

Fig. 7. Spores in the elongated rods; *a* is an example of a single spore formed at one end of each segment of protoplasm.

Fig. 8. Various phases of spore (coccus) formation in the tubes; *a* is an example of spheres in the protoplasm of an unsegmented rod; *b*, chains of spores (or cocci), in which remains of the tube, although hardly to be represented clearly in a drawing without exaggerating the appearance, are yet distinctly visible. In estimating the size of *b*, it is to be borne in mind that both the spores and the sheath make up the dimensions as they are shown.

Fig. 9. Micrococci or spores set free from scum, which is partly formed by rods in the various phases shown in the preceding figures.

III. "On the State of Fluids at their Critical Temperatures."

By J. B. HANNAY, F.R.S.E., F.C.S. Communicated by Professor G. G. STOKES, D.C.L., &c., Sec. R.S. Received May 24, 1880.

In carrying out the investigations which I commenced some years since upon the phenomena presented by the flow of different liquids through capillary tubes, the question as to what constitutes a liquid—that is in what way it differs from a gas, and how the great variance of the microrheometrical laws for the two fluids can be explained—again and again presented itself to me. Seeing that solids are soluble in gases as well as in liquids, one of the chief differences supposed to exist between the two states has disappeared; and I have been compelled to adopt as the only definition of a liquid, that it is a fluid which has cohesion. Professor James Thomson, F.R.S., has suggested to me the use of the term contractility, instead of cohesion, and this term admirably defines the liquid state, but as it suggests (in a distant way perhaps) a voluntary power, and is used in connexion with organised structures, I shall retain the term cohesion at present. We have then the two states of fluids, first, the gaseous, in which the *vis viva* or heat energy of the molecules has entirely overcome cohesion, or their mutual attraction, and they are prevented from grouping; and second, the liquid where the attractive power is greater than the *vis viva*, and the molecules are enabled to group themselves, but still are in sufficient motion to prevent the grouping from being permanent, hence we have cohesion, but no rigidity. We do not yet know that all solids are not also fluids, as many of them are known to flow, but this may be from other causes, but we know that the solid state is characterised by so much cohesion as to produce more or less rigidity. The most interesting point in the consideration of a liquid is that at which it approaches to the gaseous state, where its cohesion disappears, and we have what Dr. Andrews has termed the critical point, which is the termination of that property which distinguishes a liquid fluid from a gaseous fluid, or in other words the liquid be-

comes a gas. But a question arises. To observe this disappearance of the cohesion of a liquid, it is requisite that it should have a free surface, and this free surface has till now only been obtained by arranging the pressure that a portion of the fluid is in the gaseous state, and this only occurs at one pressure. Now, when the temperature of a liquid is raised while it is retained under very great pressure, so that it never has a free surface, but is always retained filling the vessel, does the liquid still lose its cohesion, and become a gas at the same temperature; or, as the pressure is increased, does the temperature at which the cohesion of the liquid is overcome, also rise? In the former case, the limit of the liquid state would be an isotherm, in the latter, a continuation of the boiling line. To determine which is the object of the work here described.

With proper precautions, the loss of cohesion or capillarity can be noticed very accurately, and the level of the liquid in a fine capillary tube, seen to coincide with the plane surface of the liquid just before the final disappearance of the line of demarcation. One of the precautions to be taken is to obtain equable temperature, and while in my earlier experiments, I used a double air-bath, and considered this sufficient to obtain good results, I subsequently found that by the use of a triple bath of copper, every trace of irregularity of temperature disappeared, and I obtained results in which the line of division was admirably clear and sharp, and never became broad and hazy as in ordinary experiments. Another precaution to be taken is to have pure liquids, and this at first sight might appear to be an easy matter, but I find that in transferring a portion of a pure liquid to a tube, the momentary exposure to air, especially in the vicinity of the hands, hydrates the liquid sufficiently to render the line of demarcation rounded, and show a slightly greater refractive power in the lower part of the tube after the critical point has been passed. In the case of liquefied gases, such as carbon dioxide, ammonia, sulphur dioxide, and nitrous oxide, which are easily dried, the line is beautifully sharp, and the disappearing point easily noted. Alcohol cohobated over caustic lime for a week and transferred to a tube without contact with air, shows the disappearance of the line with great sharpness, and immediately after no difference in refractive power can be detected between the upper and lower portions. The least trace of moisture is sufficient to show such a difference. Whenever I notice any difference between the upper and lower portions after passing the critical point, I attribute it to moisture or other impurity, as careful treatment always removes the difference in density. In many organic liquids there is always a difference at the critical point, and sometimes before reaching this temperature, they form several layers, each having a different critical point as they seem to give rise on heating to new compounds, or form polymeric compounds having different critical points. Besides,

many organic compounds cannot be entirely freed from impurity, as they retain it even on repeated distillation. In the following experiments, therefore, such organic compounds were never used, and only perfectly anhydrous alcohol, or carbon disulphide,* or gases which can be obtained anhydrous, CO_2 , SO_2 , and NH_3 , being chosen. The apparatus used for obtaining pressure was that described in a former paper ("Proc. Roy. Soc.," No. 201, 1880, "On the Solubility of Solids in Gases"). In order to determine, then, whether increased pressure applied above the critical point, would have the effect of reducing the gas to a liquid, as might easily be supposed, since the rates of expansion of gas and liquid become alike at the critical point, a new form of experiment was resorted to. It had been noticed that it was easy to determine whether the tube were filled with liquid or gas, by simply reducing the pressure somewhat quickly, when, if there were liquid present, it boiled, while if the contents were entirely gaseous, simple expansion was the result. The boiling only takes place when the pressure is reduced so far as to be a little under the vapour pressure at that temperature, in other words, boiling cannot be observed, unless there exists a free surface, and this free surface cannot be obtained with the liquid alone above the "critical pressure." By the introduction of a quantity of hydrogen gas over the liquid, a free surface is obtained at any pressure, and the mixture of hydrogen and alcohol vapour being of so much less density than the alcohol, it remains divided from it by a line of demarcation for some time after the latter is undoubtedly gaseous. Now, let us see what takes place on lowering the pressure. When the temperature is even only 1°C . below the critical point, when the pressure is sufficiently reduced, the alcohol boils, showing that it still has cohesion, but if the temperature be 1° above the critical point, the fluid only expands, and no boiling is seen at any pressure, from 50 up to 200 atmospheres. Here the fluid above the critical point has just as free a surface as below it, and we see that the last trace of the liquid condition has disappeared. The line dividing the mixture of hydrogen and alcohol vapour from the pure alcohol is quite sharp, for a short time, and on altering the pressure, it moves up and down quite freely, and possesses exactly the same appearance and properties as hydrogen over carbon dioxide in a bell-jar.†

Thus we see that the liquid state seems to come to an end, and the gaseous state to supervene quite independent of pressure.

* Even this, in later experiments, has been found to dissociate slightly. (June 14, 1880.)

† The experiments must be done quickly, before the alcohol has time to dissolve the hydrogen to any great extent, and the temperature must be equal all through the apparatus, otherwise mixture takes place and these phenomena are not seen. Experiments on mixtures obtained by shaking are in progress, but in these the critical point is much altered.

There is another mode of experimenting which illustrates this even more strikingly. A quantity of alcohol with hydrogen over it was raised to a temperature of 228° to 230° under a pressure of 120 atmospheres, and the pressure and temperature maintained for five hours, when it was seen that the line of demarcation was in the same place, and as sharp as before, and on lowering the pressure, the liquid boiled, showing that it had not mixed with the gas. The temperature was now raised to 240° , and the pressure as before, at 120 atmospheres, and at the end of a quarter of an hour, instead of a sharp line of demarcation there was only a faint, broad indication of a change of density near the middle of the tube, and at the end of an hour all mark of a difference had disappeared, the two gases having mixed. Doubtless, the mixture was not yet uniform, but it had proceeded sufficiently far to show that the two were miscible. Here we see plainly, that a few degrees below the critical point, the substance was undoubtedly liquid, and a few degrees above, undoubtedly gaseous. The experiment was repeated at 200 atmospheres' pressure, the temperature being 220° and 240° , with precisely the same result, and I have since repeated it several times. This shows that the limit of the liquid state depends upon temperature, and not upon pressure.

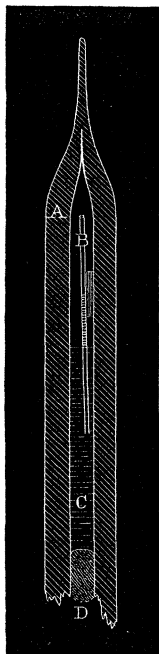
The method of examining the loss of cohesion of a liquid by means of a capillary tube was also applied at any pressure by the introduction of a permanent gas over the liquid, as in the foregoing experiments. This was done as follows.

In the working tube of the pressure apparatus A, a small piece of capillary tubing B, was cemented by fusing a minute piece of silicate of soda between it and the side of the tube. The liquid C, which was in this case carbon disulphide, was placed in the tube over the mercury, and readings taken of the height of the liquid in the capillary tube. In order that the same liquid should be used in both cases, and the experiments thus rendered strictly comparable, the point of A was broken off, and a quantity of pure dry nitrogen introduced. Pressure was then applied, and the capillarity noted, the temperature raised, and the result again noted. The following table illustrates the results obtained. The capillary heights are arbitrary numbers of the cathetometer: ten experiments were done in each case.

Liquid alone.			Liquid with nitrogen.		
Temp.	Pressure.	Height.	Temp.	Pressure.	Height.
51° ..	1 atmos. ..	53.6 ..	51° ..	81 atmos. ..	53.2
220° ..	63 ,, ..	12.2 ..	220° ..	180 ,, ..	11.9
Probable error					
of mean		0.7 ,, ..	0.2	1.1 ,, ..	0.25

The experiments were then pushed up to the critical point when, in both cases, the one at 80 atmospheres and the other at 194, the capil-

larity disappeared. This again shows that pressure has little or no effect upon the cohesion of a liquid, and that it is reduced to zero at about the same temperature notwithstanding the pressure.



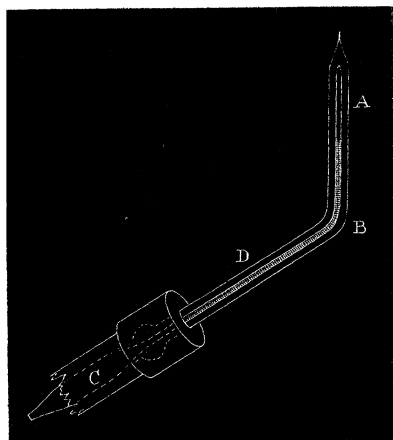
It would appear, then, that the boiling line does not extend beyond the critical point, but that the critical point lies upon an isothermal, which is the limit of the liquid state.

I have examined several liquids and liquefied gases, including CO_2 , NH_3 , SO_2 , N_2O , CS_2 , CCl_4 , Cl , CH_4O , $\text{C}_2\text{H}_{10}\text{O}$, and $\text{C}_2\text{H}_6\text{O}$, and I find that the capillarity disappears at or near the critical point, and pressure does not cause it to reappear.

I have also measured the rate of decrease of capillarity with temperature, but have not yet had time to reduce the arbitrary readings to actual measurements to find whether or not any systematic relation exists. I shall bring this work forward at some future time.

I have still another method of examination to bring before the Society. An apparatus was arranged with the tube for experimenting with the liquid bent at an obtuse angle, as shown in the sketch. The liquid was contained in the upper part, A, inclosed by the mercury, B; while the lower part, C, inclosed in the apparatus, was filled with nitrogen or other permanent gas. On applying pressure the nitrogen is compressed into small space, and by gently tapping the

tube is made to rise to about D, where it rests against the upper side of the slanting part of the tube. When the temperature and



pressure required were reached the tube was gently tapped, when the bubble of nitrogen passed round the bend up into the fluid at A. If the fluid be in the liquid state, the bubble shows a meniscus ; but if the fluid be gaseous, the bubble instantly diffuses into the inclosed space, showing that the fluid has no cohesion or has assumed the gaseous state. The same results were obtained as before. When the temperature was below the critical point the contents of the tube were liquid, and when over that temperature the reaction was always gaseous, notwithstanding the variations of pressure.

I think that we have in these experiments evidence that the liquid state ceases at the critical temperature, and that pressure will not materially alter the temperature at which the cohesion limit occurs. Dr. Andrews has, indeed, indicated his belief that such was the case ; but as far as I am aware, there has been till now no direct experimental proof of the fact. When the line dividing the fluid from the gas, and the difference in height outside and inside the capillary tube disappear, it cannot be said that this proves the total absence of cohesion, but only that the cohesion of the two portions of the fluid becomes equal ; and it is only if the gas or vapour has no cohesion that we can say that the portion which formed the liquid has none either. But by the introduction of a third substance, which, when the experiments are done quickly, acts only on one side, it seems, from the results observed, that the condition of the surface of demarcation depends mainly, if not entirely, upon the lower or liquid portion of the fluid. The critical points of liquids are thus truly the absolute boiling points, as has been aptly said, and are closely comparable to

the melting points of solids, which depend almost solely upon temperature, a very great amount of pressure being required to alter them.

The difference between the fluid and gaseous states is not then entirely dependent upon the length of the mean free path, but also upon the mean velocity of the molecule.

June 14, 1880.

IV. "On the Solubility of Solids in Gases. II." By J. B. HANNAY, F.R.S.E., F.C.S. Communicated by Professor G. G. STOKES, D.C.L., &c., Sec. R.S. Received May 24, 1880.

In a former paper* it was pointed out that a solid dissolved in a liquid was not deposited from solution when the liquid passed through the critical point into the gaseous state, and the conclusion drawn that solids are soluble in gases. I have shown in another paper † that it is probable that after a liquid passes its critical point it becomes a vapour or gas, and this quite independent of pressure, and that the cohesion limit for any one substance lies more in the direction of an isothermal line than a continuation of the boiling line. Before, however, I had carried out that work, I determined to make sure that a truly gaseous state had been reached, and the fluid containing the solid was raised to 150° above its critical point, and the gaseous solution expanded to nearly twice its liquid volume, and still the solid remained in solution. In these circumstances it was found that non-volatile solids were retained in solution in truly gaseous menstrua. In the second paper referred to, I have pointed out some of the difficulties which beset such an investigation; and when it is remembered that only air-baths can be used, the temperature being over 200° and sometimes over 300° , and that very many liquids dissociate under these temperatures, it will be seen that conclusions should be drawn only from substances perfectly free from suspicion. All the experiments, therefore, which I have performed in iron tubes cannot bear on a discussion in this matter; and I shall defer going into the natural minerals formed artificially from aqueous solution at a red-heat till another paper. For high temperatures glass does not do, as every variety of it is easily decomposed by water; but by the use of rock crystal blocks I have obtained some results of interest where the action of the water can be seen. However, I intend in this paper to treat in a fuller manner of work touched upon in former papers. One of the first pieces of work I set about to finish was to determine whether or not the critical points were altered by the introduction of a solid into solution.

In a former paper it was thought that the critical point of alcohol

* "Solubility of Solids in Gases," "Proc. Roy. Soc.," *ante*, p. 178.

† "On the State of Fluids at their Critical Temperatures," *ante*, p. 478.

