

A SYMPOSIUM ON THE CRITICAL STATE¹

THE CRITICAL STATE OF PURE FLUIDS

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If a closed tube which is only partly full of ether, alcohol, or other pure liquid is heated uniformly and not too rapidly, certain interesting phenomena may be observed. If ethyl ether is used and the tube is about one-third full when cool, the volume of the liquid does not change very much during the heating. As the temperature is raised the curved meniscus or boundary between the liquid and vapor flattens slightly and then more rapidly, becomes quite flat and indistinct, and finally fades out entirely without ebullition.

Figure 1 shows a series of instantaneous photographs² of such a tube at different temperatures. The numbers under the photographs indicate the temperatures at which the different photographs were taken, with the temperature of disappearance of the meniscus taken as the temperature of reference. This temperature is called the critical temperature, which for pure ethyl ether is almost exactly 194°C. For ordinary impure ether, the temperature may be a few degrees higher.

If, as in figure 2a, the tube is more than one-half full when cool, the meniscus rises and eventually the tube is completely full before the critical temperature is reached. If, on the other hand (figure 2b), the tube is much less than one-third full, the meniscus sinks and the liquid disappears entirely before the critical temperature is reached.

If, after the meniscus has disappeared, the tube of figure 1 is cooled and the temperature 194°C. is approached, the material in the tube becomes opalescent (see figure 3). The opalescence increases until suddenly a

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² The light required for photographing the tube creates some heat, which introduces complications. The phenomena portrayed, however, represent fairly truthfully what takes place under more ideal conditions.

cloud forms and the meniscus reappears out of the cloud. The amounts of opalescence and cloud depend on the manner of heating. If the liquid is brought very slowly just past the critical temperature and then cooled, the opalescence is slight and the cloud appears in the opalescent region. If the material in the tube is carried, say 20°C ., above the critical temperature or held a little above the critical temperature and stirred, the opalescence and cloud fill the tube. For the latter case observation has shown that the cloud forms first at the bottom of the tube and grows upward. Usually the opalescence changes to a deeper color, and becomes almost brownish; then the material suddenly turns white as the cloud forms.

The cloud persists after the meniscus forms; on careful examination it

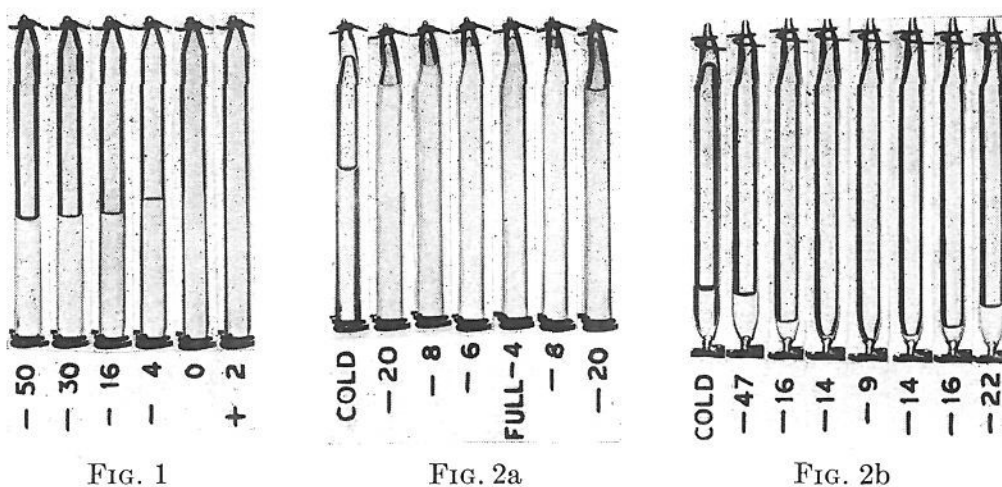


FIG. 1

FIG. 2a

FIG. 2b

FIG. 1. Phenomena observed when a closed tube partly filled with ethyl ether is heated.

FIG. 2a. Closed tube containing ethyl ether. The tube is more than half full when cold; at 190°C . the liquid fills the tube.

FIG. 2b. Closed tube containing ethyl ether. The tube is much less than one-third full when cold; at 185°C . the vapor fills the tube.

is seen that above the meniscus there are innumerable droplets of liquid falling through the vapor and that below the meniscus bubbles of vapor are rising through the liquid. The temperature of reappearance of the meniscus seems to be a fraction of a degree below that of disappearance, although it may be that this is not always true.

Figure 4 shows the difference in the appearance of the cloud for the two cases mentioned above. The tube of the first pair of photographs was heated just past the critical temperature and cooled immediately. The first photograph of each pair was taken just as the cloud formed and the second when it was at the maximum, a few seconds later. The tube of the second pair was heated 24°C . above the critical temperature and cooled.

An interesting variation of the experiment may be made by inserting a

capillary tube in the larger tube (figure 5). As the temperature rises the capillary height in the small tube diminishes, until at the critical temperature the level is that in the outer tube, when both surfaces are flat. If the heating is rapid the small meniscus may lie below the larger. This is due to unequal densities within and without the capillary.³

Even after the meniscus has become invisible when the tube is viewed directly, it may be seen from above or below, sometimes shining like a perfect mirror, sometimes appearing as a dark patch (figure 6), the appearance depending on the temperature and the angle of vision. Two photographs are shown, one taken looking down at an angle, the other horizontally. In one the meniscus is plainly seen, in the other it is invisible.

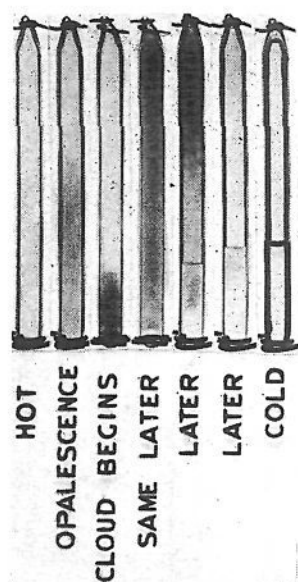


FIG. 3

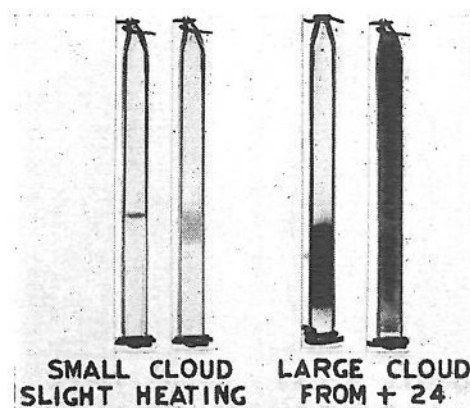


FIG. 4

FIG. 3. Phenomena observed when the tube of figure 1 is cooled

FIG. 4. Formation of cloud

The disappearance and reappearance of the meniscus at a particular temperature are known as the Cagniard de la Tour (15) phenomena. These phenomena were observed for a number of liquids by different experimenters, but until the work of Andrews (1869) their significance was not recognized. Andrews' work on carbon dioxide led to an almost complete understanding of the conditions under which a gas may be liquefied. Faraday had much earlier given the name "permanent gases" to those gases which he was unable to liquefy by the methods of his day.

The Andrews (1) experiment consisted in compressing carbon dioxide

³ Those who have been fortunate enough to see liquid helium no doubt have been struck with the extreme flatness of the surface. The liquid and vapor are so near the critical temperature that the surface tension at their interface is very small.

at constant temperature and measuring the pressure and volume over a wide range of volumes. At low pressure and not too high temperature the pressure-volume curve is not unlike that for a perfect gas. This is the unsaturated vapor pressure curve. If the volume is much decreased Andrews found that at a certain volume, varying with the temperature, the gas begins to liquefy and continues to do so as the volume is still further reduced, until the vapor is all condensed. During this part of the experiment the pressure remains strictly constant, so that the vapor pressure line is straight and horizontal. This corresponds to the two-phase equilibrium state of the substance. Further reduction of volume is attended by an extremely rapid rise in the pressure, since liquids are highly incompressible. The entire curve outlined above is an isothermal line and consists of the three parts described.

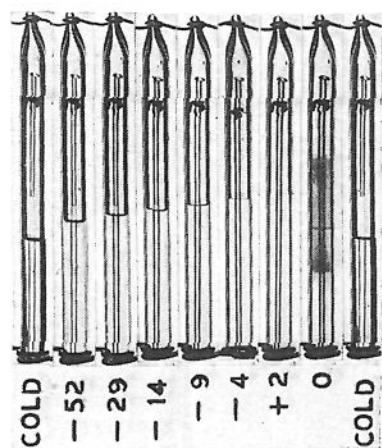


FIG. 5

FIG. 5. Disappearance of surface tension

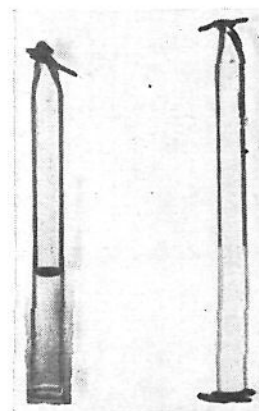


FIG. 6

FIG. 6. Photographs of the tube at the time when the meniscus is invisible when viewed directly. One photograph was taken from above, looking down at an angle; the other horizontally.

If the experiment is repeated at a higher temperature the straight part of the isothermal becomes shorter, until at a certain temperature it shrinks to a point. Andrews called this temperature the critical temperature; it corresponds to the temperature so named in the early part of this paper. The isothermal for this temperature is called the critical isothermal. The point at which the ends of the straight line have drawn together is called the critical point. The terms "critical pressure" and "critical volume" are self-explanatory. We have also critical volume, critical index, and a variety of other names for properties exhibited by the substance at the critical point. The critical temperature was called the absolute boiling point by Mendelejeff.

Van der Waals (16) in 1881 made an important contribution to the

knowledge of liquids and vapors, particularly near the critical point. He was able to give, on grounds at least partly theoretical, the first moderately satisfactory equation which gave a comprehensive description of the behavior of liquids and vapors under varying pressures and temperatures. This well-known equation is really the equation of the isothermal line with the temperature taken as a parameter.

According to the work of Andrews and of van der Waals the properties of the liquid and vapor become identical at the critical point, a most important fact about this point. Also, according to their theory, the liquid state does not persist above the critical point. At the critical point liquid becomes vapor without evaporation and no liquid is possible above this point. The densities of the two phases merge into each other at the

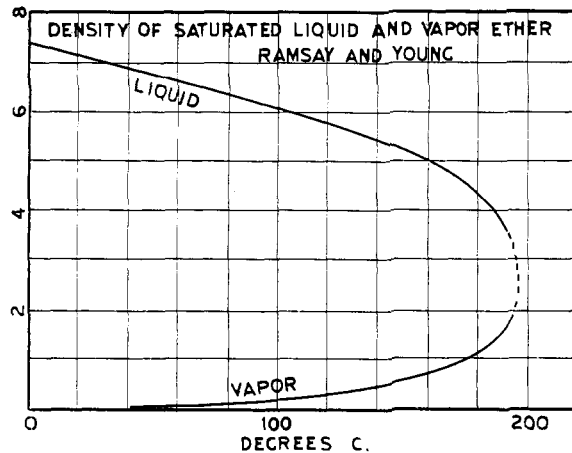


FIG. 7. Plot of the density of the saturated liquid and vapor of ether (Ramsay and Young).

critical point (figure 7). This is a very significant fact and certainly points to homogeneity at this point. It will be noticed that the most important part of the curve is dotted, which indicates that the last stages of the curve were drawn in without data. It is precisely in this region that accurate observation is required.

The work of Andrews and of van der Waals seemed not only to establish the identity of phases at the critical point but to yield the additional fact that there could be no liquid above the critical temperature. These two facts may be said to represent what has come to be known as the classical theory of the critical state.

Experiments seemed to show that the surface tension of liquid and vapor become identical at the critical point (figure 5) and that the densities

become equal also (figure 7). There can be no doubt about the existence of a surface tension at the boundary surface of a vapor. If the surface tensions of liquid and vapor become equal, the interface could hardly exist, and if the densities become equal the phases might intermingle. Equality either of surface tension or of density need not mean that liquid has disappeared entirely, but it was generally believed that such was the fact.

Presently difficulties appeared. Many observers, e.g., Cailletet and Colardeau (2), Hannay and Hogarth (8), and Hagenbach (7) (to mention only a few of the earlier ones) began to produce what seemed to be evidence that the liquid state may persist above the critical temperature, i.e., that the critical temperature does not mark the end of the liquid state. The belief grew that the vapor phase was really only largely vapor with liquid mixed with it and that the liquid phase contained some vapor mixed with it. At the critical point the two mixtures became identical. Liquid, according to these observers, persisted far above the critical temperature and gradually disappeared. Further, they claimed that at a constant temperature above the critical, the liquid part of the mixture gradually disappeared, in part if not completely.

Many different methods were employed to show the persistence of liquid above the critical point. Hannay and Hogarth added coloring matter to the liquid and found that above the critical temperature the substance in the lower part of the tube was more strongly colored than that in the upper portion of the tube. Others added a salt to the liquid to make it electrically conducting and found that above the critical temperature the lower part of the tube remained more strongly conducting than the upper part.

Another experiment, which was thought to give support to the objections to the classical theory, involved the estimation of the densities of the phases above the critical point by observing the amounts of liquid after condensation. For example, if a tube in the form of an inverted U (figure 8), in which the liquid is originally all in one arm, is heated through the critical temperature and cooled, then above the critical temperature, according to the classical theory, the vapor should be homogeneous throughout the tube and after cooling there should be equal amounts in the two arms. As a matter of fact the distribution in the arms is far from equal. Much more is found in the arm in which the liquid was present before heating than in the other, even when the heating is carried far above the critical temperature or when the heating is continued for a considerable time above the critical temperature. This seems to indicate that the liquid state has persisted above the temperature at which it should disappear.

Then there is the experiment of Cailletet and Colardeau with a contin-

uous tube in the form of an elongated O (figure 9), in which mercury or some other liquid is placed to act as a differential manometer. If more of the liquid under experiment is placed in one side than in the other the difference in the levels of the manometric liquid measures the excess. If the tube with its contents is heated above the critical temperature this

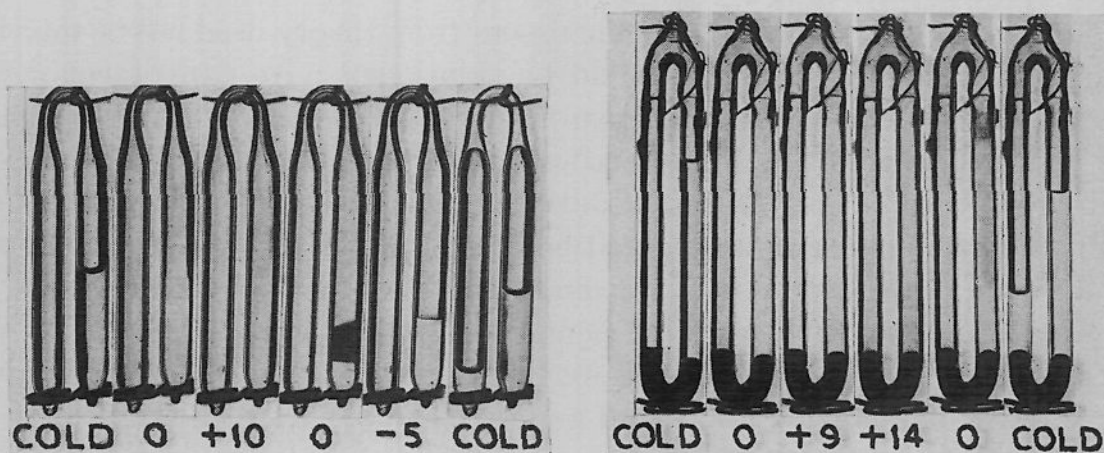


FIG. 8

FIG. 9

FIG. 8. Phenomena observed when the liquid, in an inverted U-tube, is heated through the critical temperature and then cooled.

FIG. 9. Phenomena observed when the liquid, in an elongated O-tube containing mercury to act as a differential manometer, is heated above the critical temperature.

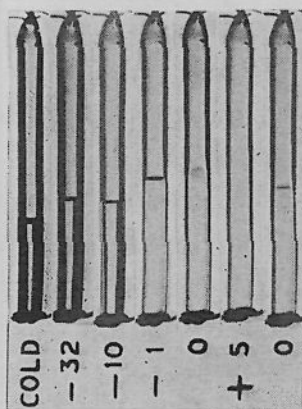


FIG. 10. Effect of temperature on the index of refraction of liquid and vapor

difference in level is maintained, at least in part, well above the critical temperature and for a considerable time.

The indices of refraction of the liquid and vapor are in general different from each other. If a straight vertical tube is partially filled with the fluid (figure 10) and the image of the tube is projected on a screen the difference in the refraction by liquid and vapor is very noticeable. The line of light above the meniscus is not of the same width as below and the break is sharp. If the tube is heated the vapor becomes denser and the

liquid less dense, and the indices of refraction change with the densities, so that the band of light alters in width. At the critical temperature the discontinuity in the line of light should disappear and the line become uniform. This does not happen, but the discontinuity persists although it is not as sharp. Even at temperatures well above the critical temperature the difference is easily seen.

Examples of the departure of experiment from theory need not be multiplied. Two more, however, should be mentioned. An experiment performed by de Heen (9), in an apparatus provided with movable pistons by which the amounts of liquid and vapor in the tube could be varied and with stopcocks to hold these amounts constant, seemed to show that the densities of liquid and vapor could be very different at the critical point and that the density was not a fixed quantity as had been supposed.

Finally, to complete the list, Teichner (14) actually measured the density of the fluid at different levels by the use of small, hollow glass spheres of different buoyancies, and found great differences between the densities at different levels in the tube.

All of these results seemed to lead to the general conclusion that the critical state is not the unique state that it had been believed to be and that the liquid state may persist above the critical temperature, as already noted. The phases may become alike, but the heavier portion of the phases might be expected to be present in the lower part of the container in relatively large quantity and the lighter portion in the upper part of the tube.

From these results came the theory of de Heen and Traube that each of the two phases, while different in composition, was made up of two components. They imagined two different kinds of molecules, the "liquidogenic" and "gazogenic", or liquid-forming and vapor-forming, molecules. The former were thought to be groups of the latter, and the process of passage from liquid to vapor was thought to be merely the breaking up of the larger molecules into the smaller.

According to this theory the liquid at ordinary temperatures is made up for the most part of the larger molecules, but there are always some of the smaller. The reverse is true for the vapor. As the temperature is raised, the number of small molecules in the liquid increases while the number of the larger type in the vapor increases. At the critical point the two phases become identical, but there are still many of the liquid-forming molecules present. These may break up slowly near the critical temperature, but they persist in considerable quantity at a relatively large distance above the critical temperature. When the vapor is cooled down through the critical temperature there is a reforming of the liquid-forming type of molecules into a true liquid.

This theory gained some support and seemed to explain most of the anomalies observed by so many experimenters. It was attacked, however, by Kamerlingh Onnes and his colleagues at Leiden and by others who claimed that the theory was not coherent and was really unnecessary. Kamerlingh Onnes and Fabius (13) repeated Teichner's experiment and seemed to prove that these marked differences of density do not exist if sufficient care be taken in filling the tubes with pure gas-free liquid.

So the problem was not entirely settled. In an attempt to settle this controversy the writer (4) began some years ago a study of viscosity in the neighborhood of the critical point. Viscosity is a phenomenon depending on the masses of the molecules and so might be expected to throw some light on the problem.

While ethyl ether from some points of view is not an ideal substance for investigation of the critical point, it has a low critical pressure and a fairly low critical temperature. Also it has been studied extensively.

A gold cylinder was suspended by a hard drawn silver wire (figure 11), in a tube in the form of an inverted U which contained the liquid. The cylinder had a small iron pin imbedded in a transverse position so that it might be oriented by means of an external magnetic field and would perform angular oscillations when released. The surface of the cylinder was highly polished and a spiral line was ruled on it. When a narrow beam of light was directed on to the cylinder, the ruled line appeared as a dark point on the line of light. When the cylinder oscillated this point moved up and down with a damped harmonic motion. By observing the excursions of this spot by means of a low-power telescope with an eye-piece scale, the decrement was easily calculated.

For the purpose in hand it is not necessary actually to calculate the coefficient of viscosity. The changes in viscosity may be followed through the values of the decrement just as well as through the changes in the coefficient itself.

Generally speaking, the decrement of the oscillations in the liquid decreases steadily with rising temperature until about the critical temperature, and then it increases. In the vapor the decrement increases slowly until near the critical temperature and then it increases more rapidly. It does not become as large, however, as the decrement in the liquid side of the tube. With falling temperature the decrement in the liquid side (figure 12) falls off rapidly and does not follow the values on the rising curve,—it is always lower. That in the vapor side is also less for falling temperature than that for rising temperature. If the amount of liquid in the tube is less than that which gives the critical volume, these four decrement curves apparently coincide.

Finally, if the temperature is maintained constant at a point slightly

above the critical temperature, the decrement in the liquid side of the tube decreases steadily, while that in the vapor side at first increases and then

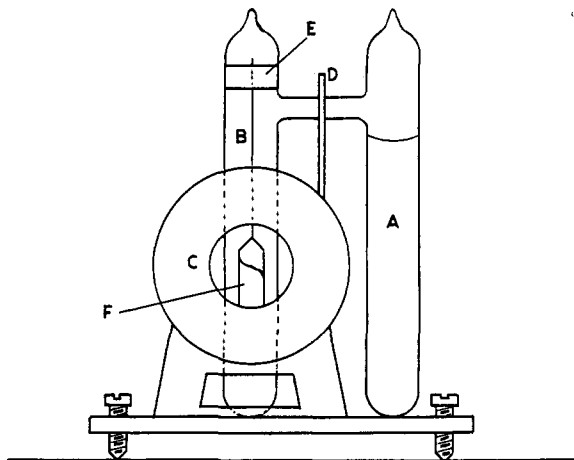


FIG. 11. Apparatus used in studying viscosity near the critical point. A, liquid; B, vapor; C, directing coil; D, support; E, suspension wire; F, gold cylinder.

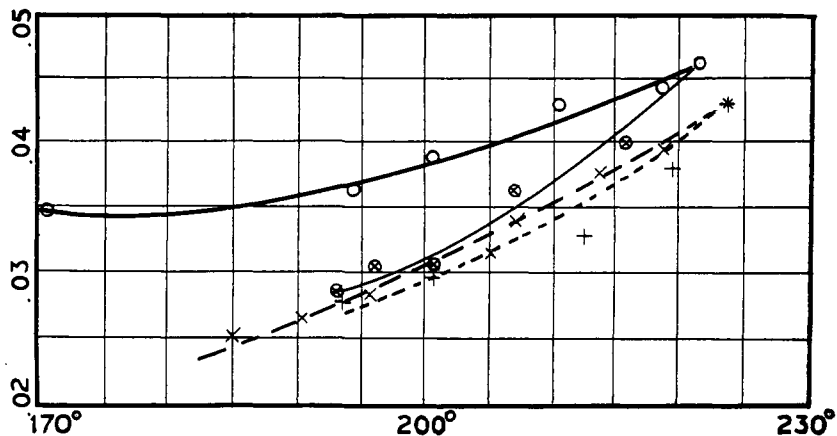


FIG. 12. Plot of the decrement of the oscillations in the liquid and the vapor against the temperature. ○, liquid up; ⊗, liquid down; ×, vapor up; +, vapor down.

decreases (figure 13). All of these results seemed to support the theories of de Heen and Traube.

As already noted, if the volume of the liquid in the tube when cold exceeds 50 per cent of the total volume, the tube is completely filled before the critical temperature is reached. Such a tube was made and results

with the liquid were the same as before, only more pronounced. The decrement on the down grade is much less than on the up. The effect seems to be present for many degrees above the critical (in one case $70^{\circ}\text{C}.$). There is a point of discontinuity on the down curve at $194^{\circ}\text{C}.$ (the critical temperature) (figure 14), which indicates that although there was no

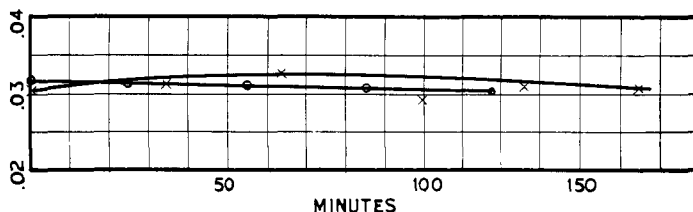


FIG. 13. Plot of the decrement of the oscillations when the temperature is maintained constant at a point slightly above the critical temperature. \circ , liquid at $194.0^{\circ}\text{C}.$; \times , vapor at $194.1^{\circ}\text{C}.$

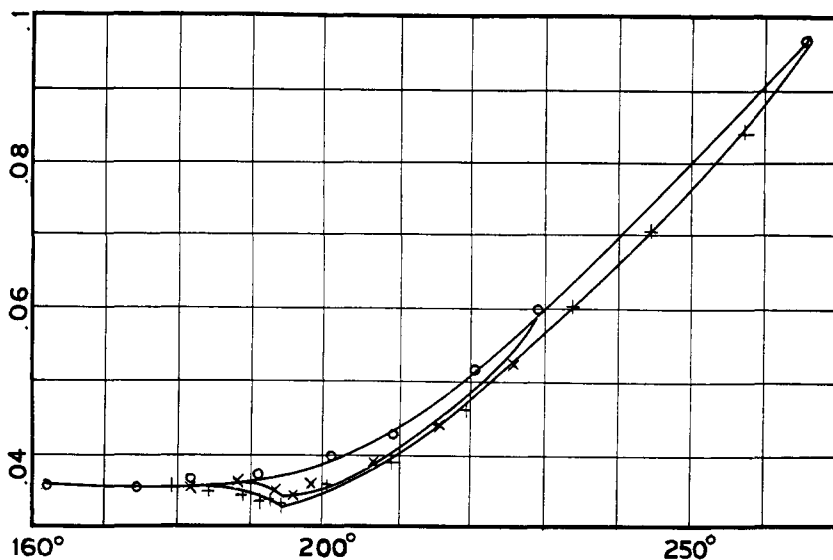


FIG. 14. Plot of the decrement of the oscillations against the temperature, using a tube containing enough liquid so that its volume when cold exceeds 50 per cent of the total volume. \circ , up; \times , down from $229.2^{\circ}\text{C}.$; $+$, down from $265.1^{\circ}\text{C}.$

opalescence or cloud, *there was a marked change in the decrement, indicating a change in structure.* Objections to these results appeared shortly, based on the claims that the liquid was not sufficiently pure and that the changes in viscosity might be caused by flow of the substance from one leg of the tube to the other.

Two points, however, were not made clear. Why does the viscosity of

the vapor after an initial increase show a later decrease when held at constant temperature, and why is the down-grade curve for the vapor always lower than for the liquid?

In accordance with a suggestion made by Kamerlingh Onnes a tube was made in the form of an elongated O and a stirring device provided so that the material in the tube could be thoroughly mixed (5). The stirrer occupied one branch of the tube (figure 15), and the cylinder of the previous experiment the other. The top of the stirrer was made of soft steel and was hollow. The stirring was accomplished by small cups like anemometer cups, on a wire attached to the steel. All was gold-plated. A flat coil placed above actuated the stirrer, and a commutator which could be run at any desired speed controlled the rising and falling of the stirrer. Rather rapid circulation resulted from the motion. The ether used was purified with extreme care.

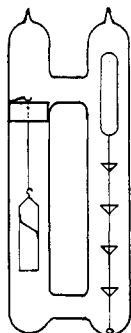


FIG. 15. Closed tube containing stirring device

Without the stirrer working, the results of the experiments were the same as before. When, however, the stirrer was operated vigorously before observations were taken, the previous results were almost absent. The values of the decrement in the liquid side and vapor side became practically the same at the critical temperature. It must be stated that the accuracy of these later results was not as great as of the earlier ones (figure 16), as the cylinders were not as well made.

The earlier work seemed to show that the liquid state does persist above the critical temperature, while the later results seemed to support the classical theory. These last results and the confirmation to some extent at least of the dicta of very weighty authorities compelled the author to accept the validity of the classical theory, but with some reluctance and misgiving.

The objections to the classical theory and the arguments against them may now be summed up.

(a) In the first place, according to the work of van der Waals, there is one and only one critical point where the temperature, pressure, and volume have unique values. So when the tube is partly filled with a liquid this liquid should, if the filling is less than for the critical volume, evaporate away before the critical point is reached, or should expand and fill the tube if the filling is greater than this value. There is, however, a wide range of amounts of filling between which the critical phenomena observed by Cagniard de la Tour are to be observed. For ethyl ether any amount of

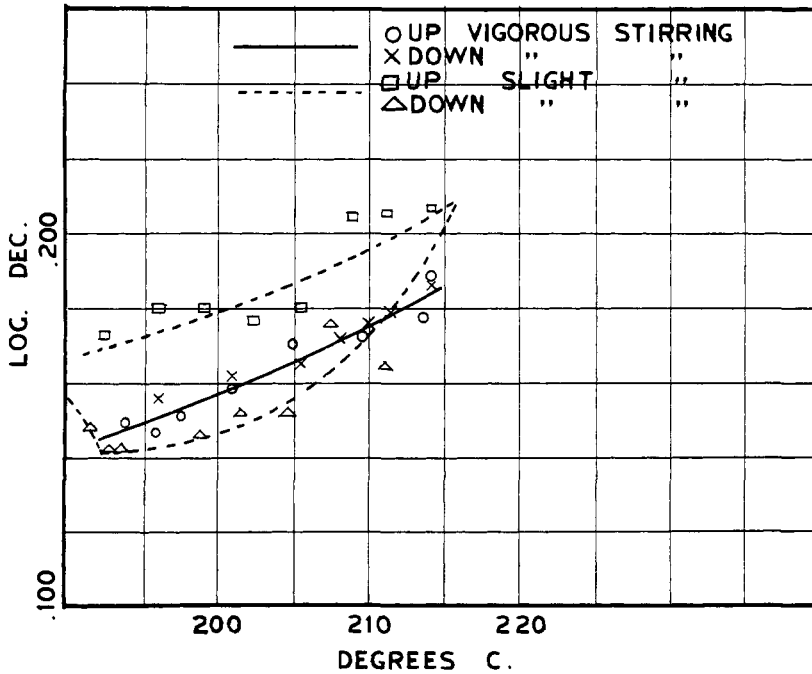


FIG. 16. Plot of the values of the decrement of the oscillations (obtained using the tube shown in figure 15) against the temperature.

filling between 28 per cent and 48 per cent (6) of the total volume will show these phenomena.

(b) The density in the lower part of the tube is very much greater than in the upper, even above the critical temperature. This is shown by actual density determinations and by the refraction of light.

(c) When the temperature is lowered through the critical temperature, fog may appear in a small portion of the tube and not throughout. The amount of fog depends on the extent to which the temperature is carried above the critical temperature and on the time of heating as well.

(*d*) Coloring matter dissolved in the liquid is unequally distributed in the tube above the critical temperature. Electrical conduction as well is unequally distributed.

(*e*) The U-tube and O-tube experiments show that more fluid is found in one leg of the tube even at temperatures considerably above the critical.

(*f*) The experiments of de Heen and Traube showed different densities at different levels in the tube above the critical temperature.

(*g*) The experiments of de Heen and Dwelhauvers-Dery (10) with complicated apparatus showed non-uniform values of the critical density.

(*h*) Finally, the results of the author's work showed that the viscosity of substances in the region originally occupied by liquid remains much larger than that of the vapor and is less in both liquid and vapor after heating. Also, when kept at uniform temperature the substance in both regions shows changes in viscosity of such a character as to indicate a change in molecular structure.

(*i*) Opalescence points unmistakably to a heterogeneity of some kind.

What has been said in reply? Kuenen (11) pointed out a very important point which should be stated first. He said that nearly all of the phenomena observed may be regarded as transition phenomena which would or do disappear upon stirring and that if final states after stirring are dealt with most of the abnormalities disappear. It has been shown by many observers that when the substance is agitated or if time enough is allowed, nearly all of the abnormalities do disappear. Not all of them disappear, however. Stirring is imperative if we are to overcome the very great sluggishness of matter near the critical point.

Owing to the very great compressibility of the substance in the critical region, gravity will have considerable effect in producing an unequal distribution of density. Then again, small amounts of impurity introduced by the experimental method or by insufficient care in preparation may cause relatively large effects.

The magnitude of the effect of gravity will depend on the height of the column of fluid. From the shape of the isothermal it is possible to calculate—roughly at least—the densities at different levels. Gouy calculated that in a tube 4 cm. long containing carbon dioxide at critical filling the density may be 6 per cent greater at the bottom of the tube than at the top. Kuenen investigated this point experimentally, and found that his results agreed with this calculation. This point then may be regarded as settled.

Kuenen also investigated the effect of impurities and found that the first traces of gas mixed with pure liquid produce relatively enormous changes in the differences in density between the bottom and the top of the tube and claimed that if the liquid is not pure the differences are ac-

counted for by the effect of gravity. From a study of the isothermals of carbon dioxide and oxygen, Verschaffelt showed that at the critical temperature with a molecular concentration of an impurity as small as 0.0001, the departure of the density from the mean may be nearly 17 per cent and that at 3°C. above the critical temperature the departure may be 5 per cent. At the critical temperature a difference of 0.001 in the concentration may cause a departure of 30 per cent from the critical density. If the density is greater or less than the critical density, as at the bottom and top of the tube, respectively, the effects are very much less.

The properties of mixtures near the critical point differ so widely from those of pure substances that conclusions drawn from results obtained by adding coloring matter or soluble salts are unreliable and in most cases open to suspicion. Kamerlingh Onnes held the view that the molecules of the impurity form attracting nuclei, which at the critical point cause rather disproportionate disturbances and modify profoundly the true critical phenomena. This opinion is entirely reasonable.

It seems perfectly clear then, that many of the abnormalities observed which affect the density greatly may be due to the effects of weight and impurities. If we deal with final states reached after stirring or long-continued heating, there is much evidence in favor of the classical theory of Andrews and van der Waals.

The experiments of a few years ago made by Callendar (3) on water and more recently the experimental evidence being accumulated by Professor Maass have reopened the question, and it now seems necessary to modify our ideas about matter in the critical region.

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