normal incidence from a normally magnetized mirror becomes of great interest, in order to decide whether Sissingh's phase has the same value at all incidences. This investigation, of great importance to judge on the exactnes of the description of the phenomena by Goldhammer's theory, is therefore prepared in the physical Laboratory of the Leiden University.

Dr. J. P. KUENEN *On the abnormal phenomena near the critical point.*

Various phenomena are seemingly opposed to Andrews's clear conception of the connection between the liquid and the gaseous states of matter and the signification of the critical point 1). In the first place the disappearing and reappearing of the liquid surface at other volumes than the critical volume, the explanation of which phenomenon Stoletow 2) finds in the smallness of the difference between the indices of refraction. Accurate observation of the phenomenon suffices to render this hypothesis improbable: at a given moment independent of the illumination the surface is seen to lose its clearness and to change into a layer of transition, as with two liquids mixing. Moreover the disappearing-temperature would not alter with the volume, which on the contrary it does (vid. below).

Cailletet et Hautefeuille 3) and Cailletet et Colardeau 4) conclude from their experiments with a solution of iodine in carbonic acid, that the liquid and vapour

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1) cf. Ramsay Pr. R. S. of L. 30 p. 323.

2) Physik. Revue II Juli 1892. p. 44. 73.

3) C. R. 92 p. 840, 1086.

4) C. R. 108 p. 1280.

still exist above ANDREWS's critical temperature, but acquire the property of mixing together. However the fact is sufficiently explained by the slow diffusion of the iodine through the carbonic acid; there is no necessity of adopting the influence of differences of temperature as STOLETOW [1]) does.

They confirmed the experiment by another with an O-tube,[2]) on which PELLAT [3]) based his distinction between the real critical temperature, at which the densities agree and the lower temperatures, at which the surface disappears. The problem was further examined experimentally by ZAMBIASI, [4]) who began by confirming the experiment with the O-tube with ether. Then he found, that the disappearing temperature increased according as the quantity of liquid was smaller. DE HEEN [5]) on the contrary finds that the temperature is higher the smaller the quantity of vapour is.

New light has been thrown upon the problem by GOUY's [6]) extensive and accurate investigation, in which he shows that a distinction should be made between the *état final* of the substance and the *états variables*, differing from it. He furthered the establishment of equilibrium by repeatedly turning the Natterer-tubes filled with CO_2 and thus found that the disappearing

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[1]) l. c. p. 63.

[2]) C. R. 108 p. 1284.

[3]) Journ. de Ph. (3) 1. p. 225.

[4]) Atti Acc. Linc. (5) I. 2. p. 423.

[5]) Bull. Ac. R. des Sc. de Belg. (3) 24. p. 96.

[6]) C. R. 116 p. 1289. June 1893.

of the surface in the état final is observed within very narrow limits of density only (0.438 and 0.470; critical density = 0.464 Amagat) and that with densities outside these limits, the disappearing is possible only when the equilibrium has not yet been attained. [1]) the fact, that even in the état final the surface disappears at different volumes and not merely at the critical volume, as follows from ANDREWS's theory, GOUY [2]) ascribes to the influence of gravitation. The truth of this conclusion is evident: it will easily be seen, that within certain narrow limits near the critical volume the surface may disappear at different heights in the tube and always exactly *at the critical temperature*, [3]) whilst there, where the surface is disappearing, we find the critical pressure and the critical density.

Two earlier observations by DE HEEN [4]) are in accordance with GOUY's experiments. One tube in which the surface had disappeared was reversed and then cooled, whereas another tube remained in its former position. In the latter the surface reappeared nearly at the same point, where it had formerly disappeared, in the former however a cloud spread through the tube. In

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[1]) The limits of the phenomenon are very wide in this case, as with the experiments with ether. Here it was observed by ZAMBIASI and DE HEEN within the volumes 2,6 and 6,2, whereas the critical volume amounts to 4,0 (ccm per gram).

[2]) l. c. and C. R. 115 p. 720.

[3]) The disappearing-temperatures seem indeed to have shown but minimal differences in GOUY's experiments too; vid. the final points of the two curves.

[4]) l. c. 24 p. 277 and 25 p. 14,15.

a second experiment a tube was heated at 35° C. for 24 hours: at cooling a cloud spread through the tube, which was dissolved into a thin liquid layer upon the mercury, though the surface had disappeared at a much higher point. In the former case the état final was brought about by reversion of the tube, in the latter by time.

Before being acquainted with GOUY's work and DE HEEN's last experiments I had concluded from the experiments which were known at that time, that with the disappearing of the surface we had to do with retardation [1]), and have succeeded in showing in a way different from GOUY's that the deviations from theory vanish if the substance is well mixed. To this end I made use of my electromagnetic stirring-apparatus, employed by me in my investigation of mixtures [2]). As I pointed out in my treatise and was also shown by DE HEEN's experiments, the cooling (resp. expansion) proves an excellent means to distinguish homogeneous from not homogeneous states. The critical volume of the carbonic acid investigated by me amounted to ± 35, expressed in an arbitrary unit. When the volume was less than 34 and the substance was rendered homogeneous bij stirring above 31° C., slow decrease of temperature pro-

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[1]) With the volume 2.9 ZAMBIASI saw the meniscus rise slowly, which is typical for a retarded process; when the O-tube was cooled an equal quantity or an unequal was observed in the branches, according as the temperature fell at once or after being raised to 196 C. etc. The influence of time was already noticed by RAMSAY l. c.

[2]) vid. Arch. Néerl. 26 p 354—422. Z. Phys. Ch. 11 p. 38.

duced at about 31° C. a cloud through the tube and then the liquid surface at the top of the tube, with volumes larger than 36 also a cloud and then the surface close to the mercury. The limits within which the surface could disappear in case of stability, are therefore no wider than 34 and 36, which distance about agrees with GOUY's.

No doubt the same result will be attained with ether, if care is taken to establish stability.

How to explain this retardation? Theoretically in a simple substance retardation may be admitted only, if one of two possible phases is entirely wanting or forms itself with difficulty, whereas observation shows, that as soon as the phase begins to form the most stable equilibrium is established in a very short time, sometimes even in the manner of an explosion. Here however we have to deal with the fact that the evaporation or condensation regularly lag behind, which reminds us of phenomena of diffusion of two substances. No doubt therefore we may assume retardation as soon as we ascribe some influence to the slight impurities of our so-called pure substances. [1])

Indeed from this point of view the phenomena may be easily explained. Only it should be borne in mind, that the amount of retardation and the direction in

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[1]) As regards ether, vid. TAMMANN. W. A. 32 p. 683. GOUY says l. c.: „Il y a lieu d'examiner si ces différences entre l'état final et les états variables ne sont pas dues à la présence d'un peu d'air mélangé au CO_2" cf. HANNAY, Pr. R. S. of L. 30, p. 478—489.

which it works depend on the nature of the impurities, in as much as some will for the greater part be found in the liquid other in the vapour. Moreover the special circumstances of the experiments (as width of the tubes rate of change of temperature, mobility of the tubes) will influence the results, so much that agreement of the results of different experimentators is not even probable (vid. ZAMBIASI and DE HEEN) [1]).

Suppose for instance some air is mixed with the ether: it will for the greater part be present in the vapour. If the volume is below v_k, the liquid will increase at rise of temperature partly because it expands partly because the vapour condenses. The latter process will now be retarded by the presence af air. Slowly according as the air is absorbed by the liquid and spreads through it by diffusion equilibrium will be attained. The liquid remains beneath its normal quantity; the densities also lay behind. Meanwhile the tube is heated above the temperature, at which all should be homogeneous; this may call forth a condition, in which the free surface between the phases is impossible. We may say, that the separating surface disappears, as soon as we attain a continuous transition between the two phases without unstable states, as the latter occasion the formation of a free surface. [2]) It is clear that a similar state of continuous transition will be attained as we approach an ordinary case of diffusion of gases.

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[1]) Consequently it is impossible to draw PELLAT's line (l. c.)

[2]) vid. v. D. WAALS. Thermodynamical theory of capillarity etc. Kon Acad. Amsterdam I, n⁰ 8. 1893.

It should be remembered in the first place, that by impurities mixed with the liquid the evaporation of the liquid will be chiefly retarded (with volumes larger than v_k); in the second place that as a rule the impurities will be so slight, that the deviations of the disappearing-temperature will be small, and even that the final state after diffusion need not necessarily differ considerably from the state of the pure substance. If we keep all this well in mind, the facts, which can be decuded from the retardation of diffusion occasioned by impurities, agree so well with observation, that we have a right to maintain this explanation as long as its insufficiency has not been proved otherwise. [1]) New theories about simple substances seem to me at present superfluous for the explanation of the critical phenomena.

Now that the great influence of retardation has once been established, we should be very careful in the acceptance of results, which have not been proved to be exempt from that influence. DE HEEN's [2]) conclusion, that vapour-density is a quantity dependent on the quantity of liquid in contact with the vapour, cannot be accepted as proved. In the first place we point out, that the vapour-densities calculated especially when they turn out so much greater, are obtained by the division of two small magnitudes and therefore must of necessity be uncertain. Besides the retardation in

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[1]) The details of the experiments with the O-tube and the other experiments mentioned are likewise in accordance with the explanation laid down here.

[2]) l. c. 24 p. 267—285.

those cases must have diminished the quantity of liquid and will so have caused a too great value for the density. The experiment with the U-tube 1) too proves nothing but that absolute homogenity is very slow in coming: from the experiments we may only conclude, that the influence of the retardation is perceptible even at temperatures far below the critical.

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1) l. c. 24 p. 278. sq.

COMMUNICATIONS
FROM THE
LABORATORY OF PHYSICS
AT THE
UNIVERSITY OF LEIDEN
BY

PROF. DR. H. KAMERLINGH ONNES.

No. 9.

Dr. C. H. WIND. Measurements regarding the SISSINGH magneto-optical phase difference in the case of polar reflexion from Nickel.

(*Translated from: Verslagen en Mededeelingen der Kon. Akad. v. Wetenschappen te Amsterdam*, **27 Januari 1894**, *p.* 116.)

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