

LIQUID ABOVE THE CRITICAL TEMPERATURE.¹

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IF the wide glass pressure tube of a Cailletet liquefaction apparatus be filled with pure carbon dioxide² and compressed, not too slowly, into progressively smaller volume, while the bath is maintained constant at some point below the critical temperature, at a certain volume the eye of the observer may notice a series of phenomena due to liquefaction.

Beginning usually at the level of the top of the mercury column, a thin, transparent cylindrical sheath mounts upward in immediate contact with the walls of the glass tube, loses width when it strikes the curve at the top of the tube, then closes together at the point. This appearance is due of course to the wetting of the interior walls of the tube. Under the circumstances named, the liquid cannot be seen to form anywhere else than on the walls of the tube, except indeed occasionally on the mercury meniscus, if the latter has sufficient area. The reason is clear. While the volume is decreasing, heat of compression maintains all of the gas at a higher temperature than that of the bath. The disparity of temperature between gas and bath is greatest in the center of the tube, and least at the walls, which conduct away the heat.³ When the volume corresponding to incipient liquefaction is reached, liquid forms in that part of the gas which is coolest—that is, on the

¹ The subject-matter of the present paper was suggested by some observations which were made during an investigation of the effect of mechanical shock upon carbon dioxide near the critical temperature. (PHYS. REV., 19, 1904, 258-272; 26, 470-482, 1908.) It may properly be considered as part of the inquiry named, which was assisted by Grant No. 104 from the Elizabeth Thompson Science Fund.

² The gas used in these experiments contained impurity, unabsorbed by potassium hydroxide solution, equal to 1 part by volume in from 30,000 to 40,000. (Cf. Journal of the American Chemical Society, 30, 1090-1096, 1908.)

³ It will be apparent that these phenomena are much more pronounced in wide tubes than in narrow ones. Our pressure tube was of 6 mm. internal diameter. (Loc. cit., p. 263.)

walls. Moreover it begins to form at that point on the walls which is cooled, in a sense, both without and within — that is, at the level of the top of the mercury meniscus — and ends at the point most affected by the heat of compression — namely, the tip of the tube, against which the convection currents set up by the heated central core of the gas are directed.¹ The process is simply a progressive wetting of the internal glass surface from below upwards.

Almost immediately the liquid can be observed flowing down the walls in ripples, which present much the same appearance as that of water flowing down a roof, or a spent wave receding on the beach.

If the initial volume is considerably greater than the volume of saturation and the compression is checked sharply at the appearance of the ripples, no accumulated liquid can be detected, as a rule, when thermal equilibrium is again established between the carbon dioxide and the bath. On the other hand when the gas is saturated, and there is any liquid present before compression, the quantity of the latter is notably increased by the newly formed liquid which flows down into it.

The new liquid of course is always warmer than that into which it runs, and therefore less dense. If there is but little of it, and its speed down the walls is slight, it stops at the meniscus or not far below. If there is considerable of it and it rushes down the glass, it penetrates more deeply below the surface, leaving the glass however after it reaches the meniscus, and curving inward more and more as it diffuses into the older liquid. In either case, its course after striking the meniscus can be followed for a little by the “*striae*” or lines of differential refraction which appear. Naturally the diffusion is seen at its best when there is considerable of the older liquid present.

Another phenomenon which may be noted by close scrutiny is a sort of agitation or tremulousness in the bottom of unsaturated gas just before the sheath “*lifts*” on the glass. This agitation seems to be limited to a few degrees below the critical temperature. When the bath temperature is 28° for instance, it is seen only occasionally and faintly, and close to the mercury, while it becomes

¹ Probably also the approximately hemispherical shape of the tip, presenting relatively less surface, contributes to the same result.

rapidly more pronounced, and may be seen at a greater height above the mercury, as temperatures nearer the critical are chosen.

There can be little doubt that the layer of gas next the mercury, being cooler than the entire system above it, is the first to feel the approach of saturation, and probably a liquid film forms on the mercury surface before it shoots up the glass. Unfortunately it was never possible to establish this priority by observation. In fact it was only once or twice that liquid was seen forming on the mercury surface at all. The difficulties of observation in this regard are very great, for liquefaction conducted on so small a scale.

Below the critical temperature these phenomena are very simply explained by the simultaneous presence of liquid and vapor in the carbon dioxide. *Every one of them persists above the critical temperature.* As will be shown, this is not only true qualitatively, but the quantitative changes which are brought about by rise of temperature present no discontinuity at the critical temperature.

The method of experimentation either above or below the critical temperature was as follows: The apparatus¹ was stationed in front of a north window so that the contents of the pressure tube could be observed by diffused, transmitted light. The gas having been already so far compressed that it was all directly subject to the influence of the bath, and the latter having been maintained sufficiently long at the desired temperature, the volume of the gas was noted. The observer then opened the needle valve to admit water slowly from the hydraulic pump into the pressure jacket of the apparatus. A dial gauge connected with the pressure jacket indicated the increase of the pressure of the carbon dioxide. In order that successive compressions might be comparable with one another in speed, an assistant read aloud the progress of the pointer around the dial, calling off equal intervals of pressure. With some practice the observer could so manipulate the needle valve as to raise the pressure not only very steadily during the course of each compression, but with practically equal speed in successive compressions. Whenever the speed became abnormal in either sense, the corresponding observation was rejected.

On the instant when the sheath of incipient liquefaction "lifted"

¹Loc. cit., p. 263.

and the rippling commenced, the needle valve was shut and the system was allowed to stand until the carbon dioxide had regained the temperature of the bath. Its volume was then noted again. Thermal equilibrium was assumed to be reached when the pointer ceased to recede upon the dial of the gauge. The mechanical lag of the pointer was corrected by gentle tapping upon some effective spot upon the gauge.

Inasmuch as for a given initial volume the final volume varies somewhat with the speed of compression, successive readings of the final volume afforded a valuable check upon the uniformity of the speed, as well as upon the personal equation of the observer.

Readings of the final volume were secured for a series of initial volumes, which varied from the largest readable volume to that

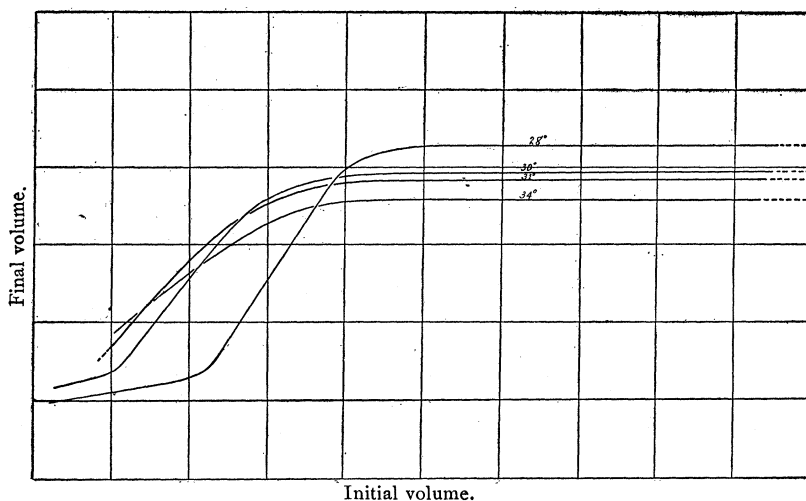


Fig. 1.

which represented nearly complete liquefaction. When one such series was complete the thermostat was adjusted to another temperature, for a second series, — and so on.

The results for four sample temperatures are given in the following table, and are plotted also in Fig. 1.

It will be noticed that the curves for all four of the temperatures begin (at the right) with a horizontal portion of considerable length. This rounds into a second rectilinear portion, which slopes in general

T.	Initial Vol. c.mm.	Final Vol. c.mm.	T.	Initial Vol. c.mm.	Final Vol. c.mm.
28°	578	267.5	31°	570.5	243.8
	385.5	263.2		403.4	242.3
	336.4	261		258	227.4
	291	240.2		204.4	194
	243.4	164		150.7	135.6
	190.8	112			
	112.5	99.5			
30°	575.5	247.8	34°	570.5	226.4
	325	248.6		459	228.5
	276	241.2		367.6	228.5
	239	218		278	225.4
	213.8	198.1		224.3	196
	185.5	162.4		183.4	168.5
	170.7	139		153.5	145.2
	139	114			
114.1	108.1				

towards the origins of the axes. This portion in turn, in the case of the lower two temperatures, curves into a third rectilinear which is more nearly horizontal and ends abruptly when the initial and final volumes are approximately the same. For the two higher temperatures this approximate equality is reached at the end of the second rectilinear.

To understand the meaning of these ripple curves, let XYZ , in Fig. 2, be a liquefaction area, whose ordinates are pressures and whose abscissas are volumes, and let $ABCD$ be the isothermal of any selected temperature below the critical. If the volume of gas at A be compressed with a measurably uniform velocity, all of the gas will become heated until the temperature gradient is such that the heat of compression flows outward into the bath as fast as it is produced. From the point where thermal equilibrium is reached the compression becomes isothermal, but its curve lies higher than that of the bath temperature. As the gas at the center of the compression tube will always be hotter during compression than that which is near the walls, its isothermal, considered separately, will be higher than that of the latter.

Let $bb'B'$ represent the isothermal of the gas at the center, and for the sake of simplicity let it be assumed that the gas at the walls follows the isothermal of the bath temperature, $ABCD$, though this

of course would never be strictly true. If compression begins at A' , $A'b'$ will represent the course of the gas at the center, and $A'a'$, the simultaneous course of gas at the walls. As the pressure at any given moment is necessarily the same on all the gas, a' and b' will be reached at the same moment. At a' , liquefaction occurs, the valve is shut, and compression ceases. The total volume now remains constant. The gas at b' , if alone, would fall vertically to the

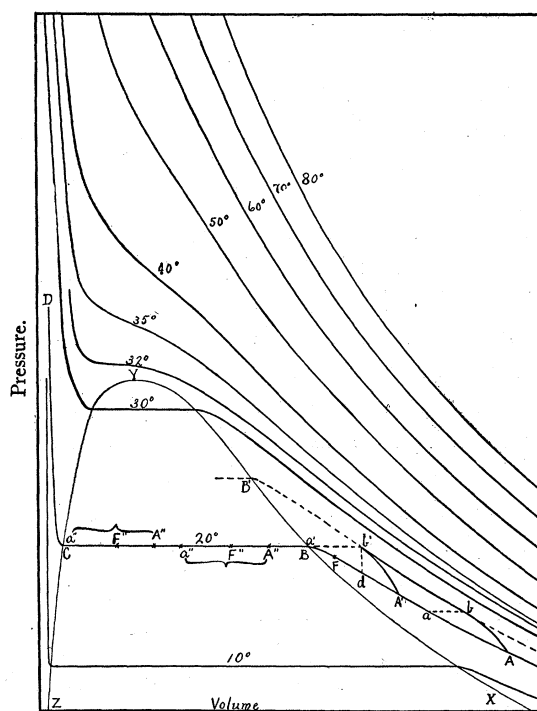


Fig. 2.

normal isothermal at d , but equilibrium will be reached when the system as a whole arrives at some point intermediate between a' and d , as F .

The point F will usually lie to the right of B , if (a) the compression valve is promptly closed at the appearance of liquid; (b) the compression tube is a wide one rather than capillary; (c) the rate of compression is not too slow; and (d) the walls conduct well. In

these experiments, indeed, residual liquid was never observed so long as the initial volume was considerably greater than the volume of saturation.

Fig. 2 makes clear also that, other things being equal, the points a' and b' , and therefore F , are independent of the initial volume A so long as the latter is greater than A' . The situation so far is represented in Fig. 1 by the horizontal portion of the curves.

When A stands sufficiently far forward on the isothermal AB , gas near the walls will reach a' before the gas in the center has reached its own isothermal $bb'B'$ at all, but stands at some point on the isobar $a'b'$. The effect is to shift F more and more towards the saturation point B . This situation is represented in that portion of the curves of Fig. 1 which is concave to the axis of volumes.

Whenever the initial volume lies at the left of B , within the liquefaction area, and not too near C , gas at the center can never rise above the normal isothermal, assuming still that gas at the walls does not, and the sole effect of decrease in volume will be liquefaction of gas at the walls. The final volume will lie at F'' between a'' , representing gas at the walls, and A'' , representing gas at the center. Moreover, the distance $A''F''$ will be constant. In other words, there will always be an increase in the liquid volume after compression, and the ripple curve becomes rectilinear, sloping toward the origins of the axes.

When the initial volume is so near to C that a'' reaches C on its own isothermal, then the distance by which F'' is in advance of A'' decreases until A'' is so near to C that ripples are no longer seen at all. This condition is represented by that portion of the curves at the left in Fig. 1 which is rectilinear and not far from horizontal.

By similar means it becomes apparent why it is that at higher temperatures than the one just now chosen for discussion, the first horizontal of Fig. 1 is longer; that the second rectilinear becomes shorter; and that the last rectilinear becomes shorter and disappears as the all-liquid portion of the isotherm diverges more and more from a true vertical, and the distance BC becomes shorter than $A''a''$.

Regarding the ripple curve of 31° it should be noted that every time ripples were observed, the system as a whole was above the

critical temperature. This was shown by the appearance of the meniscus just before thermal equilibrium was established, after compression, between the carbon dioxide and the bath. This of course was when the initial volume was not too large, as explained above. Further, when the initial volume was small enough for the existence of some liquid, compression caused at one and the same time the disappearance of the meniscus and the appearance of ripples. The latter followed the curve of the glass just as always (a fact indicative of their liquid character), and could be followed sharply to a level which rose slowly higher than that of the vanished meniscus. Having arrived at this rising level, which was thus quite sharply defined though it was itself invisible, the ripples, still descending by their acquired momentum, left the glass, curved more and more inward toward the center of the tube, became rapidly thinner and so disappeared. Presently the meniscus appeared at a level just a little higher than that at which the last ripples bent away from the glass and disappeared by diffusion. All of the phenomena of ripple curve 31° down to the minutest detail were an exact duplication of those of the ripple curves for 28° and 30° with a single exception of the visible meniscus. In the latter two curves, if a suitable initial volume was chosen, ripples ran down until they reached the rising meniscus before diffusion and their disappearance began. In the 31° curve there was no meniscus at the top of the liquid until the rippling was over. But when the meniscus did finally appear it was found at the level where the conduct of the ripples indicated that it would be.

It was difficult for an observer not to believe that at a bath temperature of 31° ripples of liquid ran down the glass until they reached the top of other liquid like themselves, with which they mixed in the usual way, with corresponding increase in the total liquid volume. Indeed in all probability a doubt would never occur, except for the commonly accepted dogma that liquid cannot exist without its cap on! We shall recur to this point later.

Again, identically the same phenomena appeared at 31.5° , 33° , 34° , 36° and 38° , though of course there was no visible meniscus at any time at these temperatures. But by watching the conduct of the ripples one might follow the accumulation of "liquid" at

each temperature, from its beginnings at the mercury until the total volume was nearly all liquid, and ripples appeared only in the extreme tip of the pressure tube. Measurements of final volume above 34° were of doubtful value however, as the needle of our gauge ran beyond its scale, and the necessary check on the uniformity of the speed of compression was lacking.

Ripples which form above the critical temperature follow the glass just like those which form at temperatures below that point. Even those which form near the tip of the compression tube take the longer way outward along the glass, instead of flowing vertically downward through the lighter gas below them. When the initial volume is too large to admit of the accumulation of liquid, they run down the entire distance to the mercury without any loss of "body." When the initial volume is too small to admit of the presence of vapor, no ripples are seen at all under compression. At initial volumes lying between these two extremes, ripples run down to some characteristic level, which is lower for larger initial volumes and higher for smaller ones. Arrived at this level, wherever it may be, the ripples at once begin to leave the glass and quickly become invisible, giving every appearance in so doing of mixing with a medium of a density allied to their own.

Ripples alone, in a region where changes of density are very great and very rapid, might be accounted for without assuming any change of physical state, but such a group of phenomena as that given above can hardly be so explained. Above the critical temperature, as below it, the ripples must be considered as consisting of *liquid*, and they flow down until they reach the top of the other *liquid*, if any, which has accumulated as the result of previous compression. When the carbon dioxide is already all liquid, ripples naturally cannot form at all.

One more phenomenon observed above the critical temperature deserves mention. As has been said, the volume of invisible liquid lying on the mercury could be gauged with approximate accuracy by observing the level on the walls at which the ripples produced by compression ceased to increase in thickness, left the walls, and began to disappear.

This level having been determined, and the heat of compression

having been allowed to disappear, a slight *increase* of volume, quite insufficient to cool any part of the system down to the critical temperature, gave rise to ripples or striæ which appeared in the "liquid" volume, except near the walls, and which worked their way rather slowly upward through the liquid to its top, and then disappeared. As they rose, they tended somewhat to recede from the walls toward the center.

Now expansion is a cooling process. The cooling takes effect chiefly in the center of the carbon dioxide, rather than at the walls, which remain approximately at the temperature of the bath. *Falling* ripples or striæ in the center of the carbon dioxide might easily be accounted for, on the basis of the orthodox theory of the critical state, by convection currents in the "gas," of which the whole volume is thought to consist. *Upward* ripples, in the coolest part of the carbon dioxide, appearing only in the lower portion of the same and ceasing abruptly at a certain predetermined level, can apparently be accounted for only as the result of a change from a physical state of greater density to one of less — that is, from the liquid to gas or vapor.¹ Indeed this conclusion is strengthened by the fact that whenever the expansion was sufficient to cool the carbon dioxide below the critical temperature, so that the meniscus temporarily appeared, it appeared always where the compression ripples would have led one to expect it, and the upward current temporarily assumed the form of true bubbles, exceedingly minute but unmistakable. In the interval before the meniscus faded out again in consequence of the inflow of heat from the bath, these bubbles could be seen to rise toward the meniscus, and disappear if they reached it. If thermal conditions were such that the meniscus faded quickly, the fog of bubbles gave way again to ripples or striæ which likewise rose no further than the level where the meniscus had been.

When there was no "liquid" present, as shown by the flow of compression ripples down the glass quite to the mercury, no upward currents were ever produced by subsequent expansion. When the carbon dioxide was all "liquid," as shown by failure to obtain compression ripples because of the small initial volume, up-

¹Cf. Ramsay, *Philosophical Magazine*, 16, 1883, 120.

ward currents, if produced at all by expansion, could be followed nearly or quite to the top of the tube. In any case intermediate between these extremes, the striæ, as already said, ceased upward at the same level as the compression ripples did downward, making, of course due allowance for the small increase or decrease in the "liquid" volume caused by the very "condensation" or "evaporation" which was under observation.

Beginning with the classic work of Andrews¹ in 1869, there have continued to accumulate, with reference to the critical state, facts which are difficult or impossible to understand except on the assumption that liquid can exist above the critical temperature. Previous to this time it had been held for nearly half a century, and apparently without question, that the disappearance of the top of a liquid was sure proof that the liquid itself had ceased to exist; and it is perhaps in part because of the age and respectability of this traditional interpretation of the critical state that comparatively few venture seriously to oppose it even now.

It may not be out of place in this connection to call attention again to some of the typical experimental facts which are not in accord with the generally accepted theory.

I. THE COURSE OF THE ISOTHERMALS FOR TEMPERATURES NOT TOO HIGH ABOVE THE CRITICAL TEMPERATURE.

At the general region where liquefaction, if any, would be expected, these isothermals exhibit in sequence the same changes in the value of pv as occur below the critical temperature. They bend at first rapidly toward the axis of pressures, with a tendency to become perpendicular thereto, and afterwards reverse the curvature with a tendency to become parallel to the same. Below the critical temperature this means the passage into, and out of, an area of progressive liquefaction. Above the critical temperature, what else can it mean? Below the critical temperature liquid and vapor are discontinuous because of their limited solubility in each other. Therefore the liquid phase not only becomes localized because of its greater density, but it possesses a meniscus. Above the critical temperature the liquid and vapor are soluble or miscible in all pro-

¹ Philosophical Transactions, 159, 1869, 575-89.

portions. Whether the two are stratified in obedience to their respective densities or not, there can never be a meniscus. If stratification exists, it is not apparent to the eye in the usual way, and it is always a temporary phenomenon subject to the ordinary laws of diffusion.

II. ANDREWS'¹ "CONTINUITY" EXPERIMENT.

Carbon dioxide is heated first to a temperature above the critical temperature and is then subjected to a pressure greater than the critical pressure. No liquefaction is observed. Then with constant pressure the "gas" is cooled below the critical temperature. Still no visible liquefaction. However, the carbon dioxide must now be *all liquid*, for the pressure is in excess of that required for liquefaction at the present temperature. And in fact it *is* all liquid, as becomes evident by the violent ebullition which occurs throughout the entire mass when the pressure is released. *Somewhere* during the process all of the gas has changed to liquid, but at no point has it been possible to see the liquid, or, let us rather say, at no point has it been possible to see the top or any other surface of liquid.

The explanation of the paradox is easy, once the possibility of the existence of liquid above the critical temperature is granted.

Beginning at that part of the compression, above the critical temperature, where the isothermals begin to curve towards the axis of pressure, liquefaction occurred, and copiously. As the liquid so formed is perfectly miscible with the vapor which remains, it does not become localized, with a visible surface to it.² Liquefaction would not be complete at this stage, except under excessive pressures. In the second stage of the experiment, while the carbon dioxide was cooling toward the critical temperature, and while the pressure continued greater than the critical pressure, liquefaction became complete. The temperature at which this could occur depends on the pressure. From that temperature downward there could of course be no expectation of a surface to the liquid other than that of the containing walls.

¹ Loc. cit.

² This is the point where liquefaction would have been betrayed by ripples, in a wide tube; but Andrews' tube was capillary.

III. EXPERIMENTS BY WHICH THE SOLVENT POWER OF INVISIBLE LIQUID IS MADE TO REVEAL THE PRESENCE OF THE LATTER.

The experiment of Hannay and Hogarth¹ is a typical one in this class. A solution of potassium iodide in alcohol was heated above the critical temperature, and the potassium iodide did *not* fall tumbling to the bottom throughout the entire former liquid volume as soon as the meniscus disappeared, though it ought to have done so if the orthodox view of the critical temperature is correct. No solid whatever appeared even at 380°, or 140° above the critical temperature of alcohol. Instead of explaining this fact by assuming that liquid alcohol was still present in the tube though not visible, it was assumed that, at sufficiently high pressures, gaseous alcohol dissolves potassium iodide.

This otherwise unsupported hypothesis was directly contradicted however by other observations of Hannay and Hogarth. If a hot iron rod was held close to the side of the hot tube, crystals formed on the inner surface of the glass, next to the rod. It is quite clear that the extra heat supplied locally by the rod could not have lessened the pressure in the tube. Doubtless it did evaporate liquid alcohol locally. It was observed further that if the volume of the solution at 350° was suddenly increased, a precipitation of solid occurred, which disappeared again when the pressure was restored. But the increase of volume was calculated to evaporate liquid alcohol, while the sudden expansion would temporarily cool that which remained and so decrease its solvent power. Altschul² afterward showed that a *general* precipitation of potassium iodide began at 356°. This is doubtless the temperature at which, by progressive evaporation of invisible liquid alcohol, his solution of potassium iodide became saturated. Probably the solution was more concentrated at the start than that of Hannay and Hogarth.

IV. The belt of irregular refraction in an undisturbed Natterer tube at the level of the vanished meniscus, showing a lighter medium above and a denser one below. The belt grows broader of course by diffusion, and in time disappears, even when the temperature is constant.

¹ Chemical News, 40, 1879, 256; 41, 1880, 103-6.

² Zeitschrift für comprimirte und flüssige Gase, I., 1898, 207-8.

V. The striæ observed when a Natterer tube which is above the critical temperature, and which has hitherto been undisturbed in its vertical position, is turned end for end. These are indicative of the mixing of miscible media of different densities, and their appearance is identical with that observed when a similar tube completely filled with stratified alcohol and water is inverted.

VI. That an undisturbed Natterer tube, cooled from a higher temperature to the critical, shows first a fog belt, then the meniscus suddenly in the midst of it, while one whose contents have been well mixed above the critical temperature shows fog through its entire length under the same circumstances. In the one case the liquid has the opportunity of remaining localized when the critical temperature is exceeded, except indeed for gradual diffusion. Naturally the depth of the fog belt, which precedes the meniscus, varies in this case with the time which has been available for diffusion. In the other case the whole liquid has a chance to mix completely with the vapor — and takes it.

VII. Experiments which show directly the persistence of differences of density as between the upper and lower portions of an undisturbed two-phase system after the critical temperature has been passed. From this very comprehensive class may perhaps be selected that of Cailletet and Collardeau with the so-called O-tube;¹ that of de Heen with his modified Natterer tube, separable by a valve into two parts;² and that of Teichner with his little glass floats of varying buoyancy.³ In this class belong also the ripple phenomena of this paper, and the definition of the vapor-liquid boundary by means of fog produced by mechanical vibration, as described in a former article.⁴

Much of the confusion now existing between the two schools of thought regarding the nature of the critical state appears to be due to a difference in the methods of observation. Those who hold to the newer view, that liquid persists above the critical temperature, base their belief principally on experiments like those catalogued above — experiments in which the pressure tube is purposely left

¹ Comptes Rendus, 102, 1886, 1202-7.

² Zeitschrift für comprimirt und flüssige Gase, 2, 1898, 97.

³ Zeitschrift für anorganische Chemie, 37, 1903, 232.

⁴ Phys. Rev., 26, 470-482, 1908.

undisturbed by any external influence while the thermal changes are taking place and where the observations are made within a reasonable time after the critical temperature has passed.

Those who hold to the older view, that at the critical temperature homogeneity ensues, find their warrant: (*a*) in experiments in which either the critical temperature is reached and passed with extreme slowness or the observations are made after the system has remained standing in thermal equilibrium for long periods after the critical temperature is passed, so that the effect of more or less complete diffusion is felt, or (*b*) in experiments in which the substance under examination is purposely given opportunity to mix, either by frequent inversions of the tube, or by the use of a mechanical stirrer inside.

Precisely the same confusion would arise over the critical solution temperature of an acetone-water system under the same circumstances. Each school is right as to its own facts, but the only theory so far which seems to include all the facts is that which assumes that at the critical temperature the miscibility of liquid and vapor ceases to be limited. This theory which has been proposed more than once¹ during the last generation, has recently found its sturdiest champion in Julius Traube.² Deserving of special emphasis is Traube's distinction between real *liquid* (liquidons) and the *liquid phase*, and between real *gas* (gasons) and the *vapor phase* respectively, whereby the liquid phase is to be understood as true liquid (liquidons) containing true gas (gasons) in solution — and the vapor phase as true gas (gasons) containing true liquid (liquidons) in solution.

¹Jamin, Comptes Rendus, 96, 1883, 1448.

Cailletet and Collardeau, Annales de Chimie et de Physique (6), 18, 1889, 269.

Batelli, Atti del Reale Istituto Veneto di scienze, lettere e arti, 50, 1893, 1615.

Wesendonck, Naturwissenschaftliche Rundschau, 9, 1894, 209.

Dwelschauvers-Dery, Bulletin de l'Académie royale de Belgique (3), 30, 1895, 570.

Pictet, Zeitschrift für comprimirte und flüssige Gase, 1, 1897, 63. Cf. also p. 207.

de Heen, Zeitschrift für comprimirte und flüssige Gase, 2, 1898, 97. Bulletin de l'Académie royale de Belgique, 1907, 859.

Ramsay and Steele, Zeitschrift für physikalische Chemie, 44, 1903, 378. Cf. Proceedings of the Royal Society, 30, 1880, 323; 31, 194. Philosophical Magazine (5), 37, 1894, 215.

²Zeitschrift für anorganische Chemie, 37, 1903, 225; 38, 1904, 399.

The proportion of gasons to liquidons in the liquid phase, and the proportion of liquidons to gasons in the vapor phase, is limited below the critical temperature by the existence of a saturation point. Above the critical temperature there is no such limit. Above the critical temperature solutions of different densities, because of different degrees of concentration, may still be stratified by various means, but such a condition is subject to the influence of gradual diffusion, just as is the case when two liquids, of different densities but perfect miscibility, are similarly stratified.

This view transforms the "area of liquefaction" on a diagram of isothermals into an "area of saturation." Outside of this area of saturation, on the side opposite the axis of pressures, liquid (liquidons) may exist, less or more according to volume, but never to the extent of saturating the gas (gasons) in which it is dissolved. Outside of the same area, but on the side next to the axis of pressures, gas (gasons) may still exist, more or less, according to volume, but never to the extent of saturating the liquid (liquidons) in which it is dissolved. Above the critical temperature, true liquid and true gas may exist side by side in any proportion, according to volume, but there can never be phases except in the loose sense of temporary stratification.

Outside of the area of saturation there is perfect continuity in every direction. The area of saturation, indeed, is after all only an exceptional case in an otherwise general continuity between the liquid and gaseous conditions of matter. Andrews' distinction between gas and vapor in terms of the critical temperature may still be retained, if the capacity for continuity is made fundamental, but not otherwise. An aëroform substance is "gas" above the critical temperature, and "vapor" below that temperature. Whether as "gas" or "vapor" it may be changed to liquid by pressure alone — as "gas," with perfect continuity, — as "vapor," only by a discontinuous process involving saturation.

SUMMARY.

I. The phenomenon of "rippling," which is observed in the wide glass compression tube of a Cailletet apparatus when the volume of saturated vapor is decreased, shows no discontinuity at the critical

temperature, but may be observed in detail, under corresponding conditions, at temperatures up to 38° , and probably higher. These ripples flow downwards in the vapor phase, adhering to the glass.

2. An increase in the volume of localized "liquid" results, above the critical temperature, in ripples or striæ which flow upward, without any tendency to adhere to glass but rather the opposite, till they reach the localized "vapor." Below the critical temperature these ripples or striæ are replaced by bubbles, rising to the meniscus. There is no break in this phenomenon at the critical temperature, except as to definiteness of outline.

3. Résumé of the evidence for the existence of liquid above the critical temperature; and a discussion of divergent views concerning the nature of the critical state, in favor of the theory of complete mutual solubility of the liquid and gas.

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