Dr. J. P. KUENEN. *Further experiments regarding the anomalous phenomena near the critical point.*

In inspecting the three Tables I, II and III of my former communication [1]) one is struck at once by the difference between the Tables I, III on one and II on the other side. While in II the values of A, i. e. the differences of density expressed in percents, are always positive and proportionally large, in I and III these differences are small and in the beginning negative. The fact, that Δ i. e. the difference of pressure has a different sign in II from that in I and III leads to the supposition that these quantities A en Δ are connected together. But one glance is sufficient to see, that the explanation of the differences of density in this way cannot be complete. The value of A in proportion to that of Δ is much too high for that in the second series compared with the 1st and 3d series, while besides the positive values of A in I and III don't agree with that suppositon [2]). Closer inspection shows

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[1]) p. 20—21.

[2]) These positive values are smaller than 1 percent; as the possible errors in my results were estimated to be as large as that, I do not think much worth ought to be attached to these positive numbers.

us, that an influence must have existed to make the density at the liquid-side too large. It lies at hand to look for that influence in the presence of the permanent gas, which was discussed in the above communication. In order to test this idea I transported the greater part of the gas to the liquid-branch and repeated the measurements (v and l indicate the same sides of the tube as in I, II and III).

IV. 4th series. At high temperature pressure higher at the vapour-side (Δ positive).

Temp.	v_v	v_l	$\frac{v_v}{v_l}$	Δ	σ_v	σ_l	$A(\%)$
195.0	64.65	20.09	3.22	13.1	0.264	0.218	—19
196.0	66.09	18.65	3.54	16.2	0.258	0.235	—9.5
198.0	66.67	18.03	3.70	17.5	0.256	0.243	—5
207.6	67.21	17.33	3.88	18.6	0.254	0.253	—0.5
223.0	67.14	17.21	3.90	18.7	0.254	0.254	+0.1
15.0	23.70	6.08	3.90	—6.6	0.72	0.72	—

Taken on itself the Table now obtained confirms the general conclusion, stated at the end of the former paper, i. e. that the differences of density become imperceptible at 10° C above the critical temperature. What regards the influence of the gas, the meaning of this Table becomes most evident bij comparing it to I. Accidently the quantities at ordinary temperature were exactly the same in I and IV and the differences between the A's must therefore entirely be ascribed to the fact, that in I the gas was for the greater part present at the vapour-side, in IV at the liquid-side of the tube: hence it appears, that a small quantity of gas, especially quite above the critical temperature, has a great influence upon the volume viz. increases it very remarkably [1]). This conclusion is confirmed by comparison with II. In both II and IV the gas was in that branch of the tube, where the pressure at high temperature was smallest. Both causes (difference of density and gas) therefore acted in the same direction and accordingly the values of A are large (naturally of different sign).

In order to show how small the quantities of gas are, that can produce differences as those between I and IV, I have, admitting that in III no gas was present at the liquid-side of the tube, calculated from the values of Δ at ordinary temperature the proportion of the gas to the ether expressed in the volume of the vapour and I have found:

	I	II	III	IV
x_v	0.000086	0.0000138	0.000095	0.000029
x_l	0.000026	0.0000015	0.000000	0.000247

Solution of the gas into the ether is not taken into account here.

I have not succeeded in calculating from the Δ's observed and the x's given above numerical values of A agreeing with those observed. This may for a part have been caused by disturbing circumstances in the experiments (viz. a small impurity of a different kind etc.) but by the uncertainty of the calculations as well,

[1]) The Δ's were smaller in IV than in I; hence the A's ought to have been smallest in IV; the conclusion about the influence of the air is thereby strengthened still more.

for which use had to be made of CLAUSIUS's formula for ether and of DALTON's law for the mixtures. It is improbable that the course of the isorthermal lines quite above the critical temperature should be rigorously rendered by CLAUSIUS's formula. It is a known fact that this formula, though in a less degree than VAN DER WAALS's equation, generally gives wrong values for the critical volume, which fact of course is very nearly connected with the course of the isothermal lines. It is equally doubtful, whether DALTON's law holds good for these small impurities quite near the critical point. I must therefore be content with the following conclusion: GALITZINE's *experiment executed with nearly gasless ether, furnishes differences of density for the greater part to be explained by the differences of pressure and the gas still present. The remaining differences are of uncertain origin and at 10° C above the critical temperature amount to nearly 2 % in one case only, to less than 1 % in the other cases.*

We must add a word about the origin of the permanent gas and its influence on the determinations of volume. In the former communication I ventured to bring forward the hypothesis, that the gas is originated by the sealing of the tube. The same opinion is expressed by RAMSAY and YOUNG in a recent note in the Philosophical Magazine [1]). I have since been able to confirm this by direct experiment: a tube of GALITZINE, of which the glass had been drawn into a very thin point in consequence of which it had to be heated only a small

[1]) Phil. Mag. (5). 37. p. 503—504.

time during the sealing, was filled in the manner explained before. This time in fact the quantity of gas appeared to be very small: the difference of pressure amounted to 1.4 mm. only. Now the point of the tube was heated for some time, in consequence of which the difference of pressure had now increased to circa 5 mm. It does not seem possible to explain this otherwise than by decomposition of the ether.

The result obtained above as to the large influence of small quantities of gas is highly important for different experiments near the critical point. It cannot be derived fom these experiments, how large the influence is of a definite quantity of gas in case of a *direct* determination of the critical volume. It is a remarkable fact however, that the direction of the slow movement of the liquid surface in the neighbourhood of the critical temperature as also observed by GALITZINE [1]) from which he concludes: »In der Nähe des kritischen Punktes sind δ und ρ keine constanten Gröszen: ρ nimmt mit der Zeit und nach mehrmaligem Erwärmen über τ_c hinaus ab und δ zu" (ρ density of the liquid, δ of the vapour) agrees, with what might be expected from the results obtained here, if this movement was to be explained by a slow solution of some gas from the vapour-phase into the liquid-phase. This circumstance gives aid to the opinion, expressed in my former papers on this subject [2]),

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[1]) Wied. Ann. 50 p. 540.

[2]) Communications etc. n°. 8, n°. 11. This opinion is also confirmed by some recent experiments of VILLARD, C. R. 118. p. 1096.

that the anomalous phenomena near the critical point depend on the presence of some permanent gas.

In connection with the result obtained above we are led to suppose, that large differences of density, as obtained by GALITZINE, may be the consequence of a large quantity of a gas in the vapour-branch of the tube. It was mentioned before [1]) that the presence of much gas in the tubes, investigated by GALITZINE, was very probable, because his observations did not change by admitting air into the tube. In order to establish this point with certainty the new tube, mentioned above, was investigated at high temperature; afterwards the point was broken, a large quantity of air was admitted by cooling the tube, the point was closed again and the measurements were repeated. The values of A are laid down in the following Tables.

a. Before adm. of air.

Temp.	Δ	A (%)
197.3	—8.6	+2.3
199.6	— 8.9	+1.4
202.3	—9.6	—0.2
204.1	—9.2	+0.5
223.5	—9.4	+0.2
15	+1.4	—

b. After adm. of air.

Temp.	Δ	A (%)
197.9	—6	+32
207.3	0	+18
223.2	+4	+ 8.8
15.0	?	—

In table *a* x_v amounts to 0.000014, a very small value. In *b* x_v cannot be determined in the same way because Δ is unknown. Table *a* entirely confirms our former

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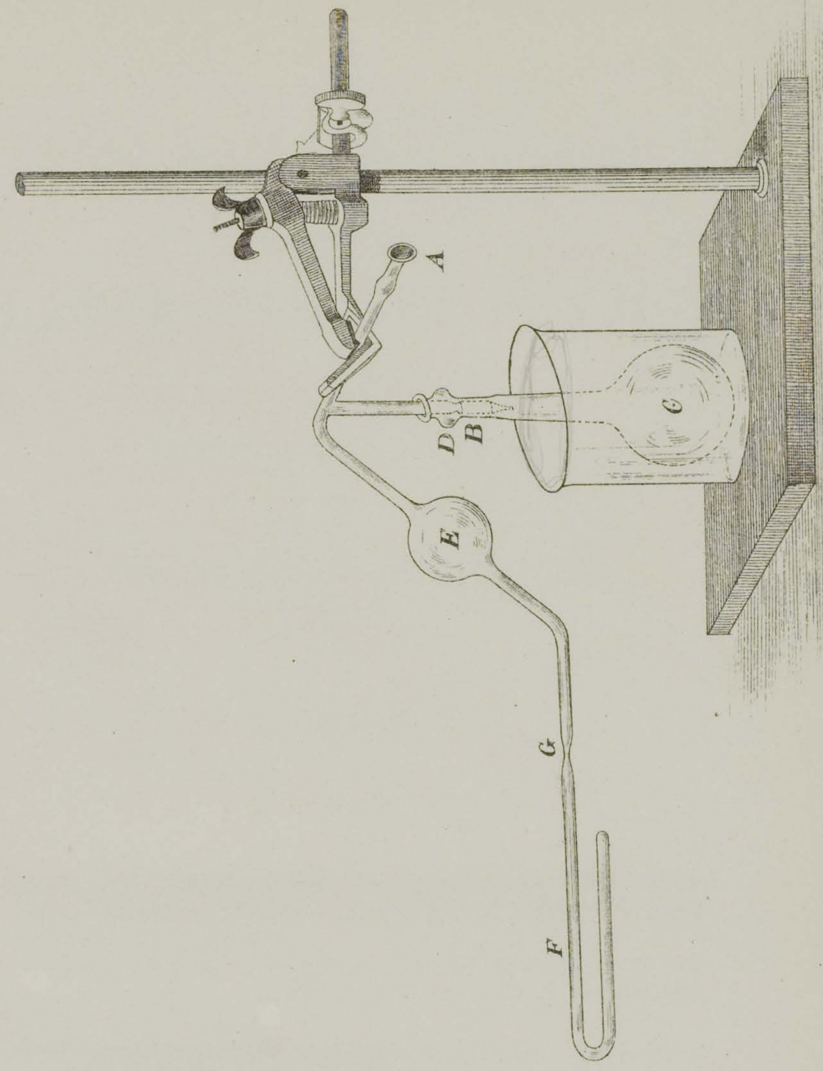
[1]) c. f. the former communication p. 9.

result; Table *b* proves our supposition about the influence of a large quantity of air to have been right. As by accident Δ was very small in this case, the large values of it must entirely be derived from the influence of the air. This result justifies the supposition, that GALITZINE'S numbers, being of the same magnitude and the same direction, must at least for the greater part be explained by the presence of gas (air?) in the vapour-branch of his tubes.



Kuenen. Critical point (25 Mei 1894).
Commun. Labor. of Physics Leiden N°. 11.