that of pure ethylene. The greatest difference is the increase of density with decrease in temperature when the cooling is started above the critical, a phenomenon that has been noted for the first time.

In order to understand the complete significance of what is to follow, a brief review of previous work and theories is given.

The classical temperature density curve has long been assumed parabolic in shape with a smooth vertex. Experimental



Isochores of air-ethylene mixtures. A, 0.93% air; B, 0.55% air.

Figure 9

TABLE VIII

% Air	Temp. °C.	Press. Atm.	Density gm/cc.
.55	9.00	50.54	.2755
.55	9.20	50.54	.2700
.55	9.40	50.54	.2636
.55	9.60	50.54	.2533
.55	9.80	50.54	.2245
.55	10.00	50.54	.1767

% Air	Temp. °C.	Press. Atm.	Density gm/cc.
.55	9.30	51.44	.2808
.55	9.50	51.44	.2772
.55	9.70	51.44	.2718
.55	9.90	51.44	.2661
.55	10.10	51.44	.2575
.55	10.30	51.44	.2430
.55	10.50	51.44	.2259
.55	10.60	51.44	.2055
.55	10.70	51.44	.1906
.55	10.80	51.44	.1788

% Air	Temp. °C.	Press. Atm.	Density gm/cc.
.93	8.80	50.54	.2781
.93	9.02	50.54	.2733
.93	9.20	50.54	.2700
.93	9.40	50.54	.2610
.93	9.60	50.54	.2481
.93	9.75	50.54	.2240

TABLE VIII - continued

% Air	Temp. °C	Press. Atm.	Density gm/cc.
.93	8.70	51.44	.2907
.93	9 20	51.44	.2823
.93	9.40	51.44	2784
.93	9.65	51.44	.2721
.93	9.95	51.44	2623
.93	10 27	51.44	.2525
.93	10.50	51.44	2181

evidence had been obtained with increasing temperatures nearly to the critical, but never quite to it. The form of the curve was therefore extrapolated by means of the Cailletet-Mathias rule regarding the critical density. Traube (19), Galitzine (8) and Teichner (20) were the first to question this procedure and recorded the observation of a density discontinuity above and below the position of disappearance of the meniscus, and that the meniscus reappeared at a temperature other than the critical. Young (9) and others failed to reproduce these results, and attempted to explain them by the theory that impurities hindered the establishment of equilibrium by slowing up of diffusion. Maass and his collaborators (41) have traced the density temperature curve through the entire critical region with very carefully purified materials, and have confirmed the first results of Galitzine et al.

It is now believed by the writer that, if this behaviour is caused by impurities, and this is regarded as improbable, a mechanism other than that proposed by Young must be assumed. Moreover, it seems doubtful that substances may be obtained pure enough for this phenomenon to disappear entirely, in the light of the work of Clark (50), and that described here.

[illegible]

Turning to the time lags of the isochore runs in Table III, we see that the order of magnitude in the establishment of equilibrium density is now quite different and much smaller. This in itself indicates that an entirely different type of phenomenon ~~to be~~ is occurring. First, either the liquid phase is destroyed and reformed, and that much more quickly in the presence of air; or second, the air causes the liquid state to persist, since it apparently is not dissolved to any great extent, by increasing the pressure on that phase. In this case, the changes of density may easily be explained by an expansion or contraction of the liquid.

A rough calculation for the .93% air mixture gives, on the assumption that the meniscus is in the middle of the tube, and that the air is immiscible with liquid ethylene, an excess pressure of three atmospheres. Certain "molecular stirring" experiments performed in the following manner support this theory.

A cooling coil was wound around the upper portion of the bomb. This coil could be maintained at 5°C. by the passage of tap water through it. The temperature of the bomb was raised to 10.0°C., the sliding thermostat partly lowered, and the upper portion of the bomb cooled. Violent distillation occurred, and after several treatments of this kind and subsequent heating to 13.5°C., the sample had a density of .2160 gm/cc. See Table IX ~~as Table IX shows.~~ The system is now probably homogeneous, and on cooling acts much like pure ethylene, ~~as is~~ shown in Figure 10, except that the temperature of condensation is now lowered. As shown above in Table V and Figure 7, when the liquid phase of pure ethylene has been even partially destroyed, or dispersed, as the case may be, no increase in density occurs on cooling. Moreover, the visual effects of an air-ethylene mixture with respect to disappearance and reappearance of the meniscus are quite different from those characteristic of pure ethylene. With air present the meniscus first becomes diffuse, a brown ring next appears, and this then disappears on further temperature increase. The phenomena on cooling is the reverse of this, and once the meniscus has reappeared, further cooling causes a noticeable contraction of the liquid, without any apparent interchange between the phases by condensation and effervescence, which would be at once remarked with pure ethylene. From this and the above experiments, one is led to the conclusion that the liquid phase had persisted many degrees above the critical, owing to the pressure caused by the inert gas. Indeed, as the figures in Table X indicate, this persistence is possible even above 34.5°C., which is twenty five degrees above the classical critical temperature. These figures were never repeated, probably because before this particular run was made, the ethylene had been immersed in liquid air, the air allowed in, and the bomb sealed off. Since no appreciable length of time was allowed for the air to dissolve in the ethylene at -80°C., before the run was performed, the density values are somewhat higher than found on repeating the lower part of the curve. However, runs made up to 24°C. with this same sample were reproducible. These figures are referred to in the next section, in conjunction with the data on compressional experiments.

To sum up, the data with air-ethylene mixtures indicated quite definitely that the persistence of the liquid state of aggregation could be extended for many degrees above the critical by pressure on that phase. This suggested the possibility of a reforming of the liquid state of aggregation, by the application of a pressure gradient along the tube. The results of the investigations along this line are presented in the following section.

The critical temperature of air-ethylene mixtures has been the point of much discussion by various experimenters in this laboratory. The critical temperature of pure ethylene samples has been agreed upon within several hundredths of a degree by the various observers. However, the meniscus of an air-ethylene mixture is apparently much more diffuse, and the reading of ~~agreement about~~ the critical temperature ~~within a tenth of~~ a varied by a tenth of a degree with different observers. ~~degree~~ has ~~depend~~ed upon the observer.

It seems safe to say that, in a stationary bomb of length sufficient to provide wall areas whose shapes are not distorted by the bending of light caused by the working of the glass at the draw-offs, the limit of visual discontinuity is within several hundredths of a degree and, independent of the observer, the same as that for pure ethylene. The temperatures reported from observations of bombs which are rotated are quite different, but the experimental treatment

TABLE IX

Molecular Stirring

Intermittent stirring nearly completely destroys liquid.

Density	Time of stirring, min.	Temp. °C.	No. of stirrings
0.2379	0	10.00	0
.2215	25	10.00	1
.2193	21	10.00	2
.2172	15	10.00	3
.2172	12	10.00	4

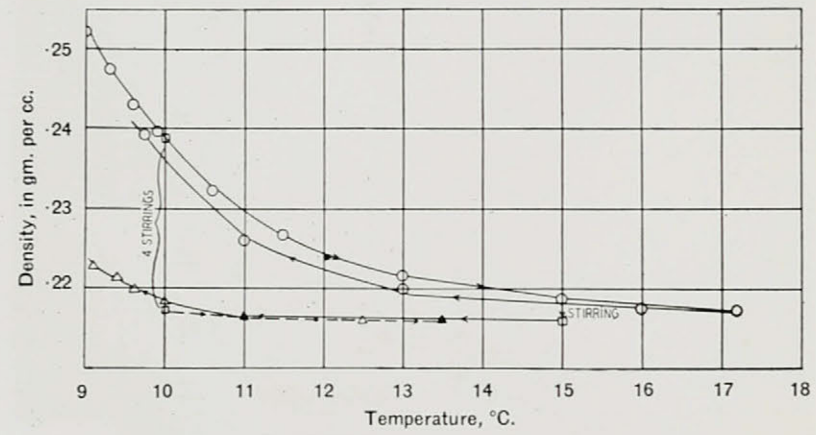
- -

System was cooled to 9.60°C. The density increased slightly to 0.2177 gm/cc. If heated to 13.5°C., after such stirring the density falls to 0.2160 gm/cc. On cooling from 13.5°C., the density changes as follows:

Density	Temp. °C.	Density	Temp. °C.
0.2160	12.50	0.2211	9.40
.2166	11.00	.2227	9.10
.2182	10.00	.2355	8.90
.2197	9.60		

- -

Condensation occurs at approximately 9.0°C.



Molecular stirring. Circles denote reference isochore; triangles denote behavior on heating to 13.5° C. after stirring, then cooling; squares denote behavior on stirring; block triangles denote behavior subsequent to stirring.

Figure 10

TABLE X

Ethylene-Air Sample

Unknown air content estimated to be about 1.5%

Temperature °C.	Density gm/cc.
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	.2392
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

is apparently the cause. With stationary bombs the temperature of disappearance as defined above may not be used as a criterion of the purity of the gas. Table XI gives figures which show this conclusively.

TABLE XI

Sample No.	1	2	3	4	5	6
Purity	100% C_2H_4	Unknown air content	100% C_2H_4	0.93% air	0.55% air	100% C_2H_4
T_c, °C.	9.50	9.50	9.50	9.49	9.50	9.50

The work described in this and the following section was done in conjunction with Mr. J. R. Dacey. The writer wishes to express his sincere thanks for the helpful collaboration during a very pleasant association.

Compressional Experiments upon the One Component System Ethylene

In many previous reports from this laboratory, the existence of a persistent heterogeneity of density has been recorded in one component systems at and above the critical temperature as defined by that temperature at which the meniscus disappears, (41).

This heterogeneity was found to be destroyed by "molecular stirring", by expansion and compression to the proper density values, by temperature fluctuations, and by heating to temperatures well above the critical. Up until now, no method of reversing this phenomenon, that is, reforming a heterogeneous system from a homogeneous one, except by a condensation below the critical temperature, has been found successful. A method of producing a heterogeneous system above the critical temperature has now been found, ~~in~~ This is accomplished by applying pressure to the lower portion of the medium in the tube, by application of a temperature gradient along the bomb.

The experimental arrangement used for the investigations has already been described. Two samples of used ?

pure ethylene were used, an average density of .1994 gm/cc. was studied in the first filling, and a higher average density of .2166 gm/cc in the second. A density temperature curve was taken for each filling, and used as a reference curve to which to relate the densities obtained subsequent to the various manipulations. In making a density measurement of the effect of compression, the top of the bomb was heated, then the whole bomb cooled to the temperature of the thermostat. Time density readings were taken until the density became constant. All compressional data were obtained upon systems which were originally in a state represented by curve B in the diagrams (Figures 11 and 12). The results were in excellent agreement, and may well be summarised before discussing the individual experiments.

(1) Above the critical temperature, compression of a homogeneous system recreates heterogeneity

(2) Below the temperature of reappearance of the meniscus, a less dense form of liquid, which appears on condensation, is changed into a denser form, and its amount is increased by the compression.

(3) Just above the temperature of reappearance of a meniscus, i.e., .03°C. higher, condensation is brought about, and a liquid separates subsequent to compression.

(4) The rate of re-establishment of uniform temperature along the length of the bomb, after application of the pressure gradient, determines the amount of density increase;

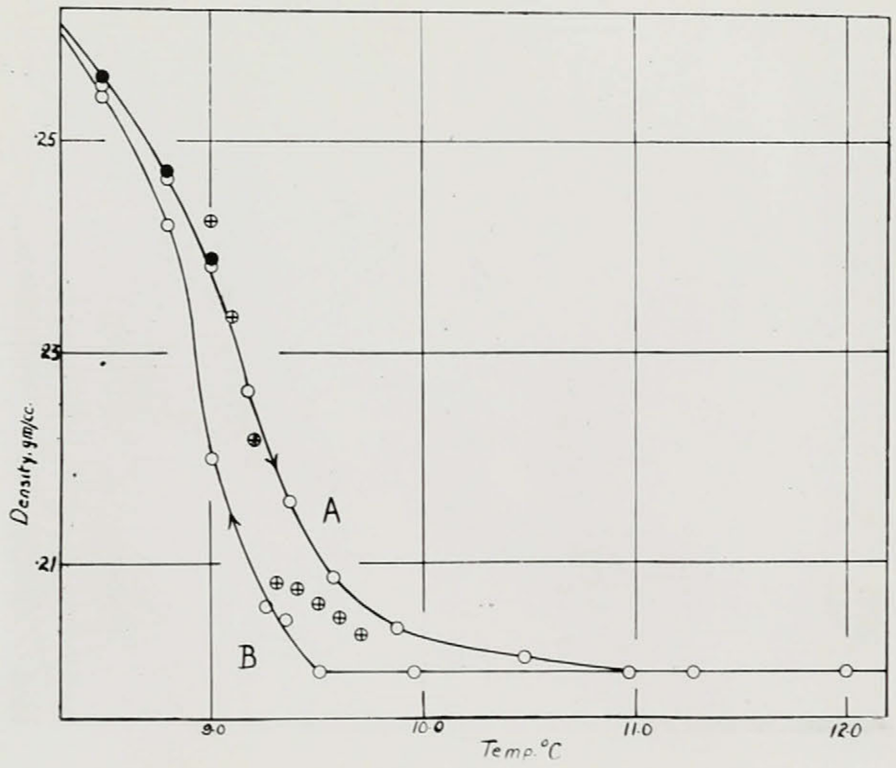


Figure 11

Density-temperature curve

Mean density 1994 gm/cc.

Crossed circles denote densities subsequent to compression with jacket on.

Solid circles denote densities subsequent to compression without jacket.

that is, above the critical temperature, heterogeneity persists only after a slow removal of the pressure gradient, while below the critical temperature, the amount of the density increase is enlarged by slow return to uniform conditions.

(5) The amount of heterogeneity which is reformed on compression appears to be independent of the magnitude of the temperature gradient, and the length of time during which it is applied. This is the case with pure ethylene, but a study of an air-ethylene mixture showed a definite increase with time.

(6) The branching of the density temperature curves for various mass volume ratios occurs for mean densities below .200 gm/cc. at some temperature below 9 00°C. For this reason, compression of the reformed liquid of the first sample (mean density .1994 gm/cc.) could create a liquid of a higher density than the original liquid. This could not be done with the sample of higher mean density (.2166 gm/cc.).

(7) Many of the experiments were repeated, and the recreated heterogeneity was found to be exactly reproduced.

(8) One experiment was performed in order to show that the heterogeneity did not tend to disappear. Density readings subsequent to compression became constant after about thirty minutes. In this particular case, observations were made for an hour and three quarters after the density had become constant. No change could be detected during this period.

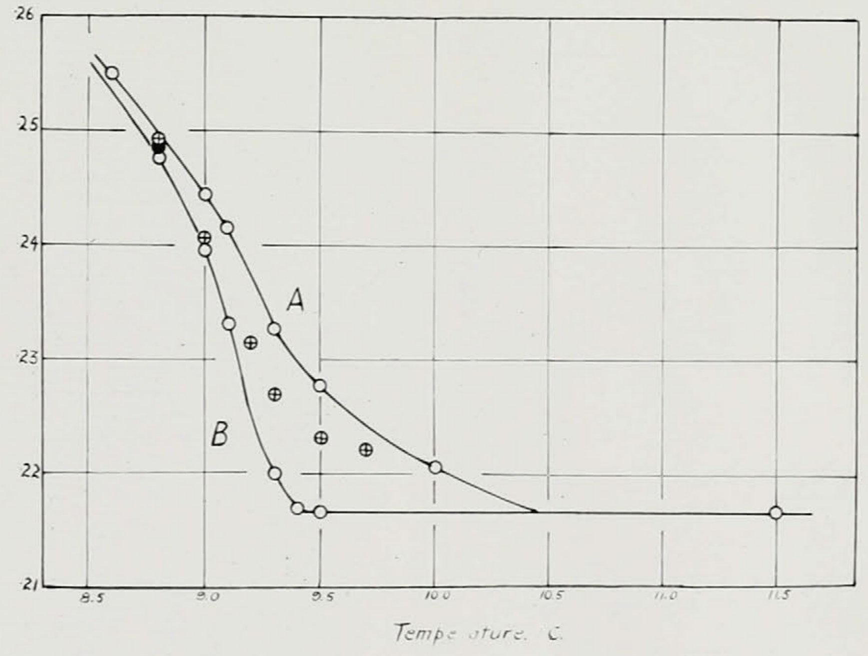


Figure 12

Density-temperature curve

Mean density 2166 gm/cc

Crossed circles denote values subsequent to compression.

Solid circle denotes value after compression without jacket

The density data for these experiments has been compiled in the following tables. Table XII gives the results for the samples of mean densities .1994 gm/cc. and .2166 gm/cc. above the critical temperature. Measurements followed by a "T" were made by compressing the medium by means of the water jacket. The other compressions were made without the jacket, by lowering the sliding thermostat until somewhat over a third of the bomb was exposed to the air at room temperature. After such compression the sliding thermostat was raised, and the bomb again completely submerged.

The interpretation of these results is difficult. For convenience the experiments have been divided into the three categories, (1) compression above the classical critical temperature, (2) compression below the critical and above the temperature of condensation, and (3) compression of reformed liquid.

For reasons that will be given fully in the next section, all ethylene systems between the mean densities of .230 gm/cc. and .214 gm/cc., at temperatures as high as 9.70°C., and whether represented by points along curve A or curve B of a typical isochore, must be considered to be two-phase systems. In the case of the macroscopically heterogeneous system, the major portion of the liquid phase is considered to be in the lower part of the tube. In the systems represented by curve B, the liquid phase is considered to be dispersed throughout the system, somewhat in the form of an emulsion of liquid and vapor.

Any explanation offered for the above experiments must take into account this background. Moreover, the compressibility of the system as a whole, although perhaps not for each phase separately, is infinite.

TABLE XII - Part 1

Density temperature reference curve
Mean density .1994 gm/cc.

Temperature °C.	Density gm/cc.
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
8.50	.2543

TABLE XII - Part 1

(continued)

Density temperature reference curve.

Mean density .2166 gm/cc.

Temperature °C.	Density gm/cc.
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

TABLE XII - Part 2

Summary of results of compression above
the critical temperature.
Average density .1994 gm/cc.

Temperature °C.	Density gm/cc.	Duration of Compression	
9.50	.2060	-----	T
9.50	.2060	30 mins.	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 mins.	-

TABLE XII - Part 3

Summary of results of compression above
the critical temperature.
Average density .2166 gm/cc.

Temperature °C.	Density gm/cc.	Duration of compression	
9.70	.2220	7 mins.	T
9.50	.2230	7 "	T

TABLE XIII

Summary of results of compression below the critical temperature and above temperature of reappearance of meniscus.

Average density .1994 gm/cc.

Part 1

Temperature °C.	Density gm/cc.	Duration of Compression	
9.40	.2074	10 mins.	T
9.30	.2081	10 "	T
9.20*	.2217	10 "	T

* Meniscus reforms, subsequent to compression.

Part 2

Average density .2166 gm/cc.

9.30	.2270	10 mins.	T
9.20*	.2314	10 "	T

* Meniscus reforms, subsequent to compression.

Turning to the data of the first division, two distinct features are at once apparent. Compression by means of the water jacket causes a reforming of a heterogeneous system, while compression with the top exposed does not. This cannot be explained away by supposing the continuance of a temperature gradient when the jacket is in position, because of the care taken to avoid this possibility in the experimental arrangement. The variance must therefore be due to the difference in rate of re-establishment of pressure uniformity. If, a reformation of more liquid has taken place, and any expansion destroys this liquid, a possible explanation has been offered. The writer, however, is uncertain as to the effect of such expansion. The work done by Geddes upon the effect of expansion was of this nature. A heterogeneous system was obtained, and allowed to expand. The measured density eventually became equal to the density of a known homogeneous system at the same temperature. This, however, did not occur until the true "vapor" region of densities had been reached.

This type of expansion does not seem comparable to that occuring in the experiment under discussion. The best explanation which the writer can offer is that, under the conditions of very great density caused by the compression, additional liquid is formed and tends to settle to the bottom of the tube. If the subsequent expansion is slow, it is not entirely redistributed, and a heterogeneity persists. On rapid expansion the heterogeneity is again destroyed. On the other hand, the great compressibility may permit the formation of a large density gradient which, on slow expansion, persists to a measurable extent because of the small resiliency of the system.

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

The liquid which condenses out spontaneously at 9.17°C. is of a different nature than the visible liquid that was present at 9.17°C. on the original heating curve, if the density measurement is truly of the liquid phase alone.

Compression changes the characteristic density and the amount of liquid as Table XIV shows. There are two possible explanations for this behaviour. The first does not postulate ~~hypothes~~ise the existence of various forms of liquid, with a frozen equilibrium between the forms. It merely assumes that below the temperature of condensation, a dispersion of vapor in the liquid causes a decrease in the apparent density. Upon compression, vapor groups in the liquid are largely transformed to liquid. In addition, liquid which is still dispersed in the vapor phase rains out, and both the density and the amount of the liquid is increased. This explanation is concordant

TABLE XIV - Part 1

Summary of results of compression below the temperature of meniscus reappearance.

Mean density .1994 gm/cc.

Temperature °C.	Density	Duration of Compression	
9.10	.2335	5 mins.	T
9.10	.2335	-----	T
9.00	.2426	-----	T
9.00	.2391	-----	-
8.80	.2472	-----	-
8.50	.2564	-----	-

Mean density .2166 gm/cc.

Temperature °C.	Density	Duration of Compression	
9.00	.2406	-----	T
8.80	.2492	-----	T
8.80	.2486	-----	-

TABLE XIV - Part 2

Compressional Experiments

Mean density 1994 gm/cc

Temp. °C.	Density after Compression	Density $Curve_A$	Density $Curve_B$	Meniscus $Curve_A$	Meniscus $Curve_B$	Meniscus after Compression
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		2339	----	21.4	18.0	20.7

Mean density .2166 gm/cc

Temp. °C.	Density after Compression	Density $Curve_A$	Density $Curve_B$	Meniscus $Curve_A$	Meniscus $Curve_B$	Meniscus after Compression
8.80	.2486	.2495	.2476	----	26.3	27.0

with the phase rule, which does not permit of the existence of two liquid phases of different densities at the same temperature and pressure. Moreover, the lower density of the liquid phase at 9.00°C. on heating up for the filling of mean density .1994 gm/cc., compared to the constancy of liquid density at this temperature for fillings of higher average densities (see Table I), is explained by the greater amount of penetration of vapor into the liquid phase. Compression of the reformed liquid at this low average density at 9.00°C. on the curve B causes an increase in density above that of the original heating curve, but never in excess of the density .245 gm/cc. which is characteristic of the fillings of higher mean density. This can be explained by the assumption that at the low mean density under discussion, the mechanism of compression does not permit as great an artificial density to be developed, and some of the vapor is left in the liquid unchanged, with a consequent lower liquid density even after compression.

The alternate explanation which may be put forward is that there are two types of liquid possible, one highly orientated, and one with much less orientation, which we shall call liquid "A" and liquid "B" respectively. On heating at constant volume, liquid "A" is gradually destroyed until at 10.5°C. a true gas system is formed. On cooling down, liquid "B" is formed, and the two-phase character of the system is again apparent. At 9.17°C. liquid "B"

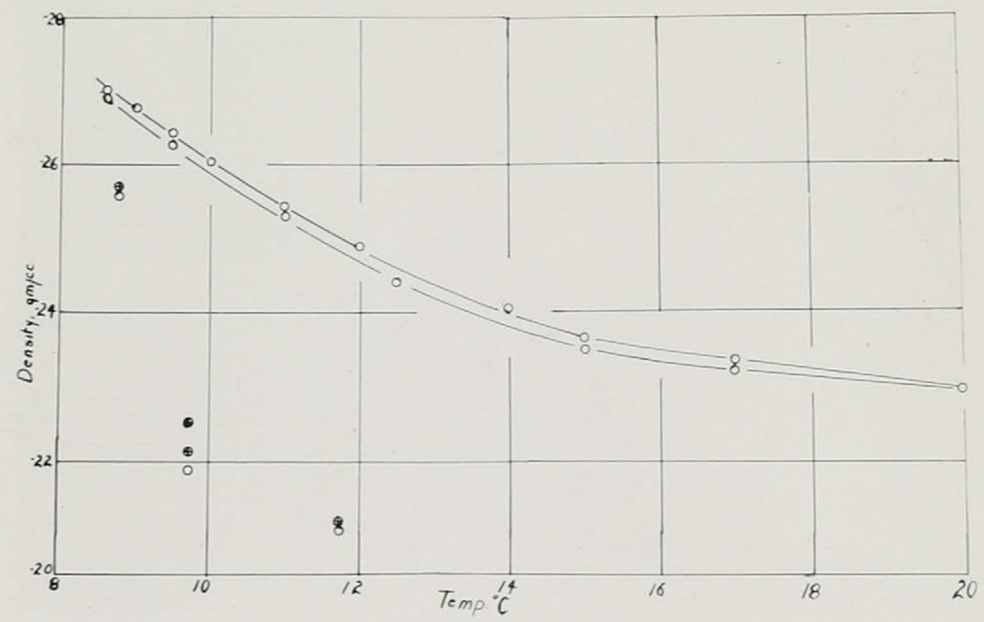


Figure 13

Density-temperature curve for for air-ethylene mixture

Plain circles denote density value after "molecular stirring". Crossed circles denote densities subsequent to "molecular stirring" and compression.

condenses out. Compression of liquid "B" causes a reconversion to liquid "A". This explanation involves the additional assumption of an equilibrium between the two types of liquid, which is not sufficiently mobile for the ethylene to act as a one component system. The first explanation is therefore preferred, particularly since surface tension measurements in this region upon other substances, made by Winkler and Maass (41), show a very real possibility of dispersed vapor-liquid systems appearing to be stable equilibrium systems.

Compressional experiments performed upon an air-ethylene mixture which was subjected to "molecular stirring", shows the same sort of behaviour. The results are given in Table XV and shown in Figure 13.

The only difference which was observed between the behaviour of ethylene alone, and air-ethylene mixtures after "molecular stirring", after these systems had been subjected to a compression, was that the amount of recreated heterogeneity was independent of time of compression in the first case, but was increased in the second case with increasing time.

An air-ethylene system at 9.50°C., which has been subjected to "molecular stirring", is considered to be macroscopically homogeneous, but to have present both liquid and vapor ethylene, while the air is now no longer concentrated in the upper section of the bomb, but is distributed

TABLE XV - Part 1

Air-Ethylene Mixture

Density-temperature relation after standing at -78°C. for 12 hours or longer.

Temperature °C.	Density gm/cc.
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 XV - Part 2

Compression of Air-Ethylene Mixture

Mean density = .2108 gm/cc.

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

evenly throughout. The system, then, is similar to pure ethylene on curve B, but has air dispersed or dissolved in it. The increase of heterogeneity with compressional time may be explained in either of two ways. The dilution caused by the air may slow down the formation of the liquid; or second, the effect of the air upon the surface tension is such as to decrease the tendency of liquid formation.

Since the proportion of air is small, i.e., less than 1.5%, the effect of dilution should be very small. Apparently, then, the second possibility is more reasonable, a conclusion which is supported by the evidence that the temperature of meniscus reappearance is appreciably altered. At a concentration of .93% air, it has already been pointed out that condensation occurred at about 9.0°C., which is over .10°C. lower than that for pure ethylene. If the condensation of a pure ethylene sample is caused by the increase of the liquid-vapor interfacial tension to a limiting value too large for complete dispersion to be possible, it would appear that the effect of air in an air-ethylene sample must be to lower the interfacial tension quite appreciably. Thus, on compression of such a system, the tendency for liquid to form being somewhat reduced, the heterogeneity created might quite conceivably be influenced in amount by the time of compression.

Pressure Volume Isothermals of One Component System Ethylene

The discovery, which was outlined above, of the constancy of pressure of a heterogeneous system with changing mass volume ratio, and the major discrepancy which this experiment indicated between the work of Geddes and the writer, necessitated a very careful investigation of pressure volume relations at constant temperature. By means of the second form of apparatus already described, very precise measurements of these relations have been obtained between 8.92°C. and 10.00°C. The results have led to a much clearer understanding of the phenomena already observed in the critical region, and are of particular value as tests of certain predictions of Mayer and Harrison (52). The experimental results will first be completely presented, and then their interpretation with respect to experimental observances of this and other workers. Direct comparison between experimental result and predictions of Mayer and Harrison will then be made.

Summarising, the experimental results show clearly:

(1) Pressure isothermals above and below the temperature of disappearance of the meniscus showed regions of density wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$. This region could no longer be observed

upon the isothermal at 10.00°C.

(2) The complete envelope of this region above T_c has been determined.

(3) The isothermal at 9.60°C. was studied and found to be the equilibrium curve at this temperature. Moreover, a hysteresis was observed on reversing the direction of measurement, i.e., from "vapor" to compressed "liquid". This hysteresis was found to be caused by the time lags which are observed in passing from the "vapor" region of an isothermal to regions of high density.

(4) The pressure of heterogeneous systems whose mean density is represented by a point within this envelope, corresponds exactly to the pressure of the horizontal portion of the macroscopically homogeneous isothermal.

(5) The pressure of such heterogeneous systems is thus seen to be independent of mass volume ratio within such limits of density.

(6) The pressure of such heterogeneous systems was found to correspond exactly to the pressure of the homogeneous system obtained by heating at constant volume to 10.5°C. or higher and cooling to the temperature at which the pressure of the heterogeneous system was measured.

(7) The region of temperature and density throughout which the homogeneous systems and heterogeneous systems have identical pressures was found to correspond to the envelope of the region for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$.

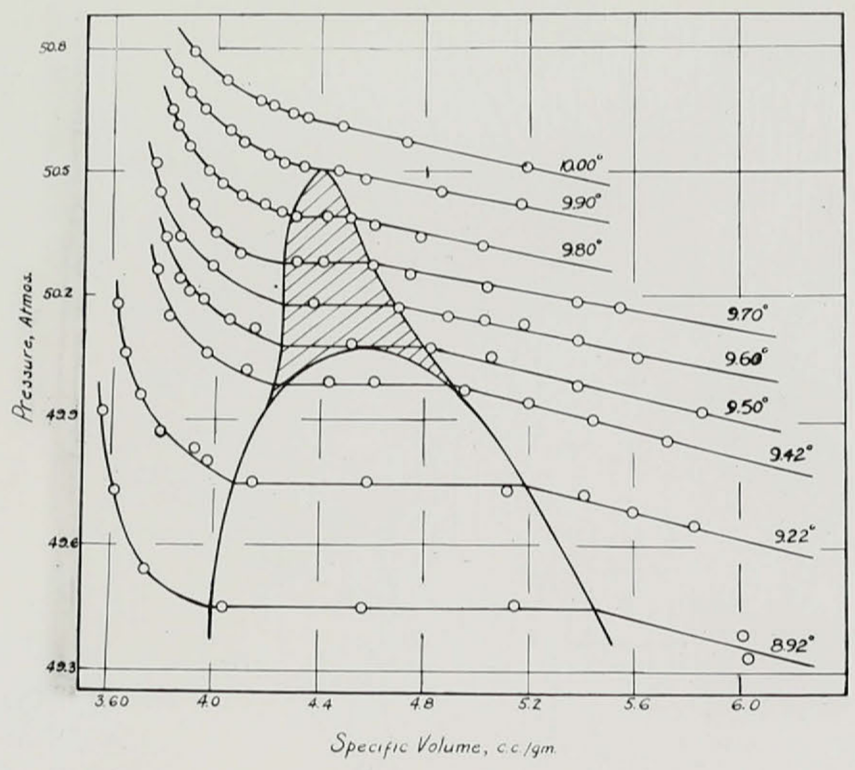


Figure 14

Isothermals of Ethylene

Shaded Area denotes region wherein $\left(\partial \frac{P}{V}\right)_T = 0$

Parabolic curve extrapolated according to classic theory

(8) A discrepancy between the value of the pressure at 9.50°C. obtained by Geddes and by the author was discovered. Moreover, the pressure temperature curves of Geddes varied, irrespective of temperature above 9.2°C., with mass volume ratio a behaviour which was not found to be duplicated by the author. The pressure temperature curves here given were independent of mass volume ratio, so long as the mean density of the system lay within the envelope of the region for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$.

(9) The pressure temperature curves were found to be reversible.

The experimental isothermals are given in Table XVI and represented in Figure 14. The envelope of the region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ is also shown and should represent the true form of density temperature curve. This density temperature curve does not coincide with that determined by Naldrett, in the opinion of the author, because of effects due to dispersion by shaking in the latter case. This point is more fully discussed later. For the moment it is sufficient to point out that in this region $\left(\frac{\partial P}{\partial V}\right)_T = 0$, and the system ethylene therefore behaves as a true two-phase system although above the classical critical temperature. Since the deduction of the existence of a two-phase system from the observation of a region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ is open to the objection that a one-phase system, if the compressibility is great enough, may simulate the behaviour of a two-phase system, and since the compressibility of liquids near the critical point is admittedly

TABLE XVI

Pressure-Volume-Temperature Relations of Ethylene

Isothermal at 8.92°C.

Exp. Vol.	Amount of Ethylene/gm.	Specific Vol.	Press. Atm.
2.532	.716	3.563	49.92
2.587	.716	3.613	49.73
2.672	.716	3.731	49.54
2.893	.716	4.040	49.45
3.271	.716	4.568	49.45
3.681	.716	5.141	49.46
4.303	.716	6.009	49.38
4.317	.716	6.029	49.34

Isothermal at 9.22°C.

2.590	.716	3.617	50.18
2.613	.716	3.649	50.06
2.655	.716	3.708	49.96
2.715	.716	3.791	49.87
2.794	.716	3.902	49.83
2.830	.716	3.952	49.80
2.970	.716	4.148	49.75
3.284	.716	4.586	49.75
3.666	.716	5.120	49.73
3.876	.716	5.410	49.72
4.006	.716	5.594	49.68
4.174	.716	5.831	49.65

TABLE XVI - (continued)

Isothermal at 9.42°C.

Exp. Vol.	Amt. of Gas	Specific Vol.	Press. Atm.
2.710	.716	3.770	50.26
2.735	.716	3.819	50.15
2.838	.716	3.963	50.06
2.950	.716	4.120	50.02
3.176	.716	4.437	49.99
3.300	.716	4.609	49.99
3.550	.716	4.958	49.97
3.723	.716	5.199	49.94
3.910	.716	5.446	49.90
4.104	.716	5.731	49.85

Isothermal at 9.50°C.

2.705	.716	3.777	50.44
2.722	.716	3.801	50.34
2.762	.716	3.857	50.24
2.789	.716	3.895	50.21
2.829	.716	3.951	50.19
2.908	.716	4.047	50.14
2.970	.716	4.148	50.12
3.235	.716	4.519	50.08
3.455	.716	4.826	50.07
3.624	.716	5.061	50.05
3.857	.716	5.386	49.98
4.197	.716	5.861	49.92

TABLE XVI - (continued)

Isothermal at 9.60°C.

Exp. Vol.	Amount of Ethylene	Specific Vol.	Pressure
2.695	.716	3.763	50.52
2.713	.716	3.775	50.45
2.756	.716	3.849	50.34
2.854	.716	3.986	50.27
3.135	.716	4.378	50.18
3.360	.716	4.692	50.17
3.512	.716	4.891	50.15
3.607	.716	5.037	50.14
3.710	.716	5.181	50.13
3.859	.716	5.389	50.09
4.020	.716	5.614	50.05

Isothermal at 9.70°C.

2.823	.722	3.909	50.42
2.884	.722	3.994	50.35
2.953	.722	4.090	50.30
3.109	.722	4.306	50.28
3.187	.722	4.414	50.28
3.318	.722	4.605	50.27
3.414	.722	4.729	50.25
3.640	.722	5.041	50.22
3.885	.722	5.381	50.18
4.004	.722	5.546	50.17

TABLE XVI - (continued)

Isothermal at 9.80°C.

Exp. Vol.	Amt. of C_2H_4	Specific Vol.	Pressure
2.761	.722	3.824	50.65
2.776	.722	3.844	50.61
2.808	.722	3.889	50.56
2.863	.722	3.965	50.50
2.902	.722	4.019	50.47
2.954	.722	4.091	50.44
3.025	.722	4.189	50.42
3.066	.722	4.246	50.40
3.108	.722	4.304	50.39
3.197	.722	4.429	50.39
3.262	.722	4.518	50.38
3.328	.722	4.609	50.37
3.464	.722	4.792	50.34
3.635	.722	5.030	50.32

Isothermal at 9.90°C.

Exp. Vol.	Amt. of C_2H_4	Specific Vol.	Pressure
2.770	.722	3.837	50.74
2.807	.722	3.890	50.69
2.854	.722	3.953	50.65
2.923	.722	4.048	50.60
2.961	.722	4.101	50.57
3.030	.722	4.197	50.54
3.072	.722	4.255	50.52
3.132	.722	4.338	50.51
3.224	.722	4.466	50.50
3.302	.722	4.574	50.48
3.512	.722	4.864	50.45
3.737	.722	5.178	50.42

Isothermal at 10.00°C.

Exp. Vol.	Amt. of C_2H_4	Specific Vol.	Pressure
2.820	.722	3.905	50.79
2.913	.722	4.034	50.72
3.005	.722	4.162	50.67
3.045	.722	4.217	50.66
3.083	.722	4.270	50.64
3.155	.722	4.370	50.63
3.236	.722	4.482	50.61
3.396	.722	4.703	50.57
3.750	.722	5.194	50.51

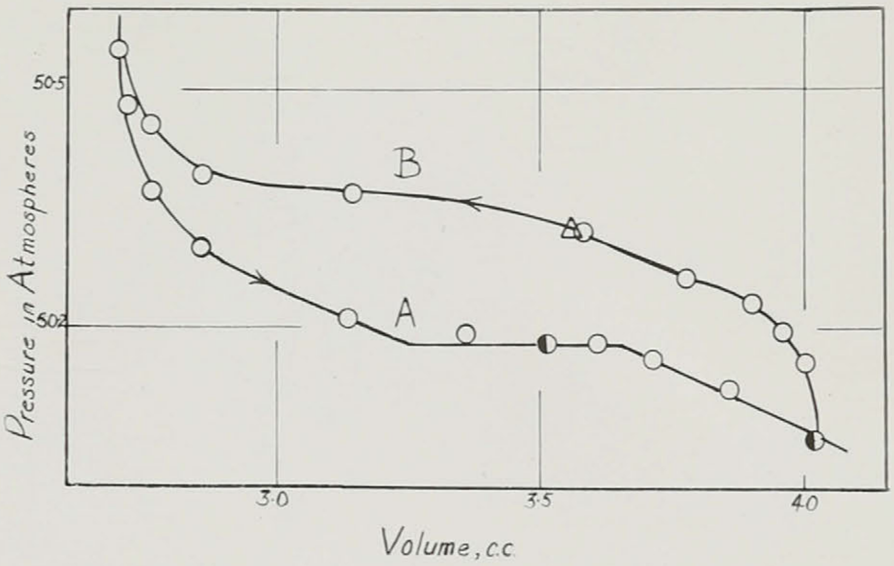


Figure 15

Hysteresis curve of isothermal at 9.60°C
Hatched circles denote repeated points
Triangle denotes value from which change in pressure with time at constant volume was measured.

enormous, the direction of measurement along the isothermal at 9.60°C. was reversed. That is, when the substance had been expanded to the last point on the isothermal, the pressure was increased. As soon as temperature equilibrium had been established, the pressure was maintained constant for 10 minutes. By following this procedure the upper curve of Figure 15 was obtained. (The volumes here have not been converted to specific volumes) See Table XVII. This showed the compressibility of the system to be dependent upon its previous history. That the points of the lower curve are not dependent upon the previous condition of the system, provided only that expansion into the true "gaseous" region has not occurred, was shown by repeating a point upon the flat portion several days later, simply by adjusting the pressure directly to the desired value. Expansion directly to this point from the high density region took place, and no change was remarked after 15 minutes. The pressure was then adjusted in order to repeat the last "vapor" point shown upon the diagram. This point was also exactly reproduced, and the system showed no tendency to undergo change.

The question as to whether the pressure on the higher curve would fall spontaneously to the value of the lower curve was then investigated. After expansion to the "gaseous" region of density the pressure on the system was adjusted to give the triangular point on the upper curve. When this point had been reached, the volume was maintained

TABLE XVII

Isothermal at 9.60°C.

Expansion from "liquid" and compression from "vapor".

Exp. Volume cc.		Pressure Atmosphere
	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
4.020		50.05
	Compression	
4.000	Thermal equilibrium only established.	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

as constant as possible, and a pressure time curve obtained. It was found that the pressure fell quite rapidly to the value of the original curve, where it remained constant. The difficulty of keeping the volume constant was very great, but it was maintained sufficiently constant to show clearly the true trend of the pressure with time. The figures are given below in Table XVIII.

TABLE XVIII

Exp. Vol.	Temp. °C.	Press. Atm.	Time
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
3.57	9.60	50.18	40

Note: Zero time was taken at about 12 minutes after the original pressure adjustment.

Pressures of Heterogeneous Systems at 9.51°C., and Homogeneous Systems Produced by Heating to 10.5°C., and Subsequent Cooling to 9.51°C.

The question of relative stability of the heating and cooling curves of a typical isochore, as measured by the pressure of the system, was then studied by measuring the pressure of the heating curve (curve A) and of the cooling curve (curve B) at 9.51°C. The volume of the system was fixed by freezing the mercury in the centre u-tube, at a value of the average density where a heterogeneous system was known to exist from previous work. The ethylene temperature was then fixed at 9.51°C., the mercury melted, and the pressure of the system, which corresponds to a point on the heating curve of an isochore, was determined. The mercury was again frozen, the temperature raised to 11.5°C, where the density of the system has been shown to be uniform. After allowing twenty minutes for the medium to reach equilibrium, the temperature was again lowered to 9.51°C , and the pressure determined.

Over the range of densities studied the pressures of curve A and curve B are identical, and, moreover, are independent of mass volume ratio. They agree, further, with the pressure which the flat portion of an isothermal must possess at 9.51°C., from the pressure temperature curve of these horizontal regions.

TABLE XIX

Average Density	Pressure_A	Pressure_B	Temperature °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 flat portion of homogeneous isothermal at 9.50°C. is 50.07 atmospheres. $\frac{dP}{dT}$ for horizontal regions is $\frac{50.51 - 50.07}{9.90 - 9.50}$

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

Range of density of horizontal region of isothermal at 9.50°C. is .231 gm/cc. to .198 gm/cc., approximately.

From these experiments then, it is at once obvious that,

(1) Pressures of homogeneous and heterogeneous systems are equal, and equal to pressure of flat portion of homogeneous isothermal;

(2) Pressure of homogeneous and heterogeneous systems are both independent of mass volume ratio over a large density range.

These facts indicate very definitely, that

(1) The heterogeneous and homogeneous systems of an isochore are equally stable, and also have the same stability as the known homogeneous and stable system of the isotherm at the same temperature;

(2) The cooling curve B of an isochore cannot be any longer considered to represent a true gas system, as was believed up to the conclusion of this experiment, for such a system would have a pressure independent of volume over a wide range. This homogeneous system, like those present in the region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ on an isotherm, must be a two-phase system.

Further evidence which has largely clarified the phenomena of the critical region was then obtained determined with a new sample of ethylene and a new experimental assembly which was ~~were~~ necessitated by an explosion.

The four isothermals at the higher temperatures were determined with this new assembly. The reproducibility of the data is shown by the excellent contiguity of the curves; the agreement ~~which~~ was shown to be real and not accidental by repeating the isothermal at 9.22°C. The agreement was exact

Pressure-temperature curves at constant volume were determined for three different mean densities, both on heating and cooling.

The data are given in Table XX.

The purpose of these experiments was two-fold.

A disagreement in the value of the critical pressure of ethylene, as measured by Geddes, and that observed by the author, had been found. Geddes (60) reported two values of the pressure at 9.50°C., of 49.98 and 50.01 atmospheres at the average densities of .2056 gm/cc. and .2302 gm/cc. respectively. The present observations, which have been checked by two samples in two different assemblies, give a critical pressure of 50.07 atmospheres over a density range of .198 gm/cc. to .231 gm/cc. The independence of pressure with volume had therefore to be more firmly established.

Secondly, although the agreement in pressure between curve A and curve B of an isochore had been established at 9.51°C., it was considered possible that a disparity might appear at temperatures either above or below this point.

Comparing the data of Table XX with the isothermals of Figure 14, we see first that

(1) so long as the mean density and temperature of the system are such as to be represented by a point within the shaded area, the pressure of the system is independent of the mass-volume ratio;

(2) this pressure corresponds to the pressure of the flat region of the isothermal at the same temperature, and thus all three systems, either represented by a point on curve A or curve B of an isochore, or by a point on the horizontal region of an isothermal, are equally stable, and since the isothermals have been shown to represent

TABLE XX

Pressure Measurements of Heterogeneous Systems

Temp. °C. Heating	Pressure Atm. density = .2046 gm/cc.	Pressure Atm. density = .2109 gm/cc.	Pressure Atm. density = .2270 gm/cc.	Pressure of Isothermals
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 $\left(\frac{\partial P}{\partial V}\right)_T = 0$ at 10.0°
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	

equilibrium systems, the other systems must also be truly stable systems;

(3) once the temperature has been attained at which the mean density lies outside the shaded region, the pressure does become a function of the volume. Thus, at 9.80°C., the pressure shows an increase with greater density. The change of .01 atmosphere which is shown is believed not to be experimental error because, at 10.50°C., the differences in pressure are now outside the range of experimental error and the trend is concordant in all three cases. Therefore, the recorded differences at 9.80°C are believed to be significant, while below this temperature the .01 atmosphere differences must be attributed to experimental error;

(4) the pressure temperature curves are reversible. This is most significant, for it shows clearly that on cooling down the two phases are reformed, as shown by the independence of pressure and mass-volume ratio, although no separation of phases or measurement of density discontinuity is possible until well below the critical temperature.

It is for this reason that in discussing the hysteresis effect at constant volume the dispersion or emulsion of gas in liquid and liquid in gas was emphasized.

A comparison of predictions of Mayer and Harrison and the experimental results of the author will now be made.

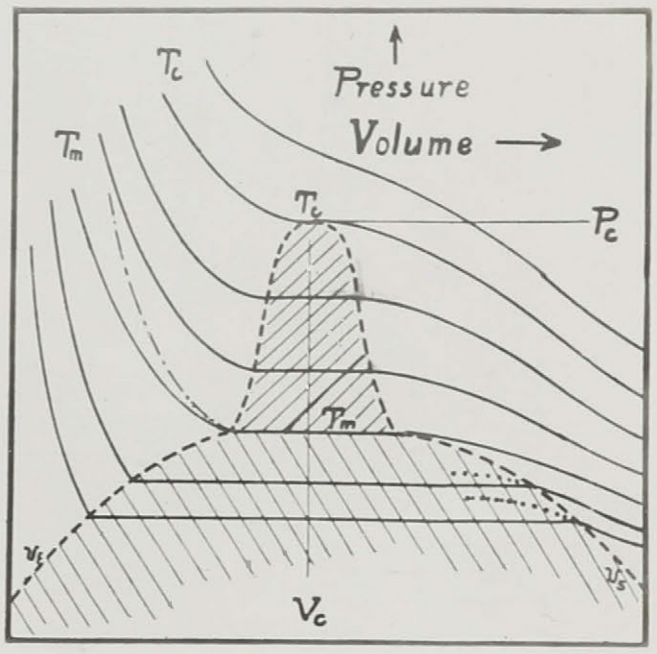


Figure 16

Predictions of Mayer and Harrison and Comparison with Experiment

Mayer and Harrison, as already pointed out, have made calculations ~~of particular interest as to the possible~~ which are applicable to to the behaviour of a one-component system in the critical temperature-critical pressure region. Figure 16 shows a reproduction of Figure 1 of their paper, page 101 of the Journal of Chemical Physics, Vol. 6, February 1938. They describe this diagram as follows: "Pressure is plotted as a function of volume at various temperatures: the heavy solid lines. The curves at two characteristic temperatures T_m and T_c are especially marked. The shaded area enveloped by the dashed line is the region in which the lines are horizontal, that is, where $\left(\frac{\partial P}{\partial V}\right)_T = 0$. The right hand boundary V_f is the volume of the condensed phase. The dotted lines inside the shaded area represent the extrapolated pressure of the supersaturated vapor. The dot-dash line on the left hand side of the shaded area at T_m represents a discontinuous transition in the properties of the condensed phase.

The part of the diagram to the right of V_c was deduced strictly from their work. "The portion to the left of V_c and below T_c represents a logical guess from the nature of the kinetic picture deduced from these equations".

Comparing this diagram to that of the experimental isothermals of Figure 14, we note a startling similarity as to general character. The continuance of the region above T_m wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ is completely verified by experiment. the suggested symmetry of this region about V_c is, however, not apparent. The experimental isotherms show a nearly perpendicular boundary for V_f, while V_s slopes very noticeably toward the higher densities as the temperature is raised.

A second difference between prediction and behaviour arises from the statement of Mayer and Harrison that, "below T_m, compression of the system through the volume region, between V_s and V_f, will be accompanied by the separation of two distinct phases of density $\frac{1}{V_f}$ and $\frac{1}{V_s}$. The microscopic density corresponding to a volume between V_s and V_f is unstable. This is indicated on the diagram by the dotted lines showing the higher pressure of the supersaturated vapor. As is well known, this phenomenon is associated with the fact that the surface tension increases the vapor pressure of very small droplets of liquid.

"Between T_m and T_c, however, the denser phase has no surface tension, and corresponding to this, the isothermals pass smoothly through the condensing region, allowing no extrapolation to a higher pressure for the supersaturated vapor. Indeed, all microscopic densities in the shaded region between T_m and T_c will correspond to the same pressure (at the same temperature) and to the same Gibbs' free energy. Compression of the system at constant temperature T, with T_m T T_c, will be accompanied by a uniform increase in density throughout the whole system, the pressure remaining unchanged between V_s and V_f".

Reversal of the direction of measurement upon the isothermal at 9.60°C. does not coincide with this picture A pronounced hysteresis has been observed, although more than sufficient time for temperature equilibrium to be established was allowed. Turning to the diagram of this isothermal, Figure 15, we see that even in the "vapor" region of the isothermal, where any evidence of a second phase, with or without surface tension, is missing, it is obvious that a decided time lag is involved in producing a change to higher density. Such a time lag points strongly to the existence of some sort of structure or association of the molecular species under these conditions of temperature and density. It is for this reason, and because of the large amount of evidence accumulated by Geddes upon time lags, that the concept due to Maass of the existence of a regional orientation must be retained.

A great deal of the evidence already given in this thesis is very simply and clearly explained by the assumption of a two-phase system, either without a surface tension for the denser phase, or with that phase possessing such a small surface tension that emulsification of the two phases is possible, and that such emulsions exist for very extended periods of time. The retention of this theory, with the elaboration that the denser or both phases are subject to various degrees of orientation, is far from impossible as the

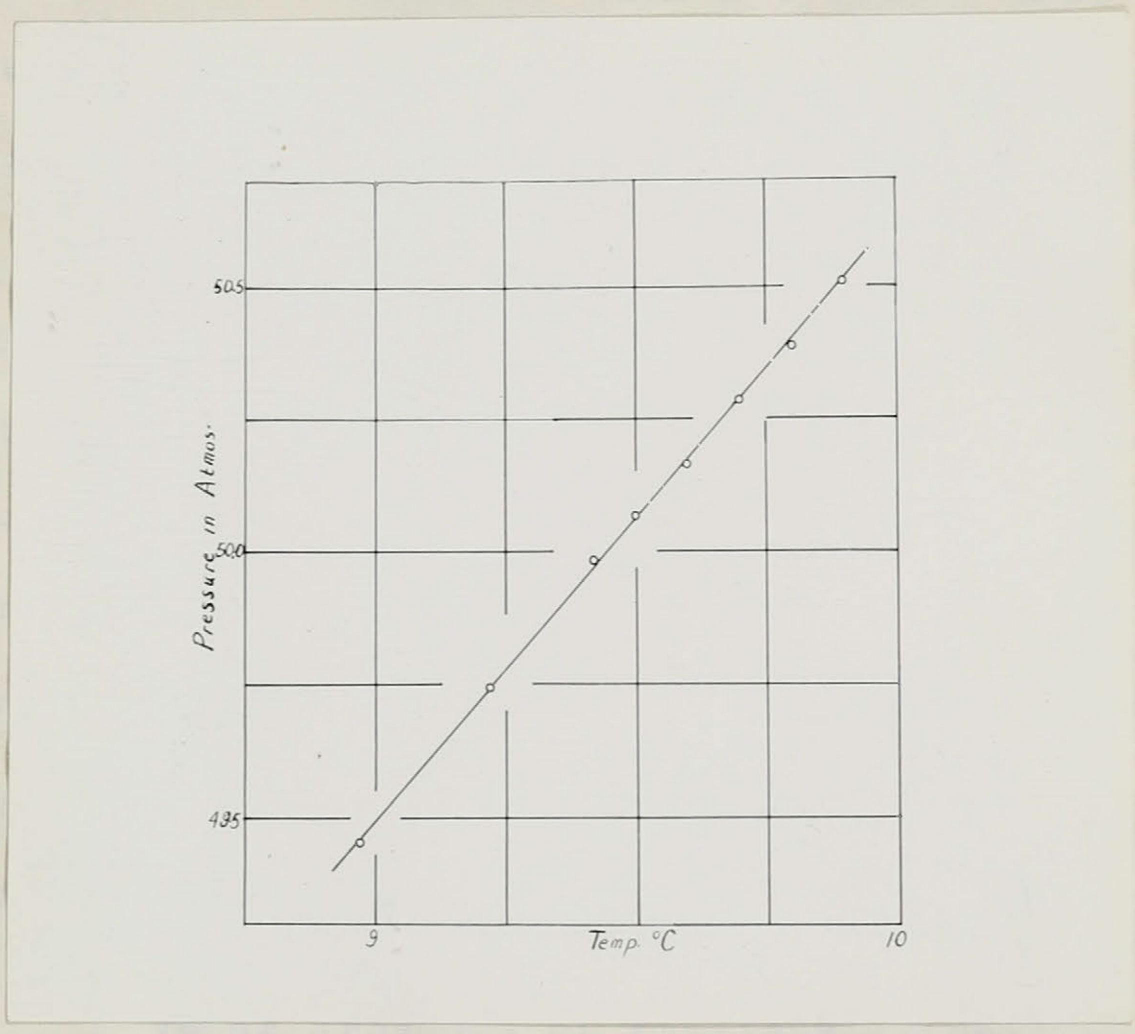


Figure 17

Vapor Pressure Curve of Ethylene

ideas are by no means contradictory.

A discrepancy in the observed temperature of reappearance of the meniscus between Geddes and the present author, i.e. 9.34°C. in the first place, and 9.17°C. in the latter, may perhaps also be explained by a statement of Mayer and Harrison. "Cooling of such a system", that is a system between V_s and V_f and above T_m, "should be expected to result in the formation of a meniscus at some temperature lower than T_m, a typical super-cooling effect. The extent of the super-cooling would be expected to be greater, the further the densities in various parts of the system were from the values corresponding to the volume V_{fm} and V_{sm} at T_m. A system with uniform density $\frac{1}{V_c}$, approximately midway between $\frac{1}{V_{fm}}$ and $\frac{1}{V_{sm}}$, would be expected to show the greatest super-cooling." Investigation of this and other points with respect to time lags is being continued by Mr J. R. Dacey.

Reverse sentence

Vapor Pressure of Ethylene between 8.92°C. and 9.90°C.

The isothermals of ethylene given above have been used to determine the vapor pressure curve of ethylene in the critical region. The values are given in Table XXI, and represented in Figure 17. The pressure for any temperature was taken as the average of the pressures of the determinations made in the region for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$ Although pressures are given in Table XVI to .01 atmosphere only, the average of the pressure readings should be somewhat better than this value, and the last figure of the pressure in Table XXI has been included for this reason, although there is some doubt of its significance ~~is held~~. As is to be expected, over such ~~a~~ narrow range of temperature, the vapor pressure as a function of temperature is excellently represented by a straight line.

TABLE XXI

Vapor Pressure of Ethylene

Temperature	Average Pressure
8.92	49.45_3
9.22	49.74_3
9.42	49.98_3
9.50	50.06_6
9.60	$50\ 16_6$
9.70	$50\ 27_6$
9.80	50.38_6
9.90	$50\ 51_0$

From Figure 17 $\frac{dP}{dT} = \frac{50.600 - 49.450}{9\ 975 - 8.960}$ atm/°C

$$= \frac{1.150}{1.015} \text{ atm/°C.} = 1.13_3 \text{ atm/°C}$$

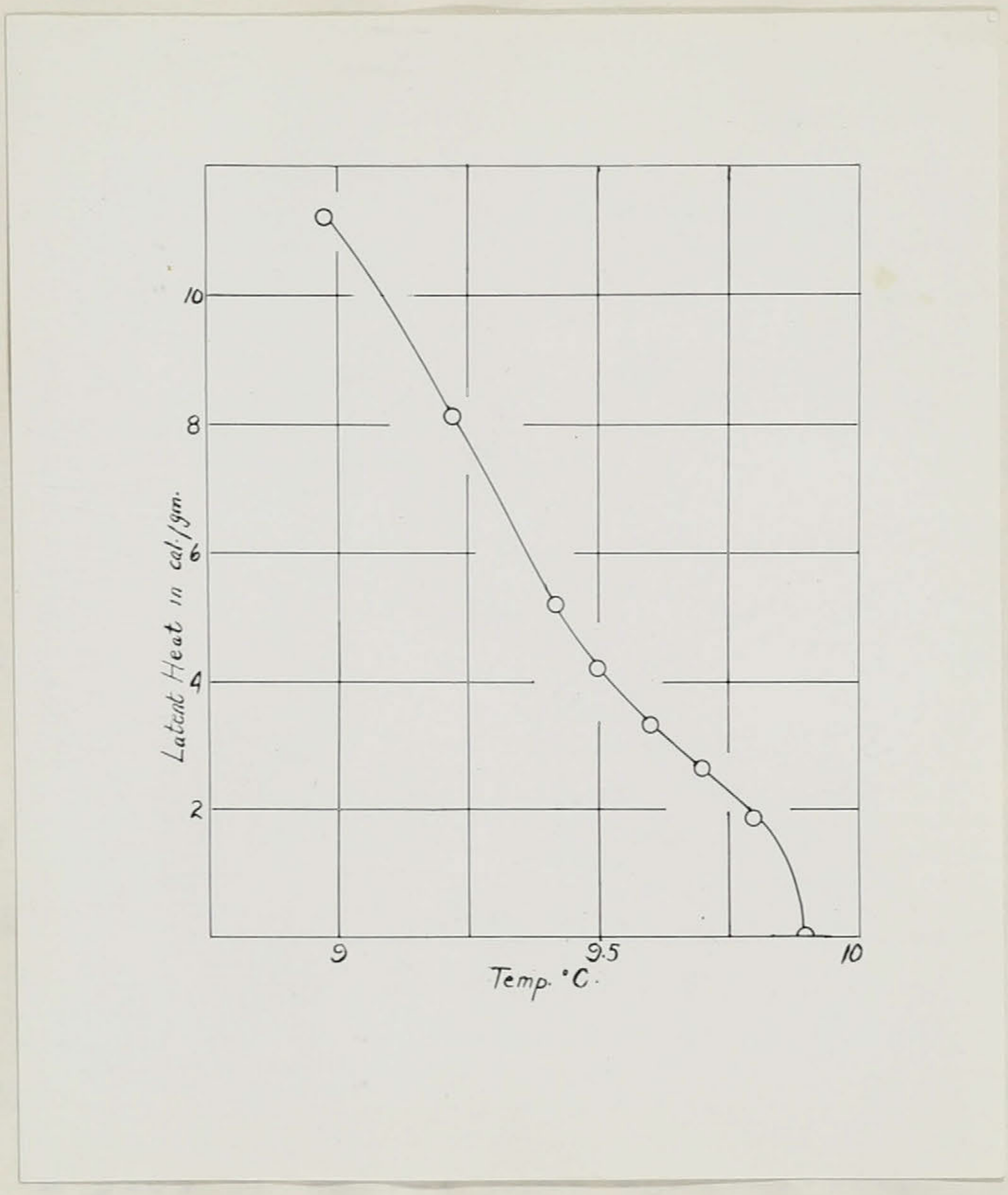


Figure 18

Latent Heat of Ethylene in

Critical Region

Heat of Vaporization of Ethylene in the Critical Region

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

$$T \frac{dP}{dT} = \frac{\lambda}{V_2 - V_1}$$

where

λ signifies the latent heat of vaporization

V_2 " " volume of the saturated vapor

V_1 " " " " " " liquid,

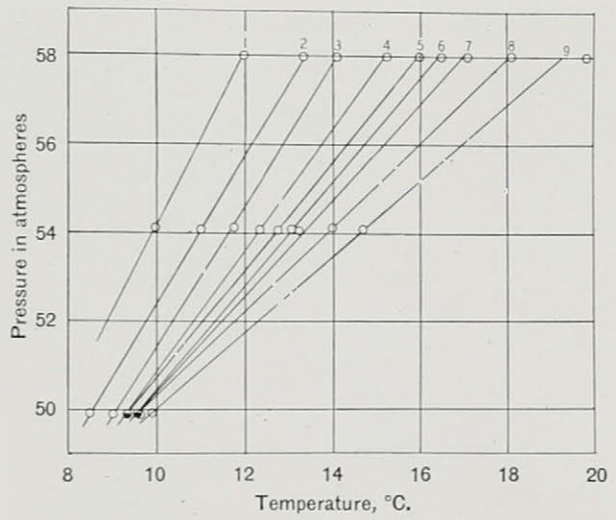
and the other symbols have their usual significance.

The value of $\frac{dP}{dT}$ was evaluated graphically from the figures of Table XXI, while the specific volumes of the saturated liquid and vapor were evaluated from the saturation curve of Figure 14. The values chosen for V_2, V_1 etc. are given with the calculated values of λ in Table XXII.

A plot of latent heat against temperature is given in Figure 18 It is seen that the latent heat does not reach a zero value at the classical critical temperature, but at 9.9 °C., that is .4°C higher.

TABLE XXIII

V_2	V_1	T	$\frac{dP}{dT}$	λ cal/gm.	V_2-V_1
5.448	4.000	282.1	1.13_3	11.19	1.448
5.176	4.072	282.4	1.13_3	8.53	1.104
4.896	4.224	282.6	1.13_3	5.20	.672
4.800	4.256	282.7	1.13_3	4.21	.544
4.688	4.256	282.8	1.13_3	3.34	.432
4.596	4.256	282.9	1.13_3	2.63	.340
4.520	4.280	283.0	1.13_3	1.86	.240
4.400	4.400	283.1	1.13_3	0	0



Pressure-temperature relations for various isochores evaluated from Geddes and Maass's isobars. Numbers denote following isochores—1, 0.290; 2, 0.275; 3, 0.262; 4, 0.240; 5, 0.220; 6, 0.205; 7, 0.190; 8, 0.170; 9, 0.148 gm. per cc. Shaded circles denote double points.

Figure 19

Pressure-Temperature Curves throughout the Critical Region and the Formula of Mills

In addition to the vapor pressure curve of ethylene given in Figure 17, the pressure temperature curves for nine different isochores are given in Figure 19. These curves were evaluated from the isobars of Geddes and Maass (51), and are all excellent straight lines. The absolute densities of these curves have been corrected to correspond to the absolute density values obtained by the author, and which are believed more nearly correct.

Since the pressure temperature curves are straight lines, it follows that equations of state, such as Van der Waals', are valid in this region. Because of this fact, an estimation of the internal pressure "$\frac{a}{V^2}$" was made from the equation

$$\frac{a}{V^2} = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Information as to the changes in "a" itself throughout this region was desired, in the hope that an indication of progressive orientation or cluster formation would be revealed. No such information was obtained, however, and the figures are not included in order to save space. The slope of the "critical" isochore has been used to test Mills' formula (58), which is that

$$\left(\frac{\partial P}{\partial T}\right)_{V_c} = \frac{2R}{V_c}$$

where R has its usual significance, and V_c is the classical critical volume.

The calculated value of $\frac{2R}{V_c}$ for ethylene is 1.26 atm/°C. while the corrected experimental value gives 1.21 atm/°C.

The Effect of Mechanical Stirring on the Heterogeneous System at 9.51°C.

In the design of apparatus used in this investigation it was possible to include a magnetic stirring arrangement in the ethylene side of the system. This was done in order to see if mechanical stirring, which has been emphasized as necessary in criticisms of work done in this laboratory, would affect the phenomena which are observed.

A heterogeneous system was therefore obtained at 9.51°C., and its pressure recorded. This system was then violently stirred by movement of the magnet up and down the length of the tube for a period of twenty seconds. Several minutes were allowed to elapse, and the pressure again observed. This treatment was repeated four times. No change in pressure could be detected. Although no mass movement of material could be seen during the stirring, the stirring was of sufficient violence to cause large visible transfers of liquid short distances into the vapor phase when the temperature was below the critical. Moreover, the fact that the phenomena reported here, and which is similar to that reported by previous workers, was observed in a tube which contained no spiral, completely refutes the argument of Ruedy (40) that the presence of a spiral acts as a deterrent to the proper mixing and diffusing of the system, and is the reason for the anomalous observations which have been made in the critical region.

Claims from the Isotherms of CO_2

by

A. Michels, B. Blaisse and C. Michels

Proc. Roy. Soc. 160, (1937) (59)

Come to our attention

Since the completion of the work described above, a paper upon the isotherms of carbon dioxide by A. Michels, B. Blaisse, and C. Michels has been found. The work is directly comparable to that just described for ethylene. The measurements of both pressure and temperature were extremely precise. The results do not agree with those for ethylene which have been tabulated above. (The temperature was controlled to better than .005°C., and pressure differences of .001 atmosphere could be detected by means of a dead weight gauge). No region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ was found above the critical temperature. The reason for this disagreement is not clear, and great weight must be attached to the measurements of these authors because of the precision of the method and the great purity of the gas investigated. There are, in addition to the possibility that a maximum sensitivity of ± .005 atmosphere, which is claimed for the present investigation of ethylene, is not sufficient to differentiate between a true two-phase system and a very compressible one-phase system, two possible explanations for the disagreement The first is the care taken in experimentation by Michels and his co-workers. For example, the isotherm at 25.07_0 °C, nearly 6°C below the critical temperature where the system should be a truly two-phase system, shows a gradual increase of pressure of nearly .02 atmosphere in the region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$. On the other hand, certain of his isothermals show a very constant pressure throughout this region. For instance, the isotherm at 29.92_9 °C reveals a maximum deviation of only .006 atmosphere from the mean value of the pressure throughout the range. No doubt greater care was taken in determining the points as the critical temperature was approached, and the degree of precision claimed was more nearly attained.

The second possibility is that the two substances under study were different and therefore being different, any generalization as to the behaviour of liquid-gas systems as a whole is unjustified.

Moreover, as will be pointed out more clearly later, the classical critical temperature appears to depend upon the point at which the surface tension drops to a value where the phases become miscible in all proportions. In some cases this temperature may actually coincide with that temperature at which liquid, under its own vapor pressure, may be unable to exist. In such a case the temperature which is the upper limit for the region in which $\left(\frac{\partial P}{\partial V}\right)_T$ equals ~~to be~~ zero, will be the same as the temperature where the visible meniscus disappears. This might well be the case for carbon dioxide, while for ethylene the temperature of complete miscibility is below that temperature at which liquid ceases to exist, and thus a persistence of liquid above the critical temperature as normally defined is observed. In any case, no mention is made by Michels of the temperature at which the meniscus is seen to disappear in a stationary bomb, which is after all, the Cagniard-La Tour temperature which has always been identified in the classical theory as the same temperature at which liquid can no longer exist under its own vapor pressure. Michels determines his critical temperature by extrapolating the minimum values of $\left(\frac{\partial P}{\partial V}\right)_T$ for temperatures above the critical back to the point of intersection with the temperature axis. This may or may not be the critical temperature as defined above.

The author feels, therefore, that the data given above for ethylene cannot be lightly dismissed, and the original interpretation of these results is given in a following section.

The Co-existence Line obtained from the Isothermals and the Density-Temperature Curve of Naldrett

The saturation line of liquid and vapor as obtained from the envelope of the region of the isothermals wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ has been plotted as a function of temperature in Figure 20 This curve should represent the saturation or solubility curve of liquid in vapor and vapor in liquid. The isothermals have been shown to be equilibrium curves, and therefore the saturation curve must be the true representation of liquid and vapor behaviour throughout the critical region. The form of the curve, which is represented by the hatched circles of the figure, does not agree with the form of the curve determined by Naldrett and Maass (57) by another method. This curve is represented by the plain circles of the figure, and except at the lowest recorded temperature lies everywhere within the saturation area as determined from the isothermals. That such a discrepancy exists is important, and an analysis of the possible cause turns out to gives excellent support to the dispersion or emulsification theory which has been used to explain many of the results outlined above.

Naldrett's experimental method must first be outlined in order that the criticism of it may be clearly understood.

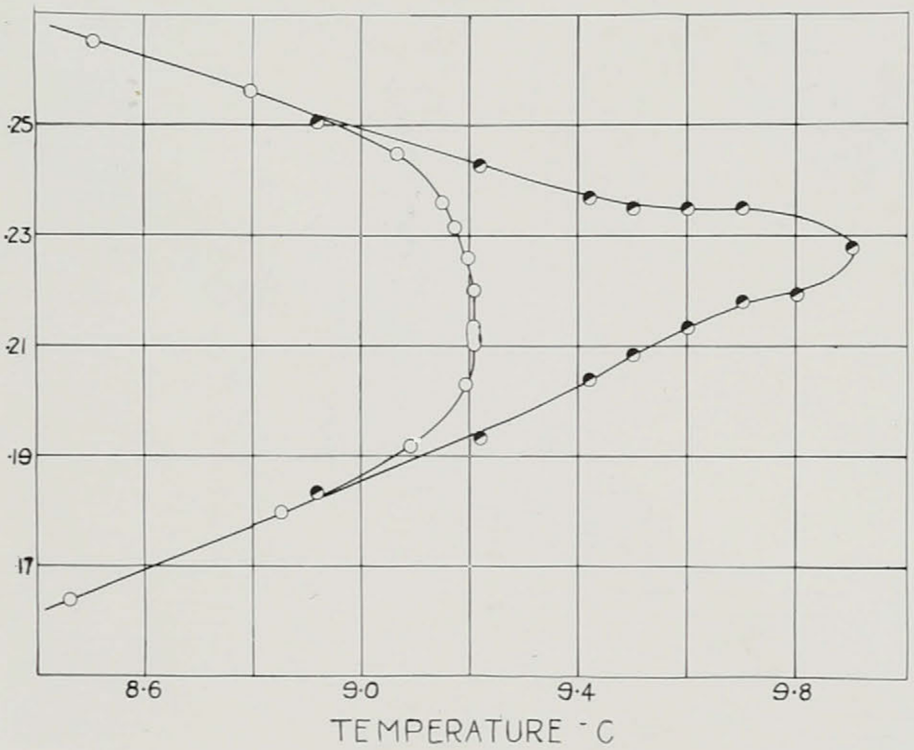


Figure 20

Density-Temperature Curve

Hatched circles denote values obtained from pressure volume isothermals

Plain circles denote values of Naldrett and Maass.

The bombs were filled with different amounts.

Surely not!

The experimental arrangement was briefly as follows. Very carefully purified ethylene was confined in small glass bombs. Each bomb was filled with varying amounts, and the mean density was determined very accurately by a gravimetric method. A bomb when filled was placed in a thermostat upon a wheel of short radius, and the wheel revolved quite rapidly. This provided violent stirring of the medium. As the temperature of the bath was raised, a bomb of density higher than the mid-point of the curve was found to fill gradually with liquid. The precise temperature at which the liquid just filled the bomb was recorded, and the density of the bomb was assumed to be the density of the liquid at that temperature. When a bomb of low density was similarly treated, vapor gradually occupied the entire space, and the temperature and density for such an occurrence was assumed to give the true vapor density for that temperature. Bombs filled to densities corresponding to the flat apex of the curve gave opalescent mixtures, and showed a definite range of density over which an apparently two-phase, but physically homogeneous, system could be obtained. This temperature was 9.20°C , and was called the "shaking critical temperature" because at this temperature the meniscus disappeared on shaking. These are the experimental facts, and the author wishes to explain them so as to bring them into agreement with the saturation curve.

The interpretation of the flat apex, which gave highly opalescent systems, was that dispersion or emulsification of one phase in the other occurred. These emulsions were apparently stable, for no restratification into layers occurred. Such an explanation is simple and reasonable, and from it the true significance of the other points may be developed.

It is a foreign concept that conditions for emulsification should be attained suddenly at some discrete temperature. A continuous approach to such conditions seems preferable. It therefore appears plausible that a certain degree of emulsification occurs at lower temperatures, either of vapor in the liquid at high average densities, or liquid in vapor for low average densities. The amount of such emulsification is dependent upon the value of the interfacial tension, and increases with rise in temperature. At 9.20°C , the extent has attained such magnitude that it becomes manifest by visual means, and the phenomena of the "shaking critical temperature" become apparent. At lower temperatures the emulsification is not apparent to the eye, and a homogeneous system of either liquid or vapor is seen to fill the tube. In reality, these systems are probably supersaturated solutions of the two phases, and have an apparent stability because of the low value of the interfacial tension at these temperatures. This concept explains neatly why the curve always lies within the saturation curve of the isothermals. Thus, at some apparent "liquid" density, a supersaturated solution of vapor in liquid is obtained, and therefore has a lower density than the true liquid density at that temperature. For apparent "vapor" densities the reverse has happened, and a supersaturated solution of liquid in vapor is obtained, with a consequently higher vapor density than that of the saturation curve. As the temperature is lowered, the degree of supersaturation which is possible is lessened, and ultimately will become negligible. This explains the agreement by the two methods at a temperature of 8.92°C

It is seen, therefore, that the apparent disagreement of results is in reality fictitious, and that strong support of the emulsion theory is presented by these two curves when properly interpreted.

DISCUSSION

The phenomena reported above and the explanations which have been offered lead to a rather interesting and somewhat novel picture of the changes which occur when ethylene is subjected to changing conditions in the critical region. As this qualitative description may well have ~~a~~ be applicable ~~wide generality with regard to~~ to all liquid gas systems, a review of the experimental behaviour and its interpretation may be of value.

The first point of interest was the pronounced hysteresis of liquid and vapor densities when the substance was heated above the critical temperature, as defined by the meniscus disappearance, and subsequently cooled. It was found that a heterogeneous system persisted for about one degree above the critical temperature, and that the density of condensed liquid did not coincide with the density of the original liquid until cooled to 8°C. The amount of heterogeneity, but not the critical temperature, was found to be a function of the mass volume ratio.

The amount of heterogeneity was found to be greatly influenced by the presence of small amounts of air (1% or less), and it was observed that with such quantities of air present, liquid could persist for as much as 25°C above the critical temperature. Air-ethylene samples which were made homogeneous by "molecular stirring" showed the same sort of hysteresis when density is plotted as a function of temperature as pure ethylene, except that the temperature of condensation was lowered.

Time lags measured upon isobars and isotherms showed a pronounced increase in time required to establish characteristic "liquid" densities by cooling or compression from the "vapor" region, above that required to produce "vapor" densities by heating or expansion from the "liquid" region. Reversing of the direction of measurement of the isothermal at 9.60°C. showed large time lags in compressing a true "vapor" to a smaller volume.

Pressure gradients produced by heating the top of the bomb were found to recreate a stable heterogeneity even above the critical temperature The amount of this heterogeneity increased as the temperature was lowered toward the condensation point. At .03°C above this temperature, a meniscus could be reformed by such compression.

Compression of the liquid which condenses out at 9.17°C., increased both the density and amount of liquid. At very low mean densities the density of this liquid could be raised above that of the original heating curve by such compression. With fillings of mean density of .200 gm/cc. or higher, the density of the liquid phase was never raised above that of the heating curve.

Accurate pressure volume relations at constant temperatures showed a persistence of a second phase above the critical temperature. This was indicated by a very definite region throughout which $\left(\frac{\partial P}{\partial V}\right)_T = 0$. The complete envelope of this region was determined and the point of inflection for the isotherms found to be at 9.90°C. The pressure of heterogeneous systems was measured in this region, and found to be unchanged by mechanical stirring, to be independent of mass volume ratio, to be the same as that of the homogeneous system obtained by heating above 10.5°C. and cooling, and to be the same as the pressure of the horizontal portion of the isothermal at the same temperatures. The homogeneous system obtained by heating and subsequent cooling was shown to have a pressure independent of volume within the limits of density defined by the co-existence curve of the isothermals. Pressure measurements at constant volume showed that curves A and B of a typical isochore had identical pressures.

The leads given by the above pressure measurements allowed of a much better explanation of the hysteresis curve at constant volume, the equivalence of pressures along curves A and B of such an isochore, the apparent stability of the experimental data, heterogeneous and homogeneous systems, and so on. The explanations heretofore given will be briefly repeated, and a general qualitative theory of the behaviour in the critical region developed from them.

The pressure-volume measurements made at constant temperature allowed but one reasonable interpretation. Within experimental sensitivity they show definitely the existence of a two-phase system between certain well defined densities even up to 9.90°C. This two-phase system can apparently be macroscopically heterogeneous or homogeneous, and either form is stable. The heterogeneous system will persist indefinitely if mixing is not caused artificially by mechanical stirring or jarring. If such treatment is applied to a heterogeneous system, the density difference above and below the position of disappearance of the meniscus is ironed out by a mixing or emulsification of one-phase in the other. In a stationary bomb a certain amount of this mixing may be brought about by the system itself, because of the tendency of the meniscus to move up or down in the tube because of the mean density of the filling The phase density relationship with mass volume ratio is thus easily explained. It is, of course, not a true phase density, as the experimental arrangement really measures the density of the one phase plus a certain admixture of the other.

The course of events on heating at constant volume is explained as follows. The liquid phase, which persists largely in the bottom of the tube, is gradually destroyed as the temperature is raised. Somewhere in the vicinity of 10°C., the system has become a true vapor system with a pressure dependent upon its volume. (The exact temperature is somewhat doubtful because the sensitivity of the experimental method is involved in its determination. Thus, in the spiral arrangement, a heterogeneity is just detectable at 10°C., while with the pressure-volume arrangement, no definite indication of a horizontal portion of an isothermal can be detected above 9.90°C). On cooling down from this temperature, liquid is formed, but is now dispersed uniformly throughout the tube. As the temperature is lowered the interfacial tension is increased, and condensation occurs at 9.17°C. Vapor is still retained in this liquid, and liquid still remains in the vapor above it. Compression causes the foreign phase to separate out of the one in which it is suspended, and both density and amount of the phase is changed. Without compression the temperature must be lowered to 8.0°C , before the amount of one phase dispersed in the other becomes negligible.

The assumption of a very small interfacial tension in this region immediately explains the pressure agreement between homogeneous and heterogeneous systems, and the apparent stability of the emulsions of one phase in the other.

The effects caused by the presence of air are explained by the fact that the air tends to remain in the upper portion of the tube, causing an artificially great pressure upon the liquid phase, which is thus caused to persist many degrees above the critical temperature. When this air is mixed throughout the system, this effect is vitiated, and the only difference in behaviour is that caused by the lowering of the interfacial tension by the air.

All the phenomena observed are therefore well explained by the assumption of a two-phase system persisting above the temperature at which the meniscus disappears, without any description of the nature of the two phases, except the phenomena of time lags. These time lags are well established from the work of Geddes and Maass (51), Pall, Broughton and Maass (47), and the present investigation. They indicate strongly that some form of orientation exists in the liquid state of aggregation. Evidence that extended time lags exist even in the true vapor region indicates that here, too, some degree of orientation is being brought about by the change of conditions. Studies by Stewart and his co-workers indicate a change of nature of the medium which is marked, only for volume changes (23). Reaction rates, studied by Holder and Maass (48), indicate again that density changes are very important, and that this importance is not due merely to the concentration effect of the reactants. All these experimental facts lend strong support to the description of the change occurring as a liquid changes to the vapor state, which was given in 1908, by Bradley, Browne and Hale (28). The sequence of occurrences is so well stated in this excellent paper that much of what is to follow is directly quoted from their writings. The author finds it difficult to understand the lack of emphasis which has been placed upon this work, unless the qualitative nature of the experiments made their value seem small to other workers in the field.

Bradley, Browne and Hale follow Traube in his distinction between real liquid (liquidons) and real gas (gasons) and between the liquid phase and the vapor phase. The liquid phase is to be considered as true liquid containing true gas in solution, while the vapor phase is supposed to contain true liquid in solution in true gas. The difference between a liquidon and gason may well be that a gason is a single molecular unit, or at least is made up of few molecules. On compression, orientation and clustering occurs at random throughout the gas and small groups of molecules form and break up as the kinetic theory demands. That is, the life of any one group is limited, but such groups are always present. On further compression, below the critical temperature, the number of such groups increases until at great enough densities saturation has been attained, and precipitation of the liquid phase occurs. This phase, as pointed out above, contains a saturation value of gasons. To quote directly from the above authors, 'This view transforms the "area of liquefaction" on a diagram of isothermals to an "area of saturation". Outside this area of saturation, on the side opposite the pressure axis, liquidons may exist, less or more according to volume, but never to the extent of saturating the gasons in which they are dissolved' The opposite, with regard to gasons in the liquid phase is the case on the side of the saturation area next to the pressure axis.

'Above the critical temperature, true liquid and true gas may exist side by side in any proportion, according to volume, but there can never be phases except in the loose sense of temporary stratification. Outside the area of saturation, there is perfect continuity in every direction. The area of saturation, indeed, is after all only an exceptional case in an otherwise general continuity between the liquid and gaseous conditions of matter. Andrews' distinction between gas and vapor in terms of the critical temperature may still be retained, if the capacity for continuity is made fundamental , but not otherwise. An aeroform substance is "gas" above the critical temperature and "vapor" below that temperature. Whether as "gas" or "vapor" it may be changed to liquid by pressure alone -- as "gas" with perfect continuity, -- as "vapor", only by a discontinuous process involving saturation'.

This continuity of state concept forms an adequate background for the phenomena which have been observed by the author, and it is hoped that more weight will be attached to such a concise and satisfactory description, now that quantitative measurements which support it so conclusively have been made.

GENERAL SUMMARY

A repetition of various curves obtained by Geddes and Maass showed that the general nature of their results ~~was~~ were in the main reproducible. For example ~~Thus,~~ the existence and nature of the extended time lags involved in the establishment of equilibrium densities has been confirmed. The persistence of heterogeneous systems above the Cagniard-la Tour temperature and the equivalence of pressures of heterogeneous and homogeneous systems was re-established. The absolute values of the densities and pressures recorded by Geddes and Maass were found to be in error, and the causes have been determined.

The work has been extended to the investigation of air-ethylene samples, and the novel behaviour of such systems has been studied. Measurements made with pure ethylene have given the relationship between phase density and mass-volume ratio at the classical critical temperature. The complete density-temperature hysteresis curve of the liquid phase has been determined for the first time.

Compressional measurements, made by establishing a higher temperature along the upper portion of the bomb, have revealed the possibility of reforming heterogeneous systems from homogeneous ones above the temperature of condensation. Moreover, a meniscus has been shown to be reformed at a temperature +.03°C higher than the temperature of spontaneous condensation, by such compression.

Pressure-volume isothermals of the system ethylene have been determined throughout the critical region. They have shown that a two-phase system exists to a temperature of 9.9°C. The true form of the density temperature curve for both liquid and vapor has been obtained from them. Pressure-temperature relations at constant volume have shown that the heterogeneous and homogeneous systems of an isochore have exactly similar pressures at the same temperature, within the density range defined by the envelope of the region of the isothermals wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ Moreover, these systems have both been shown to possess the same Gibbs' free energy, and to have the same free energy as the homogeneous system which is obtained by isothermal expansion or compression to the density region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$.

This data has been explained by the assumption of a two-phase system which becomes homogeneous above the Cagniard-la Tour temperature by grace of a zero surface tension. A general theory of the continuity of gaseous and liquids states, due to Bradley, Browne and Hale, has been extended to include the concept of regional orientation due to Dr. O. Maass. This theory is put forward to explain the behaviour of the critical region including the very important factor of time lags, originally investigated by Maass and Geddes.

CLAIMS TO ORIGINAL WORK AND CONTRIBUTIONS TO KNOWLEDGE

Two new forms of apparatus for the study of the critical region were developed. Both were based upon the principles of design due to Geddes and Maass, and incorporated the use of the "balanced pressure" principle for determining pressure values in the one case, and of a McBain-Bakr spiral and float for density determinations in the second case.

In the first design a more precise method of determining the necessary mercury level correction, by the use of a cathetometer, was employed. The total volume of the system was given by the same reading of the mercury level. Mechanical stirring of the medium was possible in this form of apparatus. Moreover, an improvement in the manual thermostating of the system was developed by means of a subsidiary water flow unit.

In the second design a water jacket was employed for the production of a temperature gradient along the bomb. By means of this arrangement the effect of compression upon the medium in the lower part of the tube was studied.

The following Contributions ~~of the following nature~~ to the knowledge of the transition from liquid to gas have been made.

(1) The cause of the hysteresis curve at constant volume and the persistence of heterogeneous systems above the

Should these not be sentences?

Cagniard-la Tour or classical critical temperature.

(2) The relation of phase densities to mass volume ratio at the classical critical temperature.

(3) The effect of small quantities of air impurity upon the persistence of the liquid state above the same temperature.

(4) Pressure-volume isothermals of a high degree of precision throughout the critical region.

(5) The true form of the density-temperature curve for both liquid and vapor phases throughout the critical region.

(6) Discovery of the region above the critical temperature within which heterogeneous systems are stable.

(7) The relative free energies of heterogeneous and homogeneous systems as measured by their vapor pressures, and the effect of mechanical stirring on the vapor pressure of heterogeneous systems.

(8) Evidence of molecular orientation in a gas system above the critical temperature.

(9) The "true" critical constants of ethylene, as indicated by the pressure-volume temperature relations.

(10) The effect of local compression upon both pure ethylene and air-ethylene samples.

(11) An explanation of the above phenomena as due to a two-phase system, the phases of which become completely miscible at a temperature 3°C below the temperature at which the meniscus is seen to disappear when observed in the conventional manner.

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