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

In a former communication on the same subject <sup>1)</sup> I was led to the conclusion, that the phenomena near the critical point observed by different experimenters do not lead to the accepting of a new theory about vapour and liquid of a simple substance, that the ordinary theory, which may be called the ANDREWS-VAN DER WAALS theory, is in harmony with all observations, if only the influence of impurities, of retardation, connected with it, and gravitation is taken into account. Since then some new investigations about the critical point have been published, of which especially those of BATTELLI <sup>2)</sup>, GALITZINE <sup>3)</sup> and WESENDONCK <sup>4)</sup> deserve to be mentioned. For the greater part these observations are the same or of the same kind as those described by ZAMBIASI, DE HEEN, GOUY etc. before, and to those therefore refer the considerations laid down in my

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<sup>1)</sup> Verslagen Kon. Akad. van Wet. Afd. Natuurkunde 1893/1894 Oct. p. 85—90. Communications etc. n<sup>o</sup>. 8.

<sup>2)</sup> Ann. Ch. et Phys. (6) 29 p. 400—432.

<sup>3)</sup> Wied. Ann. 50. p. 521—545.

<sup>4)</sup> Naturw. Rundschau 9. 209—212.

former paper <sup>1)</sup>. In the meantime an important note has appeared by RAMSAY and YOUNG <sup>2)</sup>, in which depending on experimental labour of years they unreservedly declare, that the anomalies do not belong to the real conduct of bodies and can be entirely explained by disturbing circumstances (differences of temperature, impurities etc.). The importance of this note is still more enhanced by the fact, that RAMSAY had been the first, starting from observed irregularities, to set up a new theory <sup>3)</sup> and now, with his collaborator YOUNG, declares his observations to have been caused by the presence of impurities.

In the 5th paragraph of his paper GALITZINE describes a new experiment, which he supposes to confirm, what he calls »die neueren Anschauungen über die Molekularvorgänge in Flüssigkeit und Dampf» having in view the theories as brought forward by DE HEEN <sup>4)</sup>,

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<sup>1)</sup> In WESENDONCK's paper for instance an observation is described, the explanation of which seems to be easy. A Natterer-tube heated quite above the critical temperature and therefore apparently quite homogeneous, showed mixing-phenomena (striae, cloudy appearance) by being turned at constant temperature. When it is considered, that in consequence of gravitation the density and, if some impurity is present, also the composition of the mixture varies regularly with the height in the tube, the observed fact can but appear quite natural.

<sup>2)</sup> Phil. Mag. (5) 37 p. 215—218. Vid. Young, Trans. Chem. Soc. 59, p. 128.

<sup>3)</sup> Pr. R. Soc. of L. 30 p. 323.

<sup>4)</sup> Physique Comp. 1888. Bull. Ac. r. de Belg. passim. o. a. 24 p. 281.

BATTELLI <sup>1)</sup> a. o. Into an U-shaped tube he introduces two quantities of ether separated from each other by a column of mercury; one is entirely liquid at ordinary temperature, the other in part vapour. This tube is heated beyond the critical temperature and the volumes occupied by both quantities are measured. With three tubes investigated in this manner GALITZINE finds large differences of density between both branches of the tube, diminishing with rising temperature, but at 15° or 20° C above the critical temperature still amounting to 20%; the larger density he always finds at the liquid-side of the tube independently from the relative height of the mercury in the two branches of the tube. These differences were not of a transitory nature, but did not change in the course of 1½ hour, and are supposed by GALITZINE not to be connected with the presence of air, as he derives from the fact, that admittance of air at the vapour-side of the tube did not change the phenomena to a large extent. It does not seem to me to be superfluous in connection with this experiment rigorously to formulate the »neueren Anschauungen» and to see, which form they must assume, in order not to be inconsistent with GALITZINE's and other experiments. This is necessary, because the theories of DE HEEN, BATTELLI a. o. cannot be said to have been developed very precisely, so much so that, as will appear, they lead to results contradictory to observed facts, which they are supposed to explain. If starting from GALITZINE's experiment we accept his

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<sup>1)</sup> Ann. Ch. et Ph. (6) 25 p. 38. 26 p. 394. 29 p. 239, 400.



explanation of his observations as right, we are led to the hypothesis, that at least two different kinds of ethermolecules exist, of which one is lighter and chiefly present in the vapour, the other denser and for the greater part existing in liquid ether. We may now make two different suppositions. The first is, that these two kinds of ethermolecules (liquid- and vapourmolecules) can pass into each other, that is to say that the liquidmolecules are to be considered as compounds of vapourmolecules, as is also admitted by DE HEEN <sup>1)</sup>. The hypothesis in this form we will call Hypothesis I. This Hypothesis I is not inconsistent with the ANDREWS-VAN DER WAALS's theory taken in a general sense. Many observations of late show the probability, that in many cases the transformation of a vapour into a liquid consists for a part in the formation of such complexes of molecules. The formation of these complexes can commence in the homogeneous state already and will especially take place to a large extent quite above the critical temperature, where the density changes so rapidly. Unattacked however remains, if not the form and the derivation of VAN DER WAALS's formula, still the existing of a system of unambiguously determined isothermal lines, the property that one point of the  $p$ - $v$ -diagram represents only one state of equilibrium with determined  $p$ ,  $v$ , and  $T$ , in which exists a definite proportion between the number of simple molecules and complexes of molecules. In this way it at once appears, that the hypothesis I is unable to perform, what it is meant to do, viz. to explain

<sup>1)</sup> l. c. „molécules liquidogènes”.

GALITZINE's experiment and on the other hand, that his experiment cannot confirm the hypothesis, taken in this manner. For according to this theory differences of density as found by GALITZINE in the homogeneous state at the same temperature and pressure, ought to disappear gradually, as the stable condition is attained, in which the same proportion of simple and compound molecules is found at both sides. The contrary has been observed by GALITZINE, as was mentioned above. We come to the same conclusion as to other anomalous phenomena, which are supposed to be explained by hypothesis I, as for instance the small slope of the lines, which indicate the coexistence of two phases in the  $p$ - $v$ -diagram, a well-known phenomenon, recently again observed by BATTELLI <sup>1)</sup>, who even from his observations calculates the relative number of compound molecules. The application of the thermodynamical rule for deriving the possible phases from the system of isothermal lines (GIBBS) must in this case take place in the ordinary way and at definite temperature only one pressure and one possible composition of both coexisting phases is found. In absolute contradiction with this same conclusion is one of DE HEEN's <sup>2)</sup> experimental results, viz. the difference of density of saturated vapour in the presence of more or less liquid, which fact he maintains to be entirely explained by the new theory! A clearer

<sup>1)</sup> Ann. Ch. et Ph. (6) 25 p. 66. 29 p. 242. BATTELLI's opinion, that the curvature of the straight line at the end is connected with the course of the theoretical isothermal line (J. J. THOMSON), also arises from a misconception.

<sup>2)</sup> l. c. 24 p. 281.

proof of the unsatisfactory way in which the theoretical question has been treated by the originators of the »neueren Anschauungen" is hardly possible <sup>1)</sup>.

If therefore it is thought necessary as by DE HEEN and others for the explanation of the anomalous phenomena observed to call to assistance the hypothesis of the compound molecules, only one way lies open viz. to suppose, that the two different kinds of molecules are different in nature and cannot pass into each other. We call this: Hypothesis II. According to this supposition vapour-molecules issuing from the vapour of ether might solve into liquid ether and perhaps be condensed into the fluid state, but the liquid originating thus would not be liquid ether but only condensed vapour of smaller density than real liquid ether. On the other hand ether might evaporate, but this vapour would not be vapour of ether, but evaporated liquid of larger specific gravity than real vapour and other properties, which the experimenter should learn to distinguish from those of ordinary vapour. Between these extremes in both liquid and vapour different modifications would be possible, formed

<sup>1)</sup> Independently from the questions discussed here it might be asked, whether this Hypothesis I would not have the advantage of explaining the retardation without the influence of impurities being admitted: the dividing of the liquid-molecules into the vapour-molecules might take some time. It is to be observed however, that this time ought to be extremely long (Gouy sometimes had to keep his tubes at constant temperature during a whole week!) for which supposition no analogue exists; whereas the fact cannot astonish us, if we regard the phenomenon as caused by diffusion.

by mixing the two sorts of ether-molecules, for which therefore the *laws of mixtures* would hold good. The hypothesis in this form, which admits two kinds of ether, which must be called chemically different, would perhaps succeed in explaining some observed facts and GALITZINE's result among them, but who would like to accept it with its consequences stated above? Of these two kinds of ether (and the same would be the case with many other substances) with properties differing so widely nothing has ever been discovered in the most trustworthy experiments <sup>1)</sup> and RAMSAY and YOUNG therefore do not hesitate to declare in their note, that the experiments, which compel to the accepting of such an hypothesis (as GALITZINE's experiment) must be ascribed to experimental errors, a statement against which GALITZINE and DE HEEN <sup>2)</sup> have protested without delay.

However with regard to GALITZINE's experiment, which is perhaps the most surprising, we may not content ourselves with doubt, however justified it may be; immediately after the publication of GALITZINE's paper I set myself to repeat the investigation, in order to find out, under what circumstances such results could be obtained. For discovering differences of density, as found by GALITZINE, his method being a differential-method seems to be very fit.

It seemed of high importance to follow GALITZINE's method as faithfully as possible and to take all precautions

<sup>1)</sup> REGNAULT's observation (Mém. de l'Ac. 26, p. 375, 824) has not been confirmed.

<sup>2)</sup> Phil. Mag. (5). 27. p. 423, 424.



necessary for making a pure experiment. GALITZINE states, that in his tubes in consequence of his manner of filling them some air was probably left. This quantity will probably not have been very small <sup>1</sup> because the liquid at the liquid-side never divided (at least nothing of the kind is mentioned) not even when the mercury was higher at that side, <sup>2</sup> because the phenomena did not alter by the admitting of a large quantity of air. In order to avoid the presence of air and other impurities as much as possible, the following disposition was chosen<sup>1</sup>). The *U*-shaped tube *F* (vid. Plate) (inner diameter  $\pm 3.5$  mm.) is closed at one end (liquid-branch of the tube); the other end is connected to a *T*-tube a small sphere *E* being between them. Both open ends of the *T*-tube are provided with conical glass ground joints: by aid of one (*A*) at the end of the long horizontal tube the apparatus may be connected to a mercury-pump: to the other joint *B* a sphere *C* filled with ether may be connected. This joint is made tight by aid of the small globe *D*, which is filled with mercury: in this way the use of grease is avoided. The direction of the *U*-tube is nearly perpendicular to the *T*-piece and therefore horizontal; in this way by turning the apparatus round the first joint (*A*) the *U*-tube undergoes small changes of position near the horizontal direc-

<sup>1</sup>) The description given here pertains to the last tube examined, the results of which will be given further on. The treatment of former tubes only differed in details; where it seemed to be necessary experience obtained with other tubes has been added to the description.

tion without the sphere *C* deviating too much from the vertical position; the turning of the tube is necessary during the boiling of the mercury and the ether. The liquid-branch and a part of the vapour-branch are now filled with the quantity of pure mercury required, and the mercury is made to boil in an atmosphere of nitrogen at the mercury-pump. The sphere is then provided with a quantity of pure ether distilled from pure sodium; and some fresh sodium is added: then the ether is cooled to  $-80^{\circ}$  C, made to boil at the air-pump and then distilled into the *U*-tube by cooling this until the whole tube and the sphere *E* are full. Then it is made to boil again, until the vapour-bubbles formed can be made to disappear entirely in a moment and at last the tube is sealed under the surface of the ether at *G*; the quantity of liquid remaining in the tube was chosen so that it nearly occupied its critical volume at the critical temperature, which I succeeded pretty well in doing as a rule. In the tubes, which were filled by cooling with solid carbonic acid, it sometimes happened, that some ether was found between the mercury and the glass. It soon appeared that the cause was to be looked for in the freezing of the mercury, which contracts in solidifying. Afterwards the temperature of the cooling liquid was kept above  $-40^{\circ}$  C and the phenomenon did not show itself any more.

The *U*-tube being ready the quantity of ether in the vapour-branch was measured. All measurements at ordinary temperature were made the tube being placed in a vessel with water. The readings were taken with a cathetometer. The perpendicular position of the tube

was controlled continually <sup>1)</sup> and the glass vessel was especially chosen so, that errors arising from the refraction of the glass might not influence the results too much.

In order to make the tube ready for the measurements a part of the liquid must be transported to the liquid-branch. Notwithstanding the care, with which the glass, mercury and ether had been treated, it sometimes happened, that this operation did not go on very easily because of a sort of sticking of the mercury to the glass. This was very troublesome, because the utmost care had to be taken, lest a part of the vapour should also be introduced into the liquid-branch. Probably the reason of it was to be looked for in the surface of the glass, which by repeated heating, cleaning, boiling of the mercury etc. was perhaps decomposed a little and therefore obtained other capillary properties, which supposition was confirmed by a faint bluish colour in the wide part of the tube, as is sometimes observed in old bottles. Nothing like a chemical action between the ether and the mercury could be discovered.

An important fact, which appeared without exception, consists in the presence of some permanent gas in the vapour-branch of the tube. The ether introduced into the liquid-branch remained undivided at first notwithstanding the greater level of the mercury on that side, in consequence of the ether being almost absolutely without gas: by hitting the tube or heating it the ether

<sup>1)</sup> To a slope of  $2.4^\circ$  corresponds an error of 0.001 in a measurement of a vertical distance: the error cannot have amounted to that in my experiments.

could be made to divide and then at the vapour-side a pressure of 5 or more mm. became manifest. While by inclining the tube the ether at the liquid-side could be reunited in a moment, the same could not be done at the vapour-side, without warming the tube at the other side, though before the sealing of the tube the vapour-bubbles disappeared in a moment. The hypothesis I cannot explain this, because the difference of pressure did not disappear of itself. Moreover the whole of the ether is got from boiled liquid ether and therefore cannot contain many vapour-molecules (speaking in the language of the II<sup>nd</sup> Hypothesis). Should not decomposition of the ether be supposed to be the reason of this phenomenon? As far as I know, this probability has not been taken into account till now, though in many and manifold experiments the same thing must have happened <sup>1)</sup>. Chemical analysis might perhaps decide this question (cf. p. 26, 27). The quantities of gas as calculated from the differences of pressure expressed in weight-proportion are exceedingly small, and do not exceed 0.00002 or 0.00003.

The ether being transported, the quantities on both sides were measured at ordinary temperature, first with undivided, then with divided liquid, by means of which a calibration of the ends of the tube was obtained.

<sup>1)</sup> For instance with Natterer-tubes filled with ether. The products of the decomposition of ether by conduction through a glowing tube are: ethylene, aldehyde, hydrogen, water, methane. The decomposition of methylechloride by the sealing of the tube was formerly established by myself by means of a deposit of carbon. (Arch. Néerl. 26. p. 360.)



For the observations at high temperatures a combination of a vapour- and a liquid-bath was made use of viz. glycerine being heated by purified methylic salicylate boiling under different pressures. The bath resembles that of GALITZINE and is in principle the same as the one used before by myself <sup>1)</sup> and by Dr. E. C. DE VRIES <sup>2)</sup> for his experiments on the capillarity of ether. It seems superfluous to describe it more extensively. The U-tube was fixed to a glass rod which was put into the glycerine and fixed in a stand. In this way no inequality of temperature by conduction of heat was to be dreaded, as with a metal bar. Moreover the position of the tube was now independent from the small displacements of the liquid-bath resulting from changes of pressure in the vapour-bath. The thermometers used (0.2° C) have been compared to a standard-thermometer, which has been controlled by the Phys. Techn. Reichsanstalt in Berlin.

During the heating the following difficulty arose: GALITZINE does not mention the dividing of the liquid in the liquid-branch of the tube and it seems as if during the heating such a thing did not take place, not even with the tube in which the level of the mercury was highest at the liquid-side. With my tubes however the liquid always divided at a temperature far below the critical temperature though hardly any gas was present in the liquid-branch. Happily this point does not seem to be of high interest: for, as the

<sup>1)</sup> c. f. Arch. Néerl. 26. p. 363 sqq.

<sup>2)</sup> Dissertation. Leiden 1893. p. 17 sqq., 31.

deviations found by GALITZINE have been proved by himself not to depend on retardation, the condition of the ether in both branches can only depend upon their original contents and not upon the history of the substance between the original and the final condition: therefore it cannot make any difference, whether the ether has divided or not during the heating. But in order to anticipate the objection, that here at least a difference between GALITZINE's and my experiments exists, by means of the following device the liquid at the liquid-side was kept undivided. Through a thin copper tube situated quite above the liquid-branch of the tube within the glycerine bath a stream of water is conducted. By this means the glycerine above and around the ether cools a little and the small difference of temperature arising from that is sufficient to prevent the dividing of the liquid. Comparison of readings, with or without dividing liquid, proves the validity of the above reasoning; the readings do not differ more than must be ascribed to the uncertainty of the method.

Example: volume of the ether in the vapour-branch  $v_v$ , in the liquid-branch  $v_l$  (expressed in mm. of the tube at 15° C.)

		liquid undivided	divided
at 223.3° C.	$v_v$	40.46	40.50
	$v_l$	44.32	44.24
at 206.5° C.	$v_v$	40.73	40.70
	$v_l$	44.24	44.25

The agreement is even better than might be expected. Henceforth it appeared unnecessary to prevent the





eliminated. There existed some chance of such constant differences, as the inner tube, in consequence of the continual low pressure within the vapour-bath and the giving way of the rubber stopper, had shifted a little from its coaxial position and the stream of the vapour consequently had not the same strength on all sides.

2°. The uncertainty of the form of the liquid surfaces. The form of the surfaces was not to be observed easily in the glycerine. The heights measured on different occasions above the critical temperature lay between 1.17 and 1.26, by which in the correction ( $= \frac{1}{3}$  of the height) an error of 0.02 is possible i. e. of less than 0.1% in the volumes. The influence is more important at ordinary temperature. Not only the readings were as changeable as at high temperatures, but besides the influence on the small columns of ether to be measured is much greater: an error of  $\frac{1}{2}\%$  is not impossible there.

3°. Enclosing of drops of liquid between the mercury and the glass. It was impossible entirely to collect the liquid or to determine by eye the quantity enclosed; but the size of the vapour-bubbles formed at high temperature was very small. A part of the small differences between the volumes read at different time proceeds from this source of errors.

4°. Variation of the section of the tube. From a provisional calibration it appears that the mean value of the section on both sides differed 0.8%. The variations on one side are smaller, but must have had some influence on readings at different heights of the tube.

5°. Besides we must recall here the error arising from the walls of the glass tubes used as baths on the lengths measured, together with the errors of reading, dependent from different illumination and different pointing of the telescope. The influence of these causes together may have amounted to 0.5 mm. in a single reading: it was eliminated as well as possible by repeating the measurements with different positions of the tube.

From the foregoing we conclude, that errors of  $\frac{1}{2}$  and 1% can be entirely explained by the errors of the method, but that the deviations especially in the final values will be smaller as a rule.

The results obtained with my last tube will be communicated here completely: they agree qualitatively with those afforded by former tubes. The volumes are expressed in the volume of 1 mm. of the tube at 15°. Corrections have been applied for the quantity of vapour, for the liquid surfaces, for the expansion of the glass, for the volume of the two ends of the tube, for the errors of the thermometers, for the expansion of the ether.

$v_v$  = volume in the vapour-branch.

$v_l$  = » » » liquid-branch.

$V = v_v + v_l$ .

I. Volume of the ether at 15° C, before the transport of a part of the liquid to the liquid-branch.

$v_v = V = 29.75$  mm.

II. Volume of the ether at 15° C, after a small quantity having been transported to the liquid-branch:

$v_v = 23.68$   $v_l = 6.10$   $V = 29.78$  (undivided liquid in liq. br.)

$v_v = 23.64$   $v_l = 6.09$   $V = 29.73$  (divided » » » »)

Mean value:  $v_v = 23.66$   $v_l = 6.09$ .

III. Volume of the ether at 15° C, after a larger quantity having been transported to the liquid-branch:

$v_v = 14.18$   $v_l = 15.72$   $V = 29.90$  (undivided)

$v_v = 14.06$   $v_l = 15.68$   $V = 29.74$  (divided)

Mean value:  $v_v = 14.12$   $v_l = 15.70$

IV. Volume of the ether at 15° C, again with a small quantity in the liquid-branch:

$v_v = 23.04$   $v_l = 6.68$   $V = 29.72$  (undivided)

$v_v = 22.97$   $v_l = 6.68$   $V = 29.65$  (divided)

Mean value:  $v_v = 23.01$   $v_l = 6.68$

The proportion of  $v_v$  and  $v_l$  represents the proportion of the quantity of ether present in both branches. The differences between the corresponding volumes may give an idea about possible errors.

Before communicating the complete results obtained at high temperatures, we must say a word about the expansion of the glass and the mercury. This expansion is revealed by the fact, that the sum of the entire volumes at both sides (outside the mercury) is different at high and low temperature. We found for this volume outside the mercury:

I. Before the transport of liquid at 15° C 86.69

II. 1<sup>st</sup> series at 15° C 86.76, 86.56 mean: 86.66  
at 222° C 84.22

Difference for 207° C 2.44

III. 2<sup>nd</sup> series at 15° C 86.90, 86.66 mean: 86.78

at 223° C 84.45

Difference for 208° C 2.33

IV. 3<sup>rd</sup> series at 15° C 86.71, 86.77 mean: 86.74

at 223° C 84.11

Difference for 208° C 2.63

Mean difference for 208° C 2.47

This diminution of length contains the apparent expansion of the mercury, diminished by the linear expansion of the glass. By calculation I obtain for this quantity circa 2.50, agreeing very well with the quantity derived from observation.

The results obtained with the tube are laid down in the following Tables, in which:

$v_v$  = volume at the vapour-side expressed in mm of the tube at 15° C.

$v_l$  = » » » liquid-side » » » » » » » » » »

▲ = difference of pressure between  $v$  and  $l$  expressed in mm. of mercury.

$\sigma_v$  and  $\sigma_l$  = calculated densities on both sides.

$A$  = their difference expressed in percents.

I. 1<sup>st</sup> series. At high temperatures pressure higher at the vapour-side ( $\Delta$  positive).

Temp.	$v_v$	$v_l$	$\frac{v_v}{v_l}$	$\Delta$	$\sigma_v$	$\sigma_l$	$A$ (%)
194.5	66.79	18.00	3.71	17.2	0.255	0.244	-4.5
198.9	67.34	17.43	3.86	18.5	0.253	0.252	-0.6
203.0	67.40	17.31	3.89	18.6	0.253	0.253	+0.2
207.6	67.46	17.21	3.92	18.8	0.252	0.255	+0.9
221.6	67.31	17.22	3.81	18.7	0.253	0.255	+0.6
15.0	23.66	6.09	3.88	+7.4	0.72	0.72	-



II. 2<sup>nd</sup> series. At high temperatures pressure higher at the liquid-side ( $\Delta$  negative).

Temp.	$v_v$	$v_l$	$\frac{v_v}{v_l}$	$\Delta$	$\sigma_v$	$\sigma_l$	$A$ (%)
194.7	47.74	37.50	1.273	-20.9	0.213	0.301	+35
195.0	45.53	39.67	1.148	-25.3	0.223	0.285	+24
196.7	41.80	43.19	0.968	-32.5	0.240	0.262	+8
202.4	40.80	44.14	0.924	-34.5	0.249	0.256	+2.8
206.5	40.71	44.24	0.920	-34.6	0.250	0.255 <sup>5</sup>	+2.3
223.3	40.48	44.28	0.914	-35.1	0.251	0.255	+1.7
15.0	14.12	15.70	0.900	+ 3.4	0.72	0.72	—

III. 3<sup>d</sup> series. At high temperatures pressure higher at the vapour-side ( $\Delta$  positive).

Temp.	$v_v$	$v_l$	$\frac{v_v}{v_l}$	$\Delta$	$\sigma_v$	$\sigma_l$	$A$ (%)
194.5	65.48	19.25	3.40	15.1	0.253	0.250	-1.3
196.1	65.74	18.90	3.48	15.5	0.252	0.254 <sup>5</sup>	+1.0
199.1	65.71	18.98	3.46	15.3	0.252	0.253	+0.5
205.9	65.67	18.96	3.46	15.4	0.252	0.254	+0.6
222.7	65.52	18.90	3.47	15.2	0.253	0.254 <sup>5</sup>	+0.6
15.0	23.01	6.68	3.44	+9.3	0.72	0.72	

For the critical temperature I found circa 194.3° C

While intending to discuss the above results in another paper, I wish to give here the general conclusion to be drawn from the foregoing tables.

While GALITZINE finds large differences of density between the two branches of the U-tubes, which at 15° C above the critical temperature sometimes amount to 20%, such differences here only occur in II and

even there only quite near to the critical temperature. At 3° C above the critical temperature the differences are beneath 8% already, at 10° C above the critical temperature beneath 3%, at 15° C beneath 2%. In the other cases I and III the differences are very small. Moreover GALITZINE always finds the density largest in the liquid-branch of the tube whereas the density is here found largest in the vapour-branch in I and III near to the critical temperature. The differences therefore found here are of a different magnitude and sometimes of a different direction to those in GALITZINE'S experiments.