CHANGES IN THE LIQUID STATE IN THE CRITICAL TEMPERATURE REGION[1]

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By a judiciously chosen sequence of temperature and pressure changes, the change of state from liquid to gas can be brought about in such a way that all physical properties, including that of density, vary continuously. Hence was developed the old classical theory of continuity of state, which postulates a similar structure or rather lack of structure for both gas and liquid. The results of a number of investigations which are to be described below cannot be explained on this basis. They tend rather to show that, quite apart from the question of concentration, a liquid has a structure (a dynamic structure) (10) to differentiate it from the static structure of a solid which a gas lacks. That does not mean that a continuous change from liquid to gas cannot be made to take place. For this to occur it is only necessary to assume that the change from structure to lack of structure occurs gradually under proper choice of pressure and temperature variation.

The use of the phrase "structure of a medium" implies of course a distribution involving certain regularities of its component parts. The component parts in the case of a liquid and vapor are assumed to be the molecules. In a gas these are in a completely chaotic random distribution and are free to move and rotate. In the case of a solid these gas molecules are regimented into perfect order and anchored into position. The classic theory based on the continuity of state had as its basis that the molecules in a liquid have the freedom of the gas molecules modified only by the enhancement of the forces of attraction due to greater proximity. To demonstrate that something more than this is required to explain the properties of liquids is the purpose of this paper, and it is hoped to make this evident by a review of the experiments carried out in the critical pressure–critical temperature region which are to be described.

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[1] A revised review of the subject matter presented at the Symposium on the Critical State, held by Section III of the Royal Society of Canada at Ottawa, Canada, on May 21, 1936.

The first of these experiments, and the one which gave rise to the series of critical temperature investigations in this laboratory, was the discovery that a certain reaction would take place in the liquid but not in the gaseous state. The particular reaction referred to is that between hydrogen chloride and propylene, where a homogeneous reaction occurs when the two reactants are compressed together to form a liquid medium, provided that this compression occurs below the critical temperature of the mixture. If the two substances, hydrogen chloride and propylene, are mixed as gases, heated above the critical temperature, and then compressed to a density equal to that of the liquid mixture below the critical temperature, the rate of the reaction at this temperature is less than at the lower temperature (18, 7).

Investigations were planned with the object of finding a possible explanation for this phenomenon, in particular, measurements of the P.V.T. relations of two-component systems in the critical temperature–critical pressure region. The experimental technique developed for the purpose was tested with a one-component system, and some unexpected results were obtained. It was found that a difference of density persisted between what had been the vapor and what had been the liquid above the temperature at which the visible meniscus disappeared (24, 19, 14).

After these observations had been made a survey of the literature showed that somewhat similar phenomena had been recorded before. I. Traube (21) and his collaborators, notably G. Teichner (20), showed that there was a density gradient in a tube containing a liquid and vapor heated above the critical temperature. Subsequent investigators ascribed their observations to inaccurate temperature control or to the presence of impurities. The consensus of opinion some six years ago is summed up very well by Jellinek, in his *Lehrbuch der Physikalischen Chemie* (8). He states that the results of Traube and coworkers are spurious and that in the "critical" region, where the compressibility is large, at most a gravitational effect might be expected, a suggestion first made by Guoy (5), i.e., density differences after meniscus disappearance, if not due to experimental error, can be assumed to be due to the compression caused by the weight of the medium itself.

The experimental technique developed in this laboratory made it possible to make precise density measurements in various parts of the 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 this phenomenon.

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 (24, 19). The magnitude of the density difference is dependent on the mass per volume relationship of the medium in the tube reaching a maximum when the tube is filled with an amount corresponding to the critical density as given by the Cailletet and Mathias rule. The density difference could not be destroyed by mechanical stirring, in which the lower medium was continuously carried throughout the upper part of the tube for 6 hr. (24). It was found that the difference in density persisted above the critical temperature with diminishing extent (as the temperature was increased), eventually reaching a zero value with continued rise in temperature. Some eight different substances have been investigated so far and the phenomenon found to be common to all these substances. The order of magnitude of the density difference above the so-called critical temperature varies from substance to substance, being[2] some 10 per cent for ethylene and 50 per cent for methyl chloride.

It may be emphasized that these density differences are equilibrium values in the sense that a final value is reached rapidly and then remains unaltered when the medium originally in the liquid–vapor state is heated up to the temperature at which density measurements are made. When the medium, after having been heated up to a considerable distance above the critical temperature, is cooled down these density differences are not reëstablished. This would look very much as if the density differences were perhaps merely the result of the persistence of a metastable condition.

Some weight is lent to this point of view by another observation. When the tube, in which a density difference persists above the critical temperature, is subjected to a temperature gradient in which the upper portion is kept at a lower temperature than the lower portion (sufficient to reverse the density difference and produce a circulation of medium), then, after bringing back the temperature of the medium to the original temperature, the density difference has been destroyed. Once destroyed it does not return spontaneously (24). The first inference is that the stirring induced by this procedure brought about this effect. However, the mechanical stirring mentioned above was shown to be effective in bringing about circulation throughout the tube and after 6 hr. did not even produce an indication of altering the density difference. Offhand it appears difficult to explain why a temperature gradient which produces stirring should destroy the density difference and mechanical stirring should not do so. Nevertheless an explanation will be attempted later on.

The data on which the above inferences are based were obtained by determinations in which no pressure measurements were made. The medium under investigation was confined in a fixed volume, and its pres-

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[2] Just above the temperature where the visible meniscus disappears.

sure was governed solely by this volume and the temperature to which the medium was subjected. Resource was had to a technique whereby pressure could be both controlled and measured with a relative accuracy of 1 in 1000 at the critical pressure. As a result much more information of interest was collected in regard to the P.V.T. relationships of both one-phase and two-phase systems (10).

In the first place density isobars were determined, that is, the variation in density of the medium with temperature at constant pressure measured at pressures at and above the critical pressure (10). It was found that identical density values were obtained by approaching them first from a higher density (lower temperature) and then from a lower density (higher temperature). However, a real discovery was made, namely, that the time for establishment of equilibrium was very different depending on the direction of approach. The time for establishment of equilibrium was much greater with lowered temperature (increasing density) although, as mentioned before, exactly the same final values were reached (10).

This opened up a very fruitful field of investigation. The time for the establishment of thermal equilibrium was corrected for, and data were compiled in terms of "time to half-value." This was a purely arbitrary but convenient way of representing the time lag in establishing equilibrium. Final equilibrium values are reached asymptotically and, as the final equilibrium density values are known from the isobars, this is a useful and adequate method of comparing rates. In recording the time to half-value in establishment of equilibrium subsequent to temperature changes of ±0.02°C. along isobars the maximum was found to be at the steepest part of the isobar. The time to half-value in density changes from 0.158 in the case of ethylene to various final densities along four isobars made it evident again that the time required for equilibrium is greatest when the region in the isobar is approached which is the steep part of the isobar. When the medium is cooled down to a temperature where the liquid state exists, density equilibrium is established much more rapidly than when the medium is cooled down to the intermediate density of the isobar where rapid density changes take place. Time for the establishment of equilibrium in approaching densities on the steep part of the isobar (just above the critical pressure) becomes almost infinite when the approach is made from a low density. The general conclusion of a great number of experiments with isobars in the neighborhood of the critical temperature region is that equilibrium is established fairly rapidly when a rise in temperature or a decrease in density takes place, and very slowly when an increase in density or a lowering in temperature occurs. The longest time lags occur in the region of the isobars where great density changes take place. The higher the pressure the smaller is the time lag.

These experiments on time lag in the establishment of equilibrium are most readily explained on the basis that a liquid has a structure in the sense of certain ordered regularities in the distribution of the molecules. Rise in temperature would tend to destroy such a structure, depending on regularities in the arrangement of molecules due to increased kinetic energy of the molecules. Decrease in concentration would also tend to destroy the structure, owing to the increasing distance between molecules with resultant lessened mutual influence on one another. For a given temperature a critical concentration (i.e., density) can be envisaged where the structure begins to be disrupted. The form of the isobars can then be explained. When the critical density is reached a very small increase in kinetic energy of the molecules is sufficient to bring about a large expansion where the structure is on the point of being rapidly destroyed. The steep parts of the isobars, the points of inflection, are therefore the regions in which the liquid structure is disappearing. All time lag compilations are in direct agreement with this. Rise in temperature and consequent decrease in concentration (along an isobar) mean disruption of structure; the reverse means a building up of structure. If this is the case, longer times should be required for the establishment of equilibrium in the latter, if structure means anything involving orientation. At the points of inflection of the isobars the greatest changes take place in structure, and here are found the greatest time lags. If the production of an ordered arrangement on the basis of chance and probability takes a longer time to be established than its disruption, then the "time" experiments carried out may be explained if a liquid is assumed to have a structure.

The technique involving the simultaneous measurement of pressure and density, with results given later on, was also applied to the "two-phase system." This term "two-phase system" is used not only in the classical sense of starting with a system containing liquid and vapor but also for convenience in designating this system after the visible meniscus has disappeared and a density difference persists at the point where said meniscus vanished. Although actually data obtained with ethylene are made use of, figure 1 may be taken as typical of the change in density with temperature of the liquid phase of any one-component system in the critical temperature region. Curve A of figure 1 represents the density of a liquid and its variation with temperature right through T_c where the visible meniscus disappears.[3] After heating to d above the critical temperature, on subsequent cooling the density is constant (curve B) until at e the meniscus reappears, after which the density increases rapidly (curve C) with further lowering of temperature. But the equilibrium density of the

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[3] For convenience, the temperature at which the visible meniscus disappears when the two-phase system is heated up will be called *the* critical temperature.

freshly formed liquid is less than the density of the liquid while being heated up (at equal temperatures). All points on curves A, B, and C are reproducible and can be obtained time and time again. Curves B and C were always the same provided the medium had been heated up 5°C. or more above the critical temperature.

It is convenient at this stage to consider the question of whether the density difference above the critical temperature could be due to the so-called gravitational effect (5) (i.e., due to the weight of the medium itself). One can see from figure 1 that there are density differences below the critical temperature (curves C and A) which from the continuity of the curves must be due to the same mechanism giving rise to the density differences above the critical temperature (curves B and A). The former can hardly be ascribed to the gravitational effect, hence the latter cannot either. It was always doubtful that the gravitational effect offered an adequate explanation, as it does not satisfactorily account for the sharp-

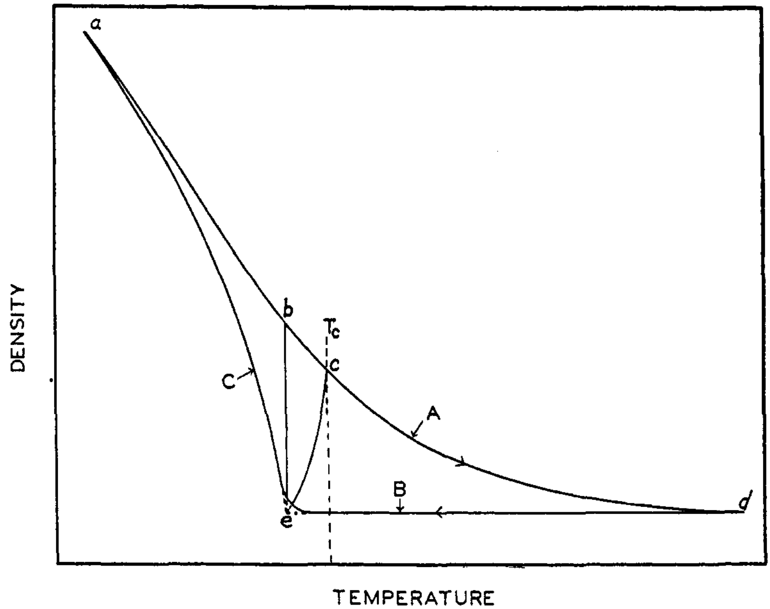

FIG. 1. Isochor (two-phase system). Curve A: variation of density of liquid with rising temperature (*ac*); *c*, critical temperature; *cd*, variation of density of medium below disappearance of meniscus with rise in temperature; *d*, disappearance of density difference. Curve B: *de*, density of medium with rise in temperature; *e*, reappearance of meniscus. Curve C: variation of density of liquid with rise in temperature.

ness of the density discontinuity (24) nor for the fact that, once destroyed, the density differences are not reëstablished by cooling or compressing the medium. Furthermore, when pressures could be accurately measured the compressibility of the medium under the density and temperature conditions was evaluated. The pressure caused by the weight of the whole medium was estimated to be only one-twentieth of that necessary to cause observed density differences, and these differences would be spread continuously between the top and bottom of the tube containing the medium and not in the narrow region within which the abrupt density changes are observed to occur. It is not disputed that there is a density gradient due to gravity superimposed on the density discontinuities, but these are of an inferior order of magnitude. Consequently the density differences must be explained otherwise, most readily on the basis of the persistence of the liquid state of aggregation with a structure above the so-called critical temperature.

It was believed to be of interest to see what would happen when temperature lowering was carried out before the (two-phase) medium had been heated up to the temperature where density differences had disappeared, and also to see what would happen to the density of the liquid formed along curve C (figure 1) when again heated. It was found that in the former case the new density curve lies below curve A and in the latter above curve B. Apparently any density in the area enclosed by curves A, B, and C can be obtained, and once obtained holds indefinitely as long as the temperature remains constant, i.e., no spontaneous change occurs subsequently.

All this can again be explained tentatively on the basis that a rise in temperature brings about a disruption of structure, which takes place rapidly, while a lowering in temperature tends to bring about a building up of a structure, which takes place slowly, and under certain temperature and pressure conditions takes place infinitely slowly. When the isochors of the two-phase system are plotted with the isobars (figure 2)[4] of the one-phase system, it is seen that the densities of the two-phase system lie on the steep parts (points of inflection of the isobars) where temperature or concentration changes tending to bring about a building up of structure take place almost infinitely slowly, as was mentioned before.

Another way in which any density in the region enclosed by curves A, B, and C can be attained by experimental manipulation has suggested an explanation of the mystery of the elimination of density differences by the temperature gradient mentioned before. This manipulation may conveniently be called "temperature fluctuations." Suppose one starts with the (two-phase) medium under a condition represented by some point on

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[4] Typical of any one-component system.

curve A and then subjects it to a slight cooling followed by a slight warming, oscillating the temperature changes around the original temperature; then the density changes found to take place are as follows: The density approaches the lower value for the mean temperature on curves B or C. Any time the fluctuations are stopped and the temperature kept constant, the density remains unchanged. It is possible to see why these results are obtained. On heating structure is presumably destroyed; on cooling it is not restored, owing to the greater time lag. It is evident then why the temperature gradient,—top cold, bottom hot,—destroys the density difference of the two-phase system above the critical temperature. It is not the stirring produced which does it, because mechanical stirring at uniform temperature does no such thing; it is a fact that the medium is subjected to alternate cooling and heating, and this is equivalent to a case of "temperature fluctuations."

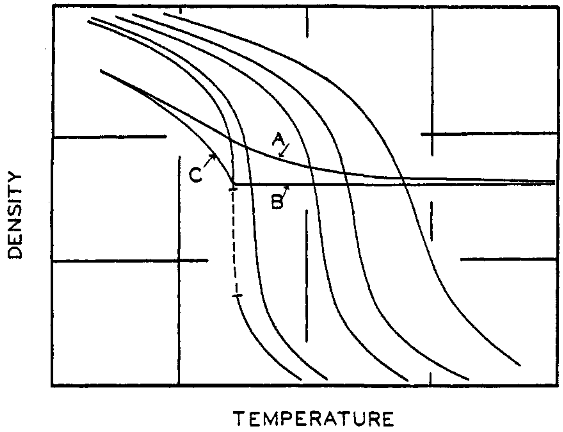

Fig. 2. Relation of isochor representing two-phase system to isobars representing one-phase systems.

In a series of experiments the two-phase system above the critical temperature was subjected to expansion and contraction. It was found that the density difference was destroyed both by expansion and by compression. Consequently in this connection it may be predicted that violent stirring such as would be produced by a rotating propeller may well bring about the same results. Such a mechanism would bring about local expansions and contractions. In the stirring previously mentioned the lower medium was continuously lifted up into the upper portion of the tube, subsequently streaming down and visibly giving a thorough stirring. This, however, was evidently accomplished without local expansion and contraction, so that after 6 hr. of such stirring the original density difference remained unchanged.

The question of the relative stability of the system as represented by curves A, B, and C of figure 1 is pertinent. Without temperature or volume fluctuations any density represented within the area enclosed by the curves A, B, and C persisted unchanged as long as measurements could be made. It was found that the density indicated by any point on curve A is gradually reduced by a process of temperature fluctuations or isothermal compressions and expansions, whereas the reverse process does not occur when starting at any point on curves B and C. This would appear to be indicative that these latter represent "the stable condition." However, it has been shown that in the critical region equilibrium is quite rapidly established when the temperature is changed in the direction of decreasing density and all it implies, whereas the time lag involved in an increase in density may be immeasurably slow. Hence, temperature fluctuations about a mean value would produce a continued decrease in density until curve B was reached. The decrease in density due to temperature fluctuations may thus be explained on the basis of a time factor and does not imply with certainty that the lower curves represent the stable condition.

The results obtained from pressure measurements on curves A, B, and C made with an accuracy of 0.005 atm. (10) do not give a conclusive answer as to the relative stability of the two curves. The results indicate that below the critical temperature the pressure on curve A is just measurably greater than that on curve C at the same temperature, since it was possible to obtain reproducibly a difference in pressure of 0.01 atm. Above the critical temperature the difference in pressure was only half that found in the previous case and was in the opposite direction. 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 this evidence it may be inferred that the stability of the system when corresponding to points on curves A, B, or C at the same temperature or any intermediate points is very nearly the same.

When a liquid is heated in equilibrium with its vapor the density of the liquid gradually decreases. Let us assume that the liquid has a structure. Both rise in temperature and decrease in concentration tend to break up this structure; a point is reached where a critical concentration is approached, "critical" in the sense that the structure of the liquid breaks down rapidly accelerating the decrease in density. For a given temperature above this point there are two limiting concentrations between which the structure rapidly decreases, and a rapid decrease in cohesive force takes place proportional to the decrease in concentration. Now the vapor pressure exerted by a liquid at a given temperature may be roughly put as being *directly* proportional to concentration in the liquid and *inversely* proportional to cohesive force existing in it. That is, it is proportional to concentration on one count and inversely proportional to concentration on another count. In the concentration (i.e., density) region, where cohesive force is proportional to concentration, the pressure is constant, i.e., the liquid can have various densities and exert the same vapor pressure. The above is of course in the nature of an approximation and is not to be taken as a quantitative representation. It gives the picture that in the critical temperature region the liquid can have a range of densities in which it will exert the same pressure. This also offers an explanation of the density discontinuities existing above the temperature at which the visible meniscus disappears, the latter being simply the temperature where the meniscus, i.e., change in density from liquid to vapor, is not abrupt enough to be visible.

Investigations other than density measurements have been published which indicate that a difference of property persists in a medium above and below the disappearance of the meniscus. These involved adsorption measurements (15, 3), surface tension measurements (23), and dielectric constant measurements (11, 12).

Apart from these, heat capacity measurements have been made which show that there is a measurable difference in the heat capacity when the system is under conditions represented by A and by B and C (figure 1) (1). Viscosity measurements are now under way (13). The influence on curves A, B, and C due to the presence of traces and of appreciable amounts of inert gases has given results which confirm the persistence of a liquid state having structure above the critical temperature (14). All this will be published shortly.

The object of presenting the above review is to indicate that measurements in the critical temperature–critical pressure region are of interest, inasmuch as the results obtained may help to evolve a hypothesis of the liquid state of aggregation.

The idea that the writer originally had, namely, that structure was in the nature of regional orientation, can be expressed by the following quotation written some fourteen years ago: "The distinction between regional orientation and a small crystal is that all the atoms in a small crystal may be looked upon as belonging to the same molecule, whereas in a region where orientation has taken place the molecules retain their identity and have translatory and rotational energy possessing only an averaged orientation for a time. The regions in a liquid are not sharply defined, but pass gradually and without any discontinuity into one another. These regions may be momentarily represented by arrows giving the direction of orientation. Contour lines around these arrows would represent the gradual diminution of orientation and blending with the direction of a neighboring region. These contour lines would be continuously shifting, orientation arrows disappearing and new ones appearing in fresh places" (9).

Stewart (16, 17) has developed somewhat similar ideas under the name of "cybotactic groups" to explain his interesting investigation of x-ray diffraction patterns of liquids.

At this stage the writer is convinced only of a few generalities. These are as follows: (*1*) that a liquid has a structure due to certain regularities of molecular distribution in a liquid which are not in the nature of association of molecules; (*2*) that the structure is a dynamic one; (*3*) that rise in temperature and decrease in concentration tend to destroy structure, a change which may be described as a tendency of the liquid state of aggregation to turn into the gaseous state of aggregation; (*4*) that what has been called the critical temperature is the temperature at which the normal density of a liquid has decreased to a point beyond which structure rapidly diminishes; (*5*) that the liquid state of aggregation can exist above this temperature when the density of the medium is increased by pressure sufficient to bring about a necessary concentration.

The interest in the nature of liquids is widespread, and among others Debye (2), Warren (22), Eyring (4), and Mayer and Harrison (6) have presented novel and valuable theories.

Mayer and Harrison, by the application of statistical mechanics to condensing systems, have arrived at certain conclusions in regard to the properties of a medium in the critical temperature region which are in striking agreement with the experimental results obtained in this laboratory. Some experiments recently carried out to test certain predictions made by Mayer and Harrison have fully confirmed these predictions.

In conclusion it may be reiterated that experiments carried out in the critical temperature–critical pressure region, where the change from liquid to gas is most pronounced, should be a deciding factor in leading to a final answer as to the nature of the liquid state of aggregation.

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