The Persistence of the Liquid State of Aggregation above the Critical Temperature. The System Ethylene

O. Maass and A. L. Geddes

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Introduction

The research described below arose from previous investigations carried out in this laboratory.* In a study of the influence of molecular compound formation on the rate of reaction (Maass and Sivertz, 1925) it was found that although propylene and hydrogen chloride apparently react in a reproducible manner when the reactants are brought together in the liquid state, no measurable reaction occurs when they are brought together as gases. At first this was ascribed to the difference in concentration between the liquid and the gaseous states. However, it was shown (Sutherland and Maass, 1931) that when propylene and hydrogen chloride are brought together at room temperature as gases and heated above the critical temperatures of the mixture, no reaction occurs even when they are compressed to a concentration as great as that of the liquid mixture slightly below the critical temperature. The rate of reaction of the liquid mixture was found to increase with rise in temperature in the usual manner up to the critical temperature, but was found to be nil in the absence of the liquid phase. The acquirement of results of a similar nature by the application of the same procedure to other systems has been delayed owing to the fact that for most systems in which a homogeneous reaction takes place in the liquid state the critical temperatures and pressures are so high as to enhance greatly the experimental difficulties. An attempt to overcome these difficulties is still in progress. In the meantime other investigations have been undertaken with the object of finding a possible explanation for a discontinuity in reaction rate at the critical temperature. The first was an attempt to discover whether or not at the critical temperature a marked discontinuity of state exists in a two-component system, in contrast to the continuous change generally accepted as taking place in a one-component system.

In the development of a technique for examining two-component systems one-component systems were first studied. It was found that when a liquid in equilibrium with its vapour is heated above its critical temperature, a difference in density persists above and below the position where the meniscus is last seen. In consequence of these observations, efforts up till now have been directed towards a study

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* Chemistry Dept., McGill University.

of one-component systems in the region of the critical point. The results which have been published on this subject by the senior author and his co-workers will be briefly summarized.

It must first be stated, however, that a survey of the literature showed that this phenomenon has been observed before. Traube (1904) and his collaborators, notably Teichner (1904), found evidence of the existence of a density gradient in a two-phase one-component system heated slightly above the critical temperature. Traube put forward a hypothesis that there is a difference in the nature of molecules when in the liquid state (liquidons) as contrasted to when they are in the gaseous state (gasons). Subsequent investigators ascribed the density difference to impurities or to inaccurate temperature control. At most, a gravitational effect due to the weight of the medium itself was conceded to be a possible cause for the density difference. This generally accepted viewpoint is summarized in a clear and concise manner by Jellinek (1928). The experimental technique developed in this laboratory made it possible to make precise density measurements in various parts of a medium above the critical temperature, when kept under accurate temperature control. This not only permitted the verification of some of Traube's experimental conclusions but also led to the discovery of other factors which are involved in the phenomenon; factors which must be taken into account in any explanation of the mechanism involved.

It was found that when a liquid is heated above the critical temperature, not only is there a difference in density above and below the point where the meniscus was last seen but there is a discontinuity in the density gradient at this point. The magnitude of the density difference is dependent on the mass per volume relationship of the material, being greater the greater the mass per volume. The density difference could not be destroyed by mechanical stirring, and it remained unchanged during a period as long as six hours of continuous stirring. That the stirring was effective was visibly demonstrated by the fact that just below the critical temperature downward streaming of the liquid in the vapour phase was produced each time the float (Winkler and Maass, 1933) was lifted above the meniscus. This showed that the liquid was actually carried up into the vapour region. This intermingling of the upper and lower " phases " due to stirring must, of course, have been just as effective above the critical temperature. It was found that the difference in density existing above the critical temperature decreases with rise in temperature and eventually becomes zero. The increase in temperature above the critical necessary for the equalization of the density is different for different substances. It was also shown that once the density difference is destroyed by an increase in temperature, a subsequent decrease in temperature is accompanied by the persistence of a uniform density throughout the tube. In other words, no density difference is re-established until the liquid phase reappears on cooling the medium below the critical temperature. Apparent equilibrium values subsequent to a temperature change were usually reached in less than thirty minutes, no further change in density being discernible either with or without mechanical stirring.

It was shown that if an expansion takes place after the medium is heated slightly above the critical temperature the existing density difference is destroyed, and it does not reappear when the medium is compressed to the original concentration. It was also shown that a temperature gradient in which the upper part of the medium is kept colder than the lower part destroys the density difference. In no case was it found that the higher density in the lower part of the medium would spontaneously recur after it has been destroyed.

The adsorption of propylene and dimethyl ether on alumina and the dielectric constants of these substances have been measured through the critical temperature critical pressure region. The surface tensions of propylene and dimethyl ether were measured to within 1·5° C. of their critical temperatures and the results obtained indicate that the total surface energy is not zero at the temperature where the visible meniscus disappears. The adsorption, dielectric constant, and surface tension measurements obtained are indicative that a difference in medium persists above the critical temperature above and below the point where the meniscus disappears.

In all the measurements that have been undertaken so far in connexion with the apparent discontinuity in density above the critical temperature there has been no experimental means of accurately controlling and measuring the pressure. The medium under investigation was confined in a fixed volume, and its pressure was governed solely by this volume and the temperature to which the medium was subjected. Whether or not discontinuities in density could still be obtained under pressures slightly above the critical was unknown. The present research was primarily undertaken to develop an experimental technique which would make this investigation possible.

Furthermore, a number of questions suggested by the results of the investigations described above remained to be answered. Is the magnitude of the density difference dependent on the polarity of the medium? Would such density differences be discernible with a substance like ethylene or carbon dioxide whose electric moment is much less than that of propylene or methyl ether? Does compression as well as expansion of the medium destroy the density difference? If a density difference exists above the critical temperature, is there evidence that this is not due to gravity in the sense of a compression brought about by the weight of the medium itself, as the compressibility near the critical temperature is admittedly enormous?

A new technique has been devised which is applicable to the investigation of any medium with a reasonably low critical temperature and critical pressure (below 150° C. and 75 atmospheres). With this apparatus any one of the three variables, pressure, volume, and temperature, may be maintained constant while the other two are varied. Only ethylene has been investigated so far. Ethylene has an exceedingly small electric moment and is interesting because of this property. The results obtained will be presented in this paper.

All the questions asked above have not been as yet fully answered, but important information has been obtained which will serve as a guide. It is hoped that further investigations with substances more polar than ethylene will lead to more definite conclusions. In order that the validity of the conclusions drawn may be more fairly judged, the experimental technique will be described in some detail. In the introduction to the experimental section, a brief summary of the principal requirements which the apparatus must fulfil will help to clarify still further the object of this research.

EXPERIMENTAL

For the investigation planned it was essential that the temperature and pressure of the system be kept under accurate control. The tolerance permissible may be stated as follows. The absolute temperatures were to be established to within an accuracy of ±0·01° C. and relative temperature variations kept considerably below this value. The pressure was to be obtained in a reproducible manner to within ±0·01 atmosphere. Relative density measurements were to be made with an accuracy of one part in two thousand. The approximate temperature, pressure, and density ranges to be covered in the case of ethylene were to be 5° to 15° C., 45 to 60 atmospheres, and 0·15 to 0·30 g./c.c. respectively.

The density measurements were made by means of a McBain-Bakr (1926) balance with attached float. This technique has been successfully employed before in this laboratory. The design of the apparatus was such that the density of the medium could be measured in the liquid state in presence of the vapour, and in the vapour state in presence of the liquid, as well as the density of the medium when only one phase was present. The temperatures were measured by means of standard Reichanstalt mercury thermometers and standardized Beckmann thermometers. The pressure was measured and controlled by the vapour pressure of stirred liquid carbon dioxide kept under accurate temperature control.

An added difficulty in fulfilling the requirements outlined above was that glass apparatus had to be employed which could be subjected to an internal pressure of 60 atmospheres. This involved a serious explosion hazard, and hence experimental arrangements had to be such that manipulation could be carried out without danger to the observer. Furthermore, provision had to be made so that the apparatus when filled could be kept for any desired time at a low temperature (—78° C.).

Experimental Technique

Fig. 1 shows the essential features of the apparatus drawn to scale. Fig. 2 is a diagrammatic representation of the complete assembly in which the various parts are not drawn quite to scale and for purposes of clarity are not shown in their actual relative positions. B and B_1 are two bombs made from a section of specially selected pyrex tubing of 11·3 mm. bore and 4 mm. wall thickness. They are connected from the bottom by pyrex capillary tubing of 3 mm. bore and 3 mm. wall thickness and shaped as illustrated in fig. 1. Before assembly, the bombs were tested with a Cailletet pump to a pressure of 75 atmospheres. The assembly was designed so that the bombs could be completely immersed in thermostats. Fig. 2 shows the bomb assembly clamped in position. Both top and bottom of each bomb are fastened firmly to a brass rod. The intervening capillary tubing and part of the available space in each bomb are filled with mercury.

The apparatus involves a new experimental principle, as far as regulating and measuring the pressure of a medium in the neigbourhood of its critical temperature

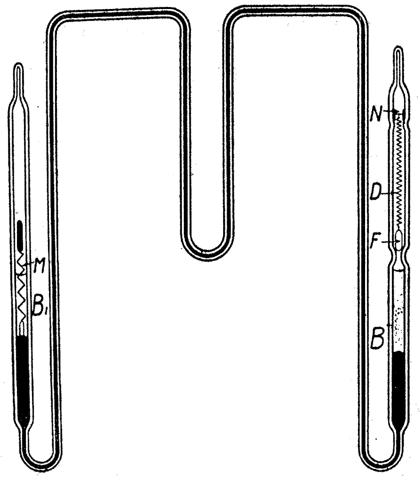

Fig. 1—Diagram of bomb assembly.

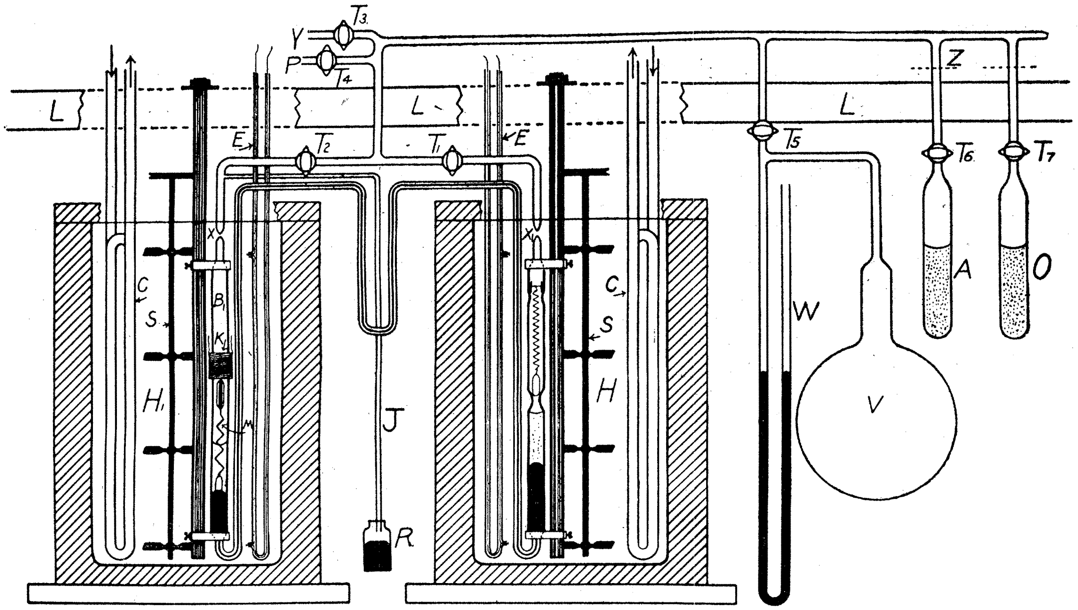

Fig. 2—Diagrammatic representation of complete apparatus.

is concerned. The pressure of the material under investigation in B is balanced by the accurately known vapour pressure of the material in B_1. In this case carbon dioxide served admirably because of the convenient temperature (approximately 15° C.) at which its vapour pressure is equal to that of ethylene at its critical temperature, and because the vapour pressure curve for carbon dioxide in this region has been accurately determined. In any case, accurate absolute measurements of pressure are not of such great interest as accurate reproducibility of relative measurements which depend only on temperature control of the carbon dioxide. The mercury of the U tube, when frozen, acts as a perfect seal, when desired, so that in the course of manipulation the media in the two bombs may be kept at different pressures.

The amount of carbon dioxide in B_1 was so chosen that the two phases, liquid and vapour, are always present throughout the range of temperature required, irrespective of the volume changes in the space above the mercury in B_1 which are induced by the expansion or contraction of the ethylene in B. As long as the temperature of B_1 is kept constant, the pressure in the system will remain constant, regardless of changes in the relative amounts of the liquid and vapour phases of the CO_2. Hence, between certain limits of volume change of the ethylene in B, its pressure can be regulated and measured indirectly by noting the temperature around B_1. For the particular bomb used in this case the volume could be varied between 16 c.c. and 32 c.c. The amount of ethylene was so chosen that density measurements could be taken through a range of 0·15 to 0·30 g./c.c.

In the range of pressures required, a change in temperature of the carbon dioxide of 0·01° C. causes a change in pressure of approximately 0·01 atmosphere. It was found possible to control the temperature to within 0·001° C. indefinitely. In the course of manipulation, momentary temperature fluctuations occasionally occurred, but this could be kept below ±0·01° C. Since the average deviations in temperature are less than ±0·01° C., the deviations in pressure are less than 0·01 atmosphere and the error involved in pressure measurements is considerably less than 0·02%. For any desired pressure the temperature of the CO_2 must be adjusted to compensate for the difference in level of the mercury.

It was of importance that a true equilibrium between the liquid carbon dioxide and its vapour could be established as rapidly as possible subsequent to changing the temperature around B_1. This involved the rate at which the temperature of the thermostat could be changed, and the rate at which B_1 and its contents got into thermal equilibrium with the thermostat. The first of these will be discussed later in connexion with the thermostating arrangements. The second was investigated by making density measurements of the ethylene when it was kept at a constant temperature and the temperature of the carbon dioxide was changed. As long as the pressure of the carbon dioxide is varying the density of the ethylene will vary likewise, and it will become constant as soon as the pressure becomes constant. This is true only when the ethylene is not undergoing a change in state. As will be seen later, it is not true at temperatures slightly above the critical where slow changes in the density of the ethylene may take place, subsequent to a change in pressure, even when it is under a constant pressure. Hence, in determining the time for thermal equilibrium in B_1 by this method, the temperature of the ethylene must be kept below the critical. Measurable density changes in liquid ethylene at a temperature just below the critical could be obtained by a variation in pressure of 0·007 atmosphere. It was found that in two minutes the temperature of the thermostat around B_1 could be brought to a constant value differing by 0·5° C. from the previous one, and that in less than five minutes after this no pressure changes as indicated by ethylene density changes could be observed. The thermal lag in B_1, subsequent to a temperature change of 0·5° C., is therefore not more than five minutes. The thermal lag in B was found to be of the same order when the pressure of the carbon dioxide was maintained constant and the temperature around B changed by 0·5° C.*

It was found that stirring of the carbon dioxide was essential for rapid establishment of vapour pressure equilibrium. For this purpose a magnetic stirrer M was constructed to break the surface of the liquid periodically.

The density measurements were made by means of a quartz spiral D with attached float F (fig. 1). The spiral and float are suspended from a glass saddle N which is held in place by a constriction in the wall of the bomb. To decrease the danger of breakage of the spiral, a constriction was made in the wall of B on which the float could rest when the spiral was extended to a point below which no readings were required to be taken. The float was made of pyrex glass and was tested to stand an external pressure of 75 atmospheres before insertion in the apparatus. The error introduced by contraction of the float under the pressures used was found to be negligible. The diameter of the float is 0·5 cm. The volume is 0·8617 c.c. and was measured with a picnometer to an accuracy of 0·02%. Its weight is 0·3500 g. and it consequently has a density of 0·4602 g./c.c. Since the ethylene would buoy up the float and break the spiral if the density was more than 0·4062 g./c.c., it was necessary to lower the mercury so that the surface of the liquid ethylene was below the float when the density was above this value. A method of manufacturing quartz spirals is described by TAPP (1932). The spiral used in this case has one hundred turns and a normal length of 3·470 cm. The diameter is approximately 0·5 cm. The sensitivity of the spiral is 0·004485 g./mm. in the range of extensions and temperatures to which it is subjected. With this instrument relative density measurements can be reproduced with an accuracy of 0·05% when the extension of the spiral is measured with an accuracy of ±0·025 mm. As the inner diameter of B is 11·3 mm., there is more than 2·5 mm. clearance all around spiral and float.

Filling

The introduction of the mercury, ethylene, and carbon dioxide into the apparatus was carried out in the following manner. B and B_1 were connected at the top by separate taps T_1 and T_2 to a source of dry air at P, a Langmuir pump backed by a Hyvac at Y, a calibrated five-litre volume V, and a manometer W. Figs. 1 and 2

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* When a test tube made of similar bomb tubing was filled with water and placed in a thermostat and the temperature of the thermostat changed by 1° C., thermal equilibrium was established in the tube to 0·01° C. within three minutes. Temperature changes were measured with Beckmann thermometers. The water in the tube was not stirred.

show the bombs sealed off from the filling apparatus after the mercury, ethylene, and carbon dioxide have been admitted. The purified ethylene contained in a tube A, cooled in liquid air, was connected to the system at Z. It could be admitted to the system through tap T_6. The purified carbon dioxide was contained in tube O, which was immersed in a carbon dioxide-acetone freezing mixture. For the admittance of the mercury to the bombs a tube J, of barometric height, was connected to the system as shown. The end of this tube dipped into a reservoir of mercury R. Before filling, the bombs were baked at 120° C. for several hours while the system was flushed out with dry air and evacuated several times. After the bombs had been completely evacuated, the desired amount of mercury was admitted to the system from reservoir R through tube J. The amount of mercury introduced into the system was calculated so that it would fill approximately half the volume of B when it was at the bottom of B_1, and thus never rise above the constriction in B.

Knowing the density of liquid ethylene up to its critical temperature, and the volume of B, the weight of ethylene required to give the desired density range could be calculated. This amount of ethylene was introduced into B by condensation when liquid air was placed around the bomb. In the first place, when the mercury was at the desired height in B, the mercury in the U bend of the capillary tube was frozen. The system was then flushed out several times with ethylene by allowing the vapour to escape through T_6. Afterwards it was completely evacuated. Tap T_6 was then opened and A slightly warmed till the desired pressure (about 1 atmosphere) was built up in the system, after which T_5 and T_6 were closed and the system again evacuated. Then T_5 was opened and liquid air was placed around B till the pressure in the system had fallen to the required amount as read on the manometer. T_5 was then closed and the bomb sealed off at X_1. The five-litre volume V and connecting tubing up to T_5 had been accurately calibrated. Thus, knowing the volume and temperature of V, the pressure required to give the desired weight of ethylene could be calculated, the aberrations from the ideal gas laws being taken into account. The volume change due to the change in level of the mercury in W was, of course, taken into account in the calculation. The error in measuring the weight of ethylene by this method was less than 0·05%. The required amount of pure carbon dioxide was introduced into B_1 by a process similar to that described above and the bomb sealed off at X. 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.

Thermostating

Since a temperature control of better than ±0·01° C. was desired, it was necessary to construct thermostats in which the temperature could be very accurately regulated. A diagram of the thermostats H and H_1, and units for regulating the temperature is shown in fig. 2. Since the temperature in H was in the neighbourhood of 9·50° C., the critical temperature of ethylene, and that in H_1 in the neighbourhood 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 consists of a cylindrical pyrex jar 18 inches high and 10 inches in diameter, well insulated with sheep's wool. The thermostats could be raised or lowered by means of a system of ropes and pulleys. A long, narrow plate glass window was cemented in the pyrex jar H, so that when the latter was placed in position the measurements of the spiral extension would not be affected by imperfections in the glass wall of the jar. Since the temperatures of the thermostats were below room temperature, the condensation of water vapour on the glass caused considerable trouble at times by decreasing the visibility. To eliminate this difficulty, a double window was placed in front of the thermostat, and a current of warm dry air was passed between the windows. The spiral was illuminated from behind with two 200-W frosted lamps. The thermometers were illuminated by front lighting. The baths were cooled to the desired temperature by regulating the flow of cold water through cooling coils C. Each bath was also supplied with a 500-W heating coil for quickly producing heat when large temperature changes were desired, and a 100-W heater for accurate temperature adjustment. All the heaters were manually controlled by means of rheostats. To detect any temperature gradient in the baths, four-junction chromel-alumel thermocouples were used, each in series with a sensitive galvanometer. A temperature gradient of $0\cdot001°$ C. along the bombs could be detected with this arrangement. This proved to be an unnecessary precaution because no temperature gradient was encountered at any time. This was due to efficient stirring and to a judicious choice of position of heating elements, cooling coils, and bombs in the thermostats. Temperatures were determined with Beckmann thermometers calibrated with two different standard Reichanstalt mercury thermometers which were found to agree in themselves. One of these was kept permanently in H. Thus absolute temperature readings could be made with an accuracy of at least $\pm 0\cdot01°$ C. and relative readings with an accuracy much better than this.

Experimental Procedure

The previous description of the apparatus will be made clearer by an account of the sequence of operations during an experiment. The Dewar flasks were slowly removed from around the bombs and the thermostats hoisted into position. Then the Dewar was lowered from the U tube and the mercury allowed to melt, after adjusting the pressure in B_1 so that it was slightly greater than in B, by reference to the vapour pressure tables of carbon dioxide and ethylene.

When it is desired to obtain a pressure-volume isothermal curve, it is necessary merely to keep B at a constant known temperature, and to vary the temperature and thus the pressure in B_1 by the desired amount. Each time the temperature of B_1 is recorded the spiral extension is also recorded. The values of the pressure obtained are in terms of the vapour pressure of carbon dioxide ('Int. Critical Tables,' vol. III, p. 235).

The volume-temperature isobars can be obtained in a similar manner. In this case the temperature of B is varied and that of B_1 is kept constant except for slight deviations in the temperature of B_1 to compensate for changes in the relative levels of the mercury.

The pressure-temperature isochores can be obtained by varying the temperatures of both baths simultaneously, so that the mercury levels remain constant. These curves are the most difficult to obtain, and involve the greatest errors because of the difficulty in adjusting the temperatures so that the volume in B remains exactly constant.

To obtain accurate density measurements at constant volume, the mercury in the U tube is frozen when the mercury is at the desired height in B. In this manner the density of the liquid in presence of the vapour and of the vapour in presence of the liquid can be accurately determined both above and below the temperature at which the visible meniscus disappears. The pressure, of course, cannot be determined during these measurements.

The density of the ethylene was calculated from the formula

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

d = density of medium,
W = weight of float,
S = sensitivity of spiral,
V = volume of float,
N = normal length of spiral,
X = extended length of spiral.

In applying this equation, a correction due to the buoyant effect of the medium on the spiral has to be considered. The volume of the spiral as found by its weight is 0·0151 c.c., and the addition of half of this value to the volume of the float is the proper correction to apply.

Purification of Materials

The sample of ethylene used was a thrice fractionated portion of 99·95% pure stock. In the course of the experimental work, a minor explosion necessitated refilling the bombs, and in the second case the sample was taken from a different cylinder and similarly treated. Density measurements, however, taken on the two samples checked exactly. The carbon dioxide was purified by several fractionations, the system being opened to the Hyvac pump at intervals to remove any foreign gases.

RESULTS

It was found that under certain pressure and temperature conditions the final value of the density was not reached until a much longer time had elasped than that required for thermal equilibrium. As it was considered to be important in connexion with the elucidaton of the results to take into account the time required for equilibrium to be reached, an exceedingly large number of observations were made. Altogether, some 3500 observations of density were recorded. As nothing would be gained by tabulating all these results, only the equilibrium values of the density are recorded here. A few time-density determinations up to the time when equilibrium was established are given as examples. The rest of the time-lag measurements are recorded in terms of time to half-value, that is, the time taken for the density to change one-half the amount from the initial value to the value eventually found, or when this would take too long to the value eventually expected from other considerations.

Isobars and Isothermals of the One-Phase System

A system of isobars of the one-phase system, obtained at pressures of 0·18 atmosphere below to 1·46 atmospheres above the critical pressure is shown graphically in fig. 3. The numerical data are given in Table I. The isothermals shown in fig. 4 were evaluated from the isobars. The experimental method of obtaining the isobars (or isothermals) has been previously described. Two of the isobars obtained were at 0·18 atmosphere and 0·08 atmosphere below the critical pressure. Only in the isobar at 0·18 atmosphere below did the two phases appear, the region being marked on the curve by cross-marks (—) (fig. 3). Most of the values were obtained by first approaching the temperature at which the measurement was made

Table I—Isobars

Temperature ° C.	49·80 Atm. Density g./c.c.	49·90 Atm. Density g./c.c.	49·98 Atm. Density g./c.c.	50·10 Atm. Density g./c.c.	50·54 Atm. Density g./c.c.	50·87 Atm. Density g./c.c.	51·44 Atm. Density g./c.c.
8·50	0·2787	0·2897	0·2912	0·2925	0·2956	0·2986	0·3021
9·10	0·2695	0·2723	0·2749	0·2777	0·2786	—	—
9·30	0·2533	0·2608	0·2646	0·2700	—	0·2838	0·2904
9·36	0·2300	—	—	—	—	—	—
9·40	0·1835	0·2472	—	—	—	—	—
9·44	—	0·2265	—	—	—	—	—
9·50	0·1717	0·1842	0·2310	0·2550	0·2720	0·2790	0·2864
9·63	—	—	—	0·2165	—	—	—
9·70	0·1596	0·1650	0·1712	0·1850	0·2628	0·2728	0·2823
9·90	—	—	0·1601	0·1665	—	0·2646	0·2774
9·98	—	—	—	—	0·2380	—	—
10·05	—	—	—	—	0·2090	—	—
10·10	—	—	—	0·1580	—	0·2523	0·2713
10·30	—	—	—	—	—	0·2190	0·2638
10·50	—	—	—	—	0·1600	0·1820	0·2528
10·70	—	—	—	—	—	0·1678	0·2335
10·90	—	—	—	—	—	0·1602	0·2027
11·10	—	—	—	—	—	—	0·1810
11·30	—	—	—	—	—	—	0·1710
11·70	—	—	—	—	—	—	0·1570

from a lower temperature and then approaching it in a similar manner from a higher temperature. In either procedure, the final values of the densities obtained at any temperature were found to be the same. The points are thus unquestionably equilibrium values. It was found that there were enormous differences in the time required for equilibrium values to be reached, and as this is pertinent to the discontinuity in density observed above the critical temperature when starting with the two-phase system, a separate section is devoted to the presentation of the time-equilibum relationships. The isobars shown in fig. 3 will be referred to later in this connexion, as the density-temperature gradient is of particular interest. These curves will be necessary as reference curves in experiments to be described later. In observations where the time was very long until the equilibrium value of the density was reached, this equilibrium value could be read from the reference isobar and the time to half-value calculated.

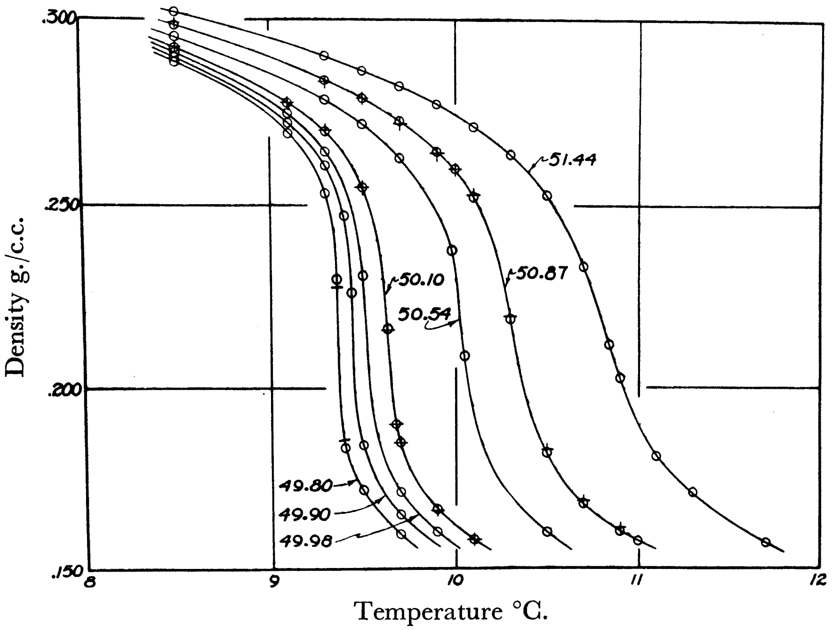

FIG. 3—Isobars. Circles represent observed values. Crosses represent calculated average densities.

The order of accuracy of the measurements made is well illustrated by the regularity with which the points evaluated from the isobars follow one another on the isothermals. Furthermore, one isothermal obtained by direct experiment at 9·80° C. was found to agree with the isothermal evaluated from the isobars (*see* fig. 4). The data are given in Table II.

It was desired to prove beyond question that during the experimental determination of the isobars the density of the medium was uniform throughout. The average density of the medium could be calculated as follows: it will be seen later that when the ethylene is heated to 5° C. above the critical temperature the density of the medium is definitely uniform, even when the two-phase system is present up to the critical

TABLE II—ISOTHERMALS AT 9·80° C.

Comparison of specific volumes observed from float and evaluated from isobars

Pressure atm.	Spec. vol. observed c.c./g.	Spec. vol. evaluated from isobars c.c./g.
49·80	6·400	6·410
49·90	6·231	6·231
50·10	5·787	5·781
50·34	4·329	4·329
50·54	3·886	3·892
50·87	3·703	3·708
51·44	3·559	3·562

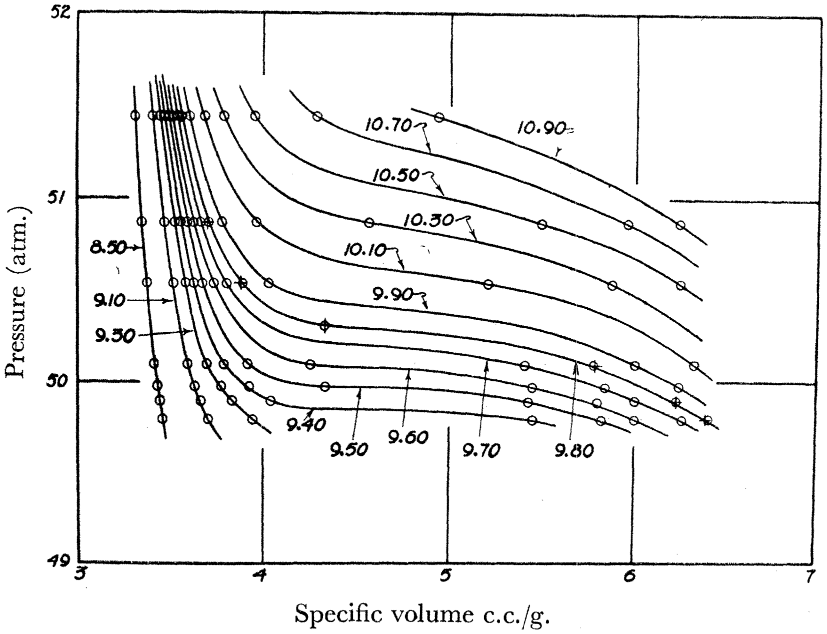

FIG. 4—Isothermals evaluated from isobars. Crosses represent observed values.

temperature. The density of the medium at 5° C. above the critical temperature was determined from the float, and as the total weight of the ethylene was known the volume that it occupied could be computed. This was repeated at a lower pressure when the mercury was at a lower level in the bomb (fig. 1). The mercury levels were measured by means of a scale beside the bomb. From this data, the volume of the bomb per unit length, and the total volume of the ethylene when the mercury was at any height could be calculated. The cross-section in the bomb had been previously measured with the original tubing and it was found to agree with the value determined from this calibration. Results of average density determinations at 50·10 and 50·87 atmospheres are given in Table III and represented in fig. 3. Evidence that the density of the system was uniform is given by the fact that the results of the average density calculations agree with the values obtained by float observations.

Rate of Establishment of Equilibrium

By rate of establishment of equilibrium is meant the rate at which the density varies in approaching a constant value, subsequent to definite temperature or pressure changes in the medium. As this final value is reached asymptotically, the time required is rather indefinite. Since the initial and final density values are definite enough, the time for the medium to reach a value half-way between the two was arbitrarily chosen as a means of comparing the rate at which equilibrum is established. This would have a very definite meaning if the rate were to follow a first order reaction equation. This is not the case, however, when the equilibrium value of the density is reached slowly.

TABLE III—ISOBARS

Comparison of densities observed by float and calculated from total volume

50·10 atm.			50·87 atm.		
Temp. ° C.	Density from float g./c.c.	Density from total vol. g./c.c.	Temp. ° C.	Density from float g./c.c.	Density from total vol. g./c.c.
8·50	0·2925	0·2928	8·50	0·2986	0·2990
9·10	0·2777	0·2776	9·30	0·2838	0·2832
9·30	0·2700	0·2700	9·50	0·2790	0·2793
9·50	0·2550	0·2550	9·70	0·2728	0·2725
9·64	0·2165	0·2162	9·90	0·2646	0·2642
9·67	0·1904	0·1904	10·00	0·2597	0·2590
9·70	0·1850	0·1850	10·10	0·2523	0·2528
9·90	0·1665	0·1661	10·30	0·2190	0·2200
			10·50	0·1824	0·1835
			10·70	0·1694	0·1700
			10·90	0·1611	0·1622
			11·00	0·1578	0·1582

At first sight it might appear that the time required to establish equilibrium is primarily a question of thermal equilibrium, because where the density gradient of the isobars is greater, smaller temperature changes bring about measurable differences in density. Consequently, for the establishment of thermal equilibrium apparently longer periods of time will elapse. For instance, at temperatures of 9·30° C. and 10·30° C. on the isobar at 50·87 atmospheres, temperature differences of 0·01° C. and 0·001° C. respectively produce the same density change of 0·0003 g./c.c. which is measurable. Hence, in the first case density changes can be detected till a temperature within 0·01° C. of the final temperature is reached, whereas in the second case variations can still be observed while the temperature is changing from 0·01° C. to 0·001° C. of the final value. However, it has been previously mentioned that a temperature within 0·01° C. of the final value is reached in less than five minutes, subsequent to a temperature change of 0·50° C., and since time lag curves were obtained in which the time to half-value had not been reached in seven hours it is evident that another factor other than thermal equilibrium is involved.

Further evidence that the time lag is not due entirely to a lag in thermal equilibrium is shown by the observation that when a point on an isobar given by a fixed temperature is approached from a lower temperature of 0·2°C. in one case, and from a higher temperature of 0·2° C. in another case, it takes much longer in the former case to reach the equilibrium value.

A few preliminary experiments showed that the time to half-value in reaching a final density depends not only on its position on the isobar (*i.e.*, the final temperature and pressure) and the direction from which it is approached (from a higher or a lower temperature) but also on the temperature and pressure of the medium from which the change takes place. This introduced a large number of variables which could be investigated, and the systematic manner in which this has been done will be discussed.

Although the visible meniscus disappears at the critical temperature, with rise in temperature the density of the medium below the point of disappearance remains greater than the density of the medium above, just as if the liquid state persisted. Hence, for purposes of discussion it has been convenient in previous papers to speak of the denser medium as the " liquid ". The nomenclature will be extended here. When referring to the isobars, the medium will be spoken of as " liquid " at temperatures below the point of inflexion of the isobar in question, even though the temperature may be above the critical. At temperatures above the point of inflexion it will be spoken of as " vapour ".

Time to Half-Value for Definite Temperature Intervals Along Isobars

In the course of the investigation of the isobars, in general, temperature intervals of 0·20° C. were chosen between density equilibrium values. By choosing these temperature intervals a relative comparison of the time lag involved in obtaining each equilibrium value could be made. The results are shown in fig. 5, where the points were obtained subsequent to temperature increases, and in fig. 6, where the points were obtained subsequent to temperature decreases. For want of a better means of illustration, temperatures are plotted as abscissae, although they serve only to show the particular temperature changes preceding the time lag observations, and as a means of referring to the isobar (*see* fig. 3) to note the density gradient at the point in question. The curves between the points are meaningless, the arrows serving only to show the direction of temperature change preceding the time lag measurements. Curves A, B, C, and D were obtained at pressures of 49·90, 50·10, 50·87, and 51·44 atmospheres respectively. In every case the time to half-value is shown to be much greater in the region of the isobars where the slope is greatest than in the " liquid " or " vapour " regions. It is also seen that the maximum value of the time to half-value becomes regularly greater with decreasing pressure toward the critical. Since the temperature at the point of inflexion of the isobars increases with increasing pressure, the curves are displaced to the right with increasing pressure. In general, for equal density gradients on an isobar, the time to half-value is greater in the " vapour " region of the curve than in the " liquid " region. The time to half-value, even at the peak of the curves in fig. 5, does not appear large, being 17·5 minutes at the highest one and 7·5 minutes at the lowest. It must be remembered that this means, however, that for the former approximately 120 minutes and for the latter approximately 60 minutes are required before no further density changes can be observed.

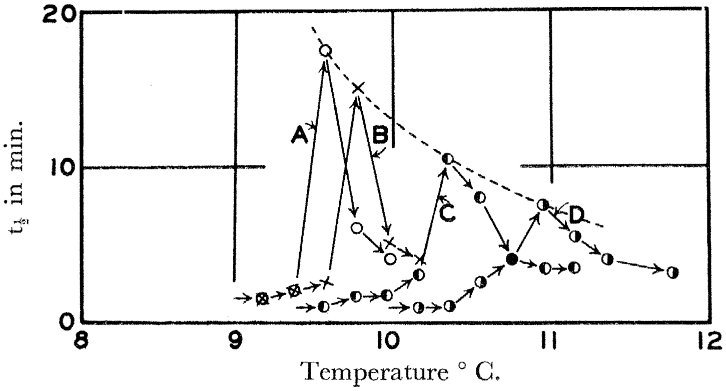

Fig. 5—Time to half-value in establishment of equilibrium subsequent to temperature changes of +0·20° C. along four different isobars. Curve A, 49·90 atm. ; B, 50·10 atm. ; C, 50·87 atm. ; D, 51·44 atm.

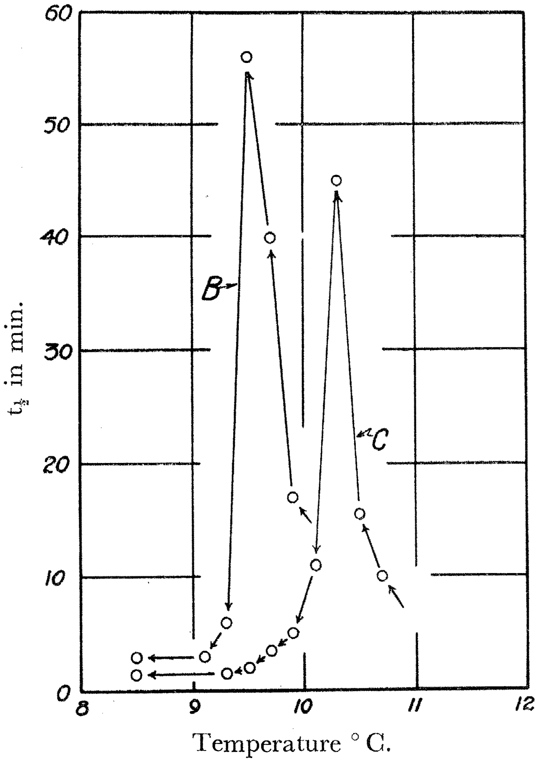

Fig. 6—Time to half-value in establishment of equilibrium subsequent to temperature changes of —0·20° C. along two different isobars. Curve B, 50·10 atm. ; C, 50·87 atm.

In fig. 6 the points in curves B and C are higher than the corresponding points on curves B and C in fig. 5. This brings out in a striking manner the difference in the time required for equilibrium to be established, when the same density is reached in the one case with decreasing temperature, and in the other with increasing temperature, the temperature interval being the same. It is seen in fig. 5 that the lowest time to half-value obtained was one minute (equilibrium value seven minutes). This is approximately the time required for thermal equilibrium to be established, so in this region of the isobars density equilibrium is established almost as soon as thermal equilibrium is established, subsequent to a temperature change of 0·20° C.

Time to Half-Value for Density Changes from the Same Initial Density to Different Final Densities

A series of time to half-value determinations were made at four pressures, subsequent to decreasing the temperature from that corresponding to a density of 0·1580 g./c.c., which is in the "vapour" region of the isobar curves, to various lower temperatures and corresponding higher densities. The form of the curves shows that the times to half-value are greatest when the final densities are at points on the isobars where the slopes are the steepest. This is in accord with previous results. These curves bring out an interesting point. The time for equilibrium to be reached is actually much greater when the "vapour" is cooled to the point of greatest gradient on the isobars, than when it is cooled, not only to a lower temperature but to a temperature below the critical where the formation of liquid in the ordinary sense of the word takes place. These observations indicate that the time until equilibrium is established is not solely dependent, as one would expect, on the

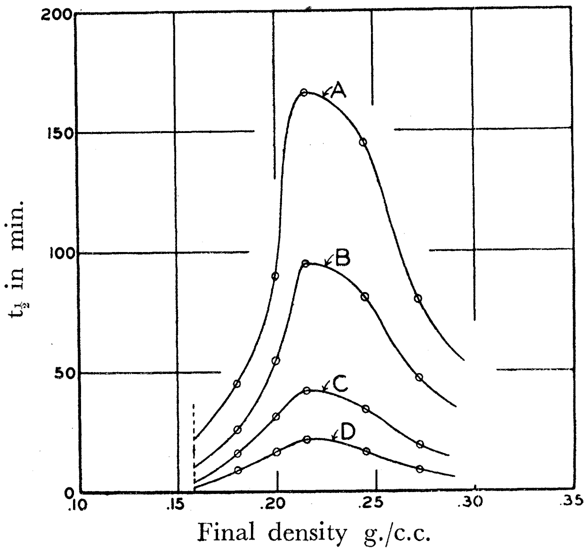

FIG. 7—Time to half-value in establishment of equilibrium during density changes from 0·1580 g./c.c. to various final densities, for four different isobars. Curve A, 49·90 atm.; B. 50·10 atm.; C, 50·54 atm.; D, 51·44 atm.

magnitude of the density or temperature changes involved. The results obtained at 49·90, 50·10, 50·54, and 51·44 atmospheres are represented by curves A, B, C, and D respectively in fig. 7, where the time to half-value is plotted against final density.

A procedure similar to that described above was carried out by starting at a density of 0·2720 g./c.c. in the " liquid " region, with the difference that times to half-value were determined subsequent to increases in temperature (decreasing density). In this case the time to half-value obtained subsequent to an increase in temperature is always less than that obtained subsequent to a decrease in temperature.

Effect of Pressure on the Time to Half-Value When the Density Change is the Same

The influence of pressure on the time for equilibrium under conditions where the system changes from the same initial to the same final densities is shown in fig. 8.

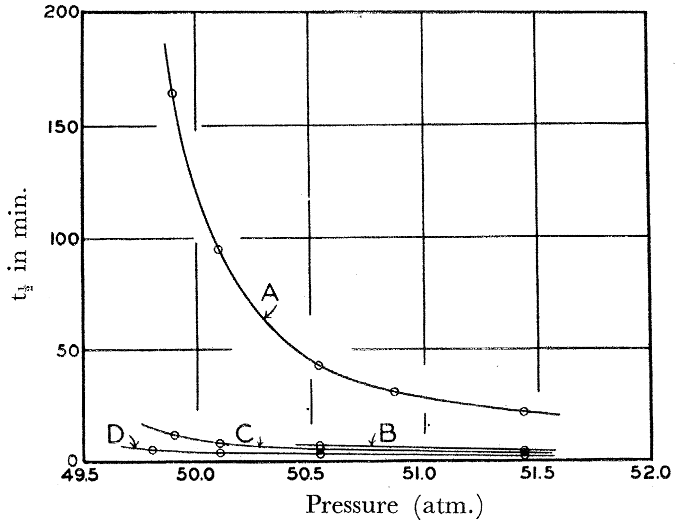

Fig. 8—Effect of pressure on the time to half-value in establishment of equilibrium during four different density changes. Curve A, " vapour " to critical density; B, critical density to " liquid "; C, " liquid " to critical density; D, critical density to " vapour ".

From the isobar curves (fig. 3) it is seen that the required temperature changes will differ depending on the isobar in question, the smallest change required being for the isobar at the lowest pressure. In all cases the density change was 0·0570 g./c.c. For curve A the initial and final densities were 0·1580 g./c.c. and 0·2150 g./c.c. respectively. This involved a change on the isobar from the " vapour " region to the point of inflexion. It is apparent that as the pressure decreases the time to half-value increases rapidly. At a pressure of 49·80 atmospheres the time to half-value was not reached in seven hours. As a matter of fact, for most points on the curve the equilibrium values could not be obtained. For instance, on the 50·54 atmosphere isobar the time to half-value of 45 minutes was taken as the time when the density had reached the half-way value to 0·2150 g./c.c. as originally measured on the isobar by decreasing the temperature. Actually the equilibrium value had not been reached in four hours, and it is estimated that at the 50·10 atmosphere isobar, which is above the critical temperature and pressure, the equilibrium would not be reached in 12 hours if at all, as indicated by the latter part of the time-density.

For curves B, C, and D, the initial and final densities were 0·2150 and 0·2720, 0·2720 and 0·2150, and 0·2150 and 0·1580 g./c.c. respectively, the changes being from the point of inflexion of the isobars to the " liquid " region, the " liquid " region to the point of inflexion, and the point of inflexion to the vapour region respectively. They all show a slight increase with decreasing pressure. They indicate that complete equilibrium would be reached in periods varying from 20 to 100 minutes as compared to less than five minutes for the establishment of thermal equilibrium. It is seen that curve B, which represents changes in the density in the direction of " vapour " to " liquid ", lies above the other two where the changes are in the other direction.

Table IV—Temperature-Density Isochores

Densities of medium below point of disappearance of meniscus. (Mercury in U tube frozen.) Volume 20·85 c.c. Average density of medium 0·2286 g./c.c.

Increasing temperature		Decreasing temperature	
Temp. ° C.	Density g./c.c.	Temp. ° C.	Density g./c.c.
9·00	0·2567	14·50	0·2286
9·50	0·2430	10·10	0·2286
9·55	0·2415	9·80	0·2286
9·60	0·2405	9·70	0·2286
9·70	0·2387	9·60	0·2289
9·80	0·2366	9·55	0·2289
10·10	0·2335	9·50	0·2289
11·05	0·2304	9·47	0·2289
12·45	0·2291	9·44	0·2289
14·50	0·2286	9·41	0·2291
		9·38	0·2294
		9·35	0·2296
		9·33	0·2314
		9·32	0·2325
		9·31	0·2345
		9·25	0·2392
		9·15	0·2451
		9·00	0·2518

Isochores of the Two-Phase System

Tables IV and V give the results which are shown graphically in fig. 9. The results in Table IV were obtained when the mercury in the U tube was frozen, and the meniscus, when present, was always above the float. The volume of the

TABLE V—ISOCHORES

Densities of medium above point of disappearance of meniscus. Volume maintained constant by adjusting CO_2 pressure. Volume 23·15 c.c. Average density of medium 0·2056 g./c.c.

Temp. ° C.	Press. atm.	Increasing temperatures Density g./c.c.	Decreasing temperatures Density g./c.c.
9·00	49·44	0·1759	0·1761
9·15	49·59	0·1795	0·1816
9·30	49·76	0·1819	0·1909
9·36	—	—	0·1978
9·40	49·87	0·1852	0·2054
9·50	49·98	0·1888	0·2056
9·70	50·19	0·1942	0·2056
10·00	50·53	0·1983	0·2056
12·00	52·66	0·2051	0·2056
14·50	55·40	0·2056	0·2056

ethylene being 20·85 c.c. Equilibrium density values subsequent to rising temperature changes were first obtained. That they were equilibrium values is shown by the fact that the density readings became constant in approximately twenty minutes after thermal equilibrium was established in the bath, and that they remained constant after a subsequent hour of observation. These results are plotted in curve A. At approximately 5° C. above the critical temperature, no further density change was observed with increasing temperature (critical temperature of ethylene is 9·50° C.). After reaching a temperature 5° C. above the critical, the temperature was lowered and the density was found to remain constant until the liquid phase reappeared. The density then rapidly increased with decreasing temperature (curve B). Even below the critical temperature with a visible meniscus present, the values of the density obtained on curve B are not the same as those on curve A at the same temperature. With decreasing temperature, however, the two curves approach one another and coincide at approximately 1° C. below the critical temperature. These results are in accord with the results of similar experiments on propylene and methyl ether obtained in this laboratory. That the values obtained on curve A are reproducible was shown by the fact that readings taken several times, between which the medium had been cooled to a temperature less than 1° C. below the critical, were found to be identical. The same reproducibility was found for curve B each time the medium was cooled from a temperature 5° C. above the critical.

The data in Table V were obtained when the volume was adjusted so that the meniscus was always below the float as long as it was visible. The measurements could have been made in the manner previously described, the mercury in the U tube being frozen. It was, however, desired to make pressure and temperature observations simultaneously in order to obtain the critical pressure, as well as pressure-temperature isochores. Therefore, the volume of the ethylene was kept constant by adjusting the pressure of the carbon dioxide as the temperature of the ethylene was altered. In this case with increase in temperature the density of the vapour was found to increase up to approximately 5° C. above the critical temperature (curve D). With subsequent lowering of the temperature it remained constant until the liquid phase reappeared, and then rapidly decreased (*see* curve C). It may be obvious, but, in order to avoid a misunderstanding, it is worth pointing out that with increasing temperature the final densities reached in the two cases must differ because the volume occupied by the ethylene is different in the two cases, being 20·85 c.c. in the first case and 23·15 c.c. in the second case. During these experiments the ethylene was not subjected to any mechanical agitation. It has been shown conclusively by Winkler and Maass (1933), however, that under such conditions stirring does not destroy the density difference in propylene.

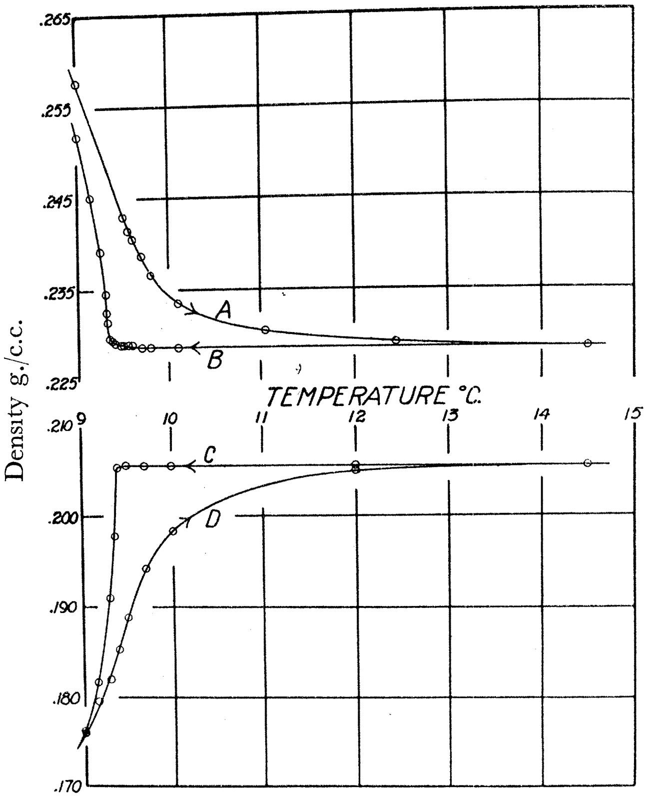

Fig. 9—Temperature-density isochores. Curves A and B float below point of disappearance of meniscus; volume 20·85 c.c. Curves C and D float above point of disappearance of meniscus; volume 23·15 c.c. Curves A and D increasing temperature. Curves B and C decreasing temperature.

Critical Temperature

In the course of the experiments just discussed, the critical temperature was determined and found to be 9·50° C. This value was reproducible to within

±0·01 and it was taken as the temperature at which the meniscus becomes completely invisible on increasing the temperature after the material has been previously cooled to at least 1° C. below the critical temperature. As will be seen later, the temperature of disappearance of the meniscus depends to a marked extent on the thermal history of the material immediately preceding the measurement.

Critical Pressure and Pressure-Temperature Isochores of the Two-Phase System

It was previously mentioned in discussing the isochores, that in procuring the density data for curve D, fig. 9, pressure measurements were made simultaneously with temperaure measurements (column 2, Table V). When these values were plotted the pressure corresponding to 9·50° C. was found to be 49·98 atmospheres. This, then, is the critical pressure if it is defined in a similar way to critical temperature, that is, the pressure at which the visible meniscus disappears on heating, after the medium has been previously cooled to at least 1° C. below the critical temperature. This pressure was reproducible to ±0·01 atmosphere. The results given in Table VI were obtained by measurements in which the float was kept below the surface of the liquid. In this case the volume occupied by the ethylene was 20·63 c.c.

The density measurements recorded in Table V were made under both increasing and decreasing temperature conditions, and differences in density as great as 10% were found between the two curves (C and D, fig. 9). Pressure measurements, however, were found to be the same in both cases (at the same temperatures) within the accuracy with which the measurements could be made. Since these results were believed to be of particular theoretical interest, the experiment was repeated with the float in the liquid region, special care being exercised in the pressure determinations. Pressures could be estimated to ±0·005 atmosphere and reproduced with an accuracy better than ±0·01 atmosphere. For example, on heating the two-phase system at a volume of 20·63 c.c. from a low temperature to a temperature of 9·25° C., a pressure of 49·705 atmospheres was obtained. One month later, during which the system was subjected to varying conditions of temperature and volume, the experiment was repeated and the same pressure of 49·705 atmospheres was again obtained. The pressure measurements made with increasing and decreasing temperature are given in Table VI. The differences are given in the last column of the table. Although the density differences are as great as 10%, the pressure differences are less than ±0·01 atmosphere or 0·02%.

Influence of Thermal History on Isochores of the Two-Phase System

It was found in the course of the experiments, that if the ethylene was cooled to less than 1° C. below the critical temperature and then heated, the equilibrium density values obtained were not so great as those obtained when the ethylene was previously cooled to a temperature lower than 1° C. below the critical. A and B, fig. 10, are reference curves obtained from the data in Table VI. E, F, and G are

TABLE VI—TEMPERATURE-DENSITY-PRESSURE ISOCHORES

Density of medium below point of disappearance of meniscus. Volume maintained constant by adjusting CO_2 pressure. ΔP represents pressure differences at equal temperature on the two isochores. Volume 20·63 c.c.

	Increasing temp.		Decreasing temp.		
Temp. ° C.	Press. atm.	Density g./c.c.	Press. atm.	Density g./c.c.	ΔP
9·00	—	0·2570	—	0·2532	—
9·15	—	0·2533	—	0·2469	—
9·25	49·705	0·2500	49·695	0·2412	+0·010
9·32	49·810	0·2480	49·800	0·2338	+0·010
9·50	—	0·2441	—	0·2307	—
9·60	50·115	0·2416	50·110	0·2304	+0·005
9·70	—	0·2394	—	0·2302	—
9·80	50·335	0·2380	50·340	0·2302	−0·005
10·50	51·150	0·2330	51·155	0·2302	−0·005
14·50	56·180	0·2302	56·180	0·2302	0

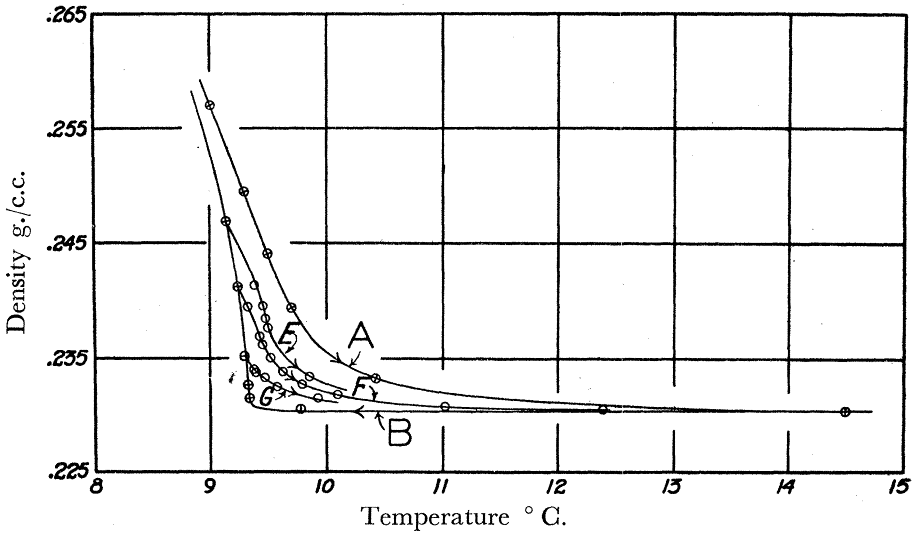

FIG. 10—Curves A and B reference isochores. Curves E, F, and G hysteresis temperature-density isochores starting from curve B. Volume 20·63 c.c.

curves obtained subsequent to heating the medium to 5° C. above the critical temperature, and then lowering the temperature to 0·36, 0·26, and 0·20° C. below the critical temperature respectively. Starting from these points, the curves were obtained by increasing the temperature. These curves are of the same general shape as the reference curve A and they attain the same final value when heated to 5° C. above the critical temperature. This is shown by curve F, which was obtained up to 14·50° C., and the final value of the density found to be identical with the final value obtained on the reference curve. It was observed that the temperatures at which the meniscus disappeared were lower than the critical temperature.

On decreasing the temperature after it had been previously raised to points less than 5° C. above the critical temperature, density values are obtained which are always below reference curve A, fig. 10.

Influence of Thermal History on Disappearance and Reappearance of Meniscus

As has been previously mentioned, the temperature of disappearance of the meniscus depends on the thermal history of the medium. The temperature of reappearance, on the other hand, is not measurably influenced by previous heat treatment. It was found in all cases to be 0·16° C. lower than the critical temperature when the volume was 20·63 c.c.

Observations on the disappearance of the meniscus were made for each of the curves E, F, and G (fig. 10), as well as for a similar curve (not shown in the figure) starting at 0·16° C. below the critical temperature. The results are given in Table VII. It is seen that the temperature of disappearance of the meniscus varies from 9·39° C. to 9·50° C. depending on the extent of the previous cooling along curve B (fig. 10).

Table VII

Influence of thermal history on temperature of disappearance of meniscus. ΔT represents the amount of cooling below the critical temperature along curve B (fig. 10) previous to heating to the temperature of disappearance of meniscus.

Curve followed during heating (fig. 10)	ΔT° C.	Temperature of disappearance of meniscus ° C.
Not shown	0·16	9·39
G	0·20	9·41
F	0·26	9·45
E	0·36	9·48
A*	1·00	9·50

* Curves A and B, fig. 10, coincide at approximately 8·5° C.

Isothermals of the Two-Phase System

Starting with the two-phase system at a volume of 20·63 c.c., the isothermals were investigated at a temperature 0·3° C. above the critical. At this temperature the reference curves (fig. 10) show the density of the medium to have two different values. The density of 0·2380 g./c.c. on curve A decreases to 0·2302 g./c.c. on curve B after the medium has been heated to a temperature 5° C. above the critical temperature and then cooled to the initial temperature.

It was desired to discover what would happen when the medium in either case was subjected to either expansion or compression at constant temperature. Curve

B (fig. 11) was obtained by starting on the upper reference curve (fig. 10) and decreasing the pressure, curve C by starting at the same point and increasing the pressure. Curve A is an isothermal determined under conditions where the density of the medium was known to be uniform. It is seen that both increasing and decreasing the pressure tend to destroy the density difference between the upper and lower regions of the bomb. An increase in pressure of 0·04 atmosphere is sufficient to eliminate it entirely in this case. A decrease in pressure of 0·12 atmosphere destroys the density difference, and on increasing the pressure again the density values agree with those found on curve A where the density of the medium is uniform. When the medium was expanded or compressed at a temperature of 9·80° C. on the reference curve B, fig. 10, the density values obtained subsequent to pressure changes were found to be identical with the values on curve A, fig. 11, at corresponding pressures.

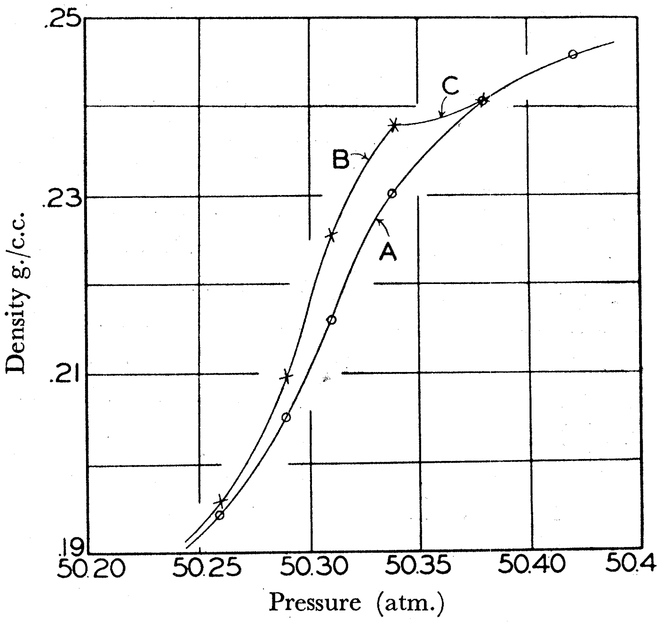

FIG. 11—Isothermals at 9·80° C. Curve A standard isothermal when density of the medium is uniform.

Similar experiments were carried out at a temperature of 9·25° C., *i.e.*, below the critical temperature. Starting with a density on curve A (fig. 10) corresponding to 9·25° C., it was found that an increase in pressure raised the level of the meniscus and increased the density of the system. A considerable time lag was involved in the establishment of equilibrium. After the meniscus reached the top of the tube, the time lag was considerably diminished. On subsequent expansion to the original pressure, the original density was re-established. On expanding the medium from the initial conditions mentioned above, it was found that subsequent compression to the original pressure left the medium with a lower density.

Starting with a density on curve B (fig. 10) corresponding to 9·25° C., it was found that when the medium was compressed, subsequent expansion to the original pressure re-established the original density. When the medium was expanded, subsequent compression to the original pressure was accompanied by a large time lag. The equilibrium density value could not be determined.

Temperature Fluctuations

A study of the influence of temperature fluctuations on the density of the system was suggested by the observations of Winkler and Maass, that the density difference existing above the critical temperature can be destroyed by maintaining a temperature differential along the bomb, the upper part being kept colder than the lower, and the discovery that the rate of establishment of density equilibrium, subsequent to a temperature change, is dependent on the direction from which the final temperature is approached.

By temperature fluctuation is meant periodic, alternate, temperature changes in the system, the temperatures differing by a small and definite amount (0·20° C. or less), and the average temperature remaining constant. It was found that although the average temperature remains the same as the initial, there is a directional change in density when the two-phase system is subjected to the fluctuation process. Above the critical temperature, any density value on curve A, fig. 9, will decrease towards the value at the same temperature on curve B when the temperature of the medium is fluctuated. A rapid decrease in density occurs at first, the rate of decrease becoming less as the lower density is approached. Starting with a density at any point on curve A (fig. 9) below the critical temperature, a continuous decrease in density occurs until the density on curve B corresponding to the minimum temperature of the fluctuations is reached. If the amplitude of the temperature fluctuation is then decreased by a definite amount, the density will decrease until another final value is reached in the same manner as before. Consequently, it appears that if the amplitude of the fluctuations approaches zero, the density at any point on curve A below the critical temperature will decrease to the corresponding value on curve B. For this condition, however, an infinite time would be required because the smaller the amplitude of the fluctuations the less the rate of decrease in density. Also, the nearer the density approaches the value on curve B the less the rate of decrease in density. To save space, the data on which the above conclusions are based are not given.

DISCUSSION

When the two-phase system is heated above the critical temperature, a discontinuity in density persists. The question of whether or not a density difference of the order of magnitude found is brought about by the weight of the medium itself can now be answered with more certainty. Apart from the arguments advanced in previous publications from this laboratory against the concept of the gravitational effect, considerably more evidence against it can be found from the results of the present investigation.

Although in the course of the determination of the isobars the relative amounts of the medium above and below the float varied considerably, the density values obtained by the float method agreed within experimental error with the average density values estimated in the manner previously described (Table III). Furthermore, it was found that isothermal compression or expansion destroys the density difference, and once destroyed no density difference is re-established under any subsequent pressure condition. Perhaps the most convincing evidence opposed to the concept of the gravitational effect is found from the following calculations based on actual compressibility measurements. When the two-phase system is heated above the critical temperature under a volume condition such that the float is approximately at a central position in the medium, the additional pressure at this point produced by the weight of the medium itself is not more than 0·0025 atmosphere. The density difference under these conditions between the lower and upper regions of the medium is approximately 6% at a temperature 0·3° C. above the critical, and it was found by actual measurement that to produce a density difference of this magnitude would require an additional pressure of 0·05 atmosphere, *i.e.*, twenty times the pressure exerted by the weight of the medium itself (fig. 11). In this connexion it must also be remembered that the density difference of 6%* occurs within a small range throughout the medium. It is not intended to deny that there is a density gradient throughout the medium due to the weight of the medium itself, but to show that it is of a much smaller order of magnitude than the density differences found above the critical temperature.† Finally, the density difference between the liquid produced by heating from a low temperature to a temperature just below the critical and the liquid produced at the same temperature after cooling from a high temperature must be due to the same phenomenon which gives rise to the density difference above the critical temperature, and the density difference between these liquids cannot readily be explained on the basis of the gravitational effect.

The question of the relative stability of the densities of the medium above and below the meniscus, as represented by curves such as A and B (fig. 9), is of interest. The density represented by any point on these curves does not undergo a spontaneous change. If, however, the medium is subjected to a temperature fluctuation process when at a density indicated by any point on curve A the density is gradually reduced, whereas the reverse process does not occur when starting with a density corresponding to any point on curve B. This would appear to indicate that B is the stable

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* The density at 9·80° C. on curve A (fig. 10) is 0·2380 g./c.c. and that on curve B is 0·2302 g./c.c., giving a density difference of 0·0078 g./c.c. This must be doubled to give the density difference between the upper and lower media.

† It is estimated that for the temperature and other conditions cited in the above example a continuous density variation would occur throughout the tube due to the weight of the medium itself giving a maximum density difference of 0·6%. Although this effect is superimposed on all density measurements made both in this and former investigations, it becomes still less significant when it is remembered that the density differences were found within a small region in the tube.

curve. However, when curves A and B are plotted together with the isobars (fig. 3), it is found that the density region enclosed by curves A and B includes the steepest portion of the isobars. It has been shown that in this temperature-density region equilibrium is established very much more rapidly when the temperature is raised than when it is lowered. Hence, temperature fluctuations about a mean value would produce a continual decrease in density until curve B is reached. Since a decrease in density due to temperature fluctuation can be explained on the basis of a time factor, they do not necessarily imply that the lower curve represents the stable condition. Incidentally, the phenomenon of temperature fluctuations explains the observations made in previous investigations in this laboratory that the density difference above the critical temperature is destroyed when the medium is subjected to a vertical temperature gradient in which the upper region is colder than the lower region. If the temperature gradient is sufficiently large, the density in the upper region becomes even greater than the density in the lower region and a circulation of matter is brought about due to the influence of gravity. Any part of the medium is subjected to alternate changes in temperature above and below an average value. The effect of a temperature gradient on the system is thus essentially the same as that involved in temperature fluctuations. It is not the stirring brought about by the temperature gradient which produces the levelling out of the density difference.

When the two-phase system is heated above the temperature of disappearance of meniscus and then the volume of the system as a whole is increased or decreased, the density difference is destroyed and, as is to be expected, an isothermal of the one-phase system results (fig. 11). In this connexion it may be predicted that violent stirring (such as that produced by a rotating propeller) may well bring about the same result. If portions of the medium are continuously subjected to expansion and contraction, an effect analogous to temperature fluctuations is brought about. In the stirring previously reported, the lower medium was continuously lifted up into the upper portion of the tube by the motion of a glass bulb, which motion, however, was not violent enough to produce local expansion and contraction, and as a result, even after six hours, the density difference remained unchanged.

By starting with a density corresponding to any point on curve A and subjecting the system to temperature fluctuations of 0·05° C. amplitude, the density is lowered. However, the moment the fluctuations are stopped and a constant temperature is maintained, the density becomes constant and does not change spontaneously. Hence, any apparently stable density in the area enclosed by curves A and B may be obtained.

Pressure measurements (*see* Table VI) made along curves A and B at the same temperature indicate a maximum difference of +0·01 atmosphere above the critical temperature and of —0·005 atmosphere below the critical temperature. However, as the pressure measurements depended on the reproducibility of the volume of the medium as well as on the accuracy of the pressure measurements themselves, the difference must be considered as being within the limit of experimental error.

From the evidence it may be inferred that the stability of the system when corresponding to points on curves A and B at the same temperature or any intermediate points is very nearly the same.

From all the above considerations it is possible tentatively to explain the persistence of density differences above the temperature at which the visible meniscus disappears on the basis that the liquid state persists above this temperature, if the liquid state of aggregation is differentiated from the gaseous state of aggregation by the existence of an appreciable amount of dynamic structure in the liquid. Starting with a liquid in equilibrium with its vapour, at a temperature well below the so-called critical temperature, the classical idea of the nature of the equilibrium between the two phases can be considered to hold with the additional concept that the cohesive forces holding the molecules together in the liquid are influenced by the existence of a structure in the liquid. With rise in temperature a decrease in concentration in the liquid will tend to break up the structure and a temperature region is reached where the concentration is such that the structure breaks down rapidly, accelerating the decrease in concentration with rise in temperature. The density of the vapour increases rapidly and the change in density at the border between liquid and vapour becomes more and more diffuse. The densities of liquid and vapour are not identical at this point but approach one another asymptotically with further heating. The temperature region where the structure of the liquid is rapidly breaking down with rise in temperature may be called the critical temperature region. At any temperature in this region a decrease in the concentration of the " liquid " means a disruption of structure and a decrease in the cohesive force between molecules. Thus, a decrease in vapour pressure due to the one factor (decrease in concentration) may be counteracted by an increase in vapour pressure due to the other factor (decrease in cohesive forces), and it is conceivable that in this region the liquid may have various densities at the same temperature and yet exert the same pressure.

The hypothesis of assigning a dynamic structure to a liquid is a particularly helpful one in accounting for the time required in the establishment of equilibrium.

It was found that in the critical temperature-critical pressure region large differences in time were required for the establishment of density equilibrium subsequent to temperature or pressure changes. With rise in temperature, longer times were required in all cases than with decrease in temperature for the same temperature intervals. For each temperature a critical concentration was found where these times were a maximum. If the idea of structure in a liquid implies a distribution involving certain regularities of its component parts, presumably the molecules, then all the results obtained on the rate of establishment of equilibrum can be explained on the basis that the production of any ordered arrangement takes a longer time than its disruption.

The picture of the structure which has been alluded to in a number of the papers on critical temperature phenomena published from this laboratory is that of regional orientation.

Stewart (Benz and Stewart, 1934 ; Spangler, 1934) has developed a similar picture under the name of "cybotactic" groups in liquids to explain the X-ray diffraction patterns. The interesting results obtained by STEWART and his collaborators have been looked upon by the authors as evidence in favour of the existence of regional orientation. DEBYE and MENKE (1931) and GINGRICH and WARREN (1934), however, have shown that the X-ray diffraction pattern of a fluid at various densities can be accounted for by a distribution of atoms about any one atom chosen for the calculation. In the opinion of the writers, this does not prove the absence of regional orientation but weakens the significance of the X-ray diffraction results as a corroboration of their hypothesis of the existence of regional orientation.

Investigations in the critical temperature region are being continued in order to obtain further information in regard to the phenomena described in this paper.

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