

Citation:

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friction of the sphere in vapour 20° K. with $\mu = 0.0012$ ¹⁾ and $\eta = 0.000011$ ²⁾ a decrement $\sigma = 0.00015$ was calculated. We conclude from this that the decrement caused by the friction of the liquid alone was $\sigma_1 = 0.00334$. The liquid was under a mean pressure of 766 mms. mercury; the temperature was thus $20^{\circ}.36$ K.³⁾ and the density 0.0708 ⁴⁾. From this it follows that $\eta = 0.000117$.

This determination was made before the investigation of the suitability of the method was completed (see Comm. N^o. 151d). From that investigation it appears probable, that the value found for η was a few percent too high, but the data are wanting by which the necessary correction might be estimated. We therefore give as the approximate value of the viscosity of liquid hydrogen $\eta = 0.00011$.⁵⁾

Physics. — "*Critical point, critical phenomena and a few condensation-constants of air*". By J. P. KUENEN and A. L. CLARK. (Communication N^o. 150b from the Physical Laboratory of Leiden).

(Communicated at the meeting of February 24, 1917).

The critical temperature and pressure of air have been determined by OLSZEWSKI⁶⁾, WROBLEWSKI⁷⁾, and WITKOWSKI⁸⁾. Their results do not agree amongst each other as well as might be desired:

	OLSZEWSKI	WROBLEWSKI	WITKOWSKI
t_k	-140°	about -140.5	-141°
p_k	39 atm.	„ 37 à 37.5	39

The main object of our investigation was to obtain reliable values for the critical constants, including the critical density, which involves a detailed study of the condensation-phenomena in the critical region. WROBLEWSKI noticed that air behaves differently near its critical point

¹⁾ The vapour still behaves approximately as an ideal gas.

²⁾ According to H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER. Comm. N^o. 134a.

³⁾ Normal boiling point: $20^{\circ}.33$ K., $\frac{dp}{dt} = 200 \frac{\text{m.M}}{\text{degree}}$ (see Comm. N^o. 137d).

⁴⁾ See Comm. N^o. 137a.

⁵⁾ This value agrees satisfactorily with that calculated in Comm. N^o. 148b on the basis of the law of corresponding states.

⁶⁾ K. OLSZEWSKI. C. r. 99, p. 184, 1884.

⁷⁾ S. v. WROBLEWSKI. Wied. 26, p. 134, 1885.

⁸⁾ A. W. WITKOWSKI. Phil. Mag. (5) 41, p. 288, 1896.

from other substances: this he correctly ascribed to the circumstance that air is a mixture, but the special phenomena which he describes were largely due to insufficient mixing. It was therefore necessary to repeat the investigation with all those precautions which in previous investigations on mixtures have proved necessary and amongst others to try and realise "retrograde" condensation¹⁾, which is characteristic of mixtures. So far an investigation of that sort had never been carried out but at the ordinary and at higher temperatures.

As expected the investigation proved to be beset with great experimental difficulties. Generally speaking these difficulties all originate in the circumstance that the mixture cannot as a whole be cooled down to a low temperature, at least, if the possibility must be left open — and this is an essential condition in the experiments here contemplated — of changing the volume of the substance gradually. A substance which at the very low temperatures could play the part which is otherwise fulfilled by mercury, viz. that of enclosing a fixed quantity of the substance in a variable volume, is unfortunately not known. It is therefore necessary to compress the mixture in a small tube which is closed at the bottom and cooled to the low temperature, by means of a piezometer, thus using the same method as followed with pure substances, so that every time a different fraction of the total quantity of substance is present in the observation-tube. With pure substances this does not involve any fundamental difficulty; by measuring the quantity of gas present in the part of the piezometer which is outside the cryostat, the quantity in the observation-tube can at each measurement be derived by subtraction from the total quantity, even when the substance is partly liquefied. With mixtures this is different: in the condensation of a mixture new mixtures are formed each time of different composition; in a series of observations in which the mixture is alternately compressed and expanded the mean composition of the mixture in the observation-tube will thereby very soon become different from that of the whole and the observations lose all definite meaning as referring to mixtures of varying and unknown composition. Taking air, the mixture dealt with in our investigation, as an instance, when it has been partly liquefied and is now re-evaporated, in the beginning the nitrogen will principally boil away and disappear from the tube, whereby the mixture, which remains behind, becomes richer and richer in oxygen and no longer has the same mean composition as air.

¹⁾ J. P. KUENEN. Comm. Leiden 4. 1892.

It is therefore necessary in the experiments to lay down the general rule when partial condensation has once set in not again to increase the volume¹⁾ and, if the observations have to be repeated or a new series has to be started at a different temperature, it is necessary — in order to obtain complete homogeneous mixing — several times in succession to lower the pressure in the apparatus to normal and recompress to the high pressure. Otherwise in consequence of the very slow diffusion in the capillary connecting tubes with the supply-tube of the piezometer a mixture of higher boiling point remains behind in the small experimental tube, so that the succeeding observations are bound to be incorrect and amongst others the condensation will set in too soon. The importance of all this was not sufficiently realized in our experiments to begin with, so that a great number of our earlier observations had to be rejected later on.

The electro-magnetic stirring also involves greater difficulties at low temperature than otherwise, in consequence of the great width of the cryostat which brings with it a corresponding size of the electromagnet surrounding the cryostat. The observation-tube, capillary and stirrer were the same as used by CROMMELIN²⁾ in his investigation of argon. In this tube the difficulty just referred to is got over by the small piece of iron on which the electro-magnet acts being placed in an enlargement above the glass capillary of the experimental tube; to this piece of iron by means of a long glass thread running down through the capillary the stirrer inside the observation-tube is attached. By this means the stirrer can be moved up and down by means of a small hand-electromagnet.

This arrangement involved the difficulty for our purpose, that the glasscapillary referred to has to be comparatively wide in order to leave room for the glassthread and that this is connected with greater danger of mutual diffusion between the different mixtures inside and outside the observation-tube and that greater uncertainties arise in the determinations of the densities. It also happened more than once that the stirrer got stuck in consequence of the flexibility of the glassthread and perhaps of microscopic deposits of solid substances. It goes without saying that the air had been freed as well as possible of water-vapour and carbon-dioxide: possibly the sticking of the glassthread indicates that traces of these substances had remained after all; in any case the disturbance usually became

¹⁾ In the neighbourhood of the critical point, where the two phases have nearly the same composition, small expansions cannot be objected to.

²⁾ C. A. CROMMELIN. Comm. 115 § 2. See also Comm. 83. Plate IV.

worse as more air was condensed and therefore had passed through the capillary. Usually the disturbance could be reduced or obviated entirely by operating the stirrer while the air was being compressed into the observation-tube.

The uncertainty in the computation of the density arises in the following manner: beside the observation-tube a long piece of the glass capillary is inside the cryostat, in our experiments about 35 cms with a volume of a quarter of the tube. Only a part of this length is immersed in the cold liquid; as previous experiments have shown, the temperature of the tube above the liquid increases pretty rapidly and near the top approaches the normal. A considerable correction has to be applied to the measurements for the gas inside this capillary. Assuming that the experiments are exclusively conducted with compression, the air which enters the capillary will retain its composition in the incompletely cooled part and will have to be taken into account as air. In the lower part on the other hand the air will separate into liquid and vapour and, if the liquid flows down properly, this part will finally contain saturated vapour. Still, owing to the circumstance, that thorough stirring can only take place in the observation-tube at the bottom, there is no guarantee, that the vapour in the capillary has the correct composition, while on the other hand the stirring in the capillary has the disadvantage of a partial mixing of the gases in the cold and the warmer parts of the capillary. As the extent to which these factors come into play is unknown, it is impossible to take them into account and the upper portion has to be taken as air, the lower portion as saturated vapour. In our case there was the additional difficulty, that the density of the saturated vapour was not yet accurately known, as it can only be found by interpolation from measurements of the vapour-density of a number of mixtures. In the mean time we had to be satisfied with an estimate. It may be added, that in a determination of a vapour-density, i.e. with only a trace of liquid in the tube, the entire cooled portion (observation-tube + part of capillary) has to be considered as containing saturated vapour; similarly in a measurement near the critical point, when on stirring the liquid surface flattens out and disappears, the same volume has to be assumed in the calculation as being filled homogeneously. The various uncertainties arising from the sources mentioned show themselves in small irregularities in the results which were obtained.

On the above grounds it is our intention in future experiments to return to the ordinary method of stirring notwithstanding the clumsy dimensions of the electro-magnet which it involves: the glass

capillary can then be taken very narrow, so that the influence of the diffusion will be imperceptible and the determinations of the volume will obtain greater accuracy. But the rule, that in a set of readings, after the condensation has once begun, no expansion must be applied, will always remain valid.

Finally it may be remarked that, whereas air is, properly speaking, a ternary mixture of nitrogen, oxygen and argon, the amount of the latter gas is so small and its properties differ so little from those of the other two components, that a perceptible influence on the phenomena cannot be assumed and our mixture may thus be actually looked upon as being a binary mixture.

Apparatus. The apparatus which we have used agree in the main with former apparatus in use in the cryogenic laboratory: we may therefore refer to previous communications (for the piezometer compare Comm. 69). Between the observation-tube and the compression-apparatus a steel three-way stopcock was inserted by means of which the apparatus could be connected with a separate reservoir (pipette) filled with pure air: by this means, if required, measured quantities of air could be introduced into or removed from our piezometer; this arrangement was chiefly made with a view to density-determinations of liquid air at temperatures far below the critical, where the quantity present in the compression-tube would not have been sufficient. But as we were obliged to confine ourselves to experiments in liquid ethylene, there was after all no necessity for drawing on the pipette.

The pressures were measured on a closed hydrogen-manometer (Comm. 78), a metal gauge being used as a control during the measurements. Two platinum-thermometers (Comm. 141a) served for reading the temperatures. The cryostat was described in Comm. 83.

Critical point and critical phenomena. As shown by the theory of mixtures a distinction has to be made between two different critical points: the "plait-point", where the two coexisting phases become identical and where thus the critical phenomena will be most conspicuous and secondly, corresponding to a somewhat higher temperature, the "critical point of contact", i.e. the limit for the separation into two phases. In the temperature-range between those two points the condensation is "retrograde", in this case of the first kind. We have succeeded in confirming these several theoretical conclusions for air and have thus been able to show, that at these very low temperatures the phenomena are no other than what theory leads to expect. The experiments were far from easy, as the two points lie very close together, which is connected with the circum-

stance that the condensation-loop in the $p-T$ figure turned out to be comparatively narrow. The plait-point was found at

$$t = -140^{\circ}.73 \quad p = 37.25 \text{ atm.}$$

the critical point of contact at

$$t = -140^{\circ}.63 \quad p = 37.17 \text{ atm.}$$

The special kind of condensation which is characteristic of mixtures is thus confined to a range of $.1^{\circ}$, and it is therefore necessary to make the compression proceed extremely slowly, if the observation is to succeed. High demands as regards constancy during a long period are thus made on the temperature and the success of our endeavours was no doubt due to the excellent appliances and arrangements which are available for this purpose in the cryogenic laboratory.

In order not to extend this paper unduly we shall not describe our observations in all detail. An exception may be made for a phenomenon which was observed at $-140^{\circ}.64$ and a pressure of 37.26 atmospheres and which shows very clearly the extreme sensitiveness of the substance in the critical region to changes of temperature and pressure. At the above pressure the surface between liquid and vapour was just no longer visible; by lifting the stirrer — as in other corresponding states in this temperature-range — a mist was produced which, however, in this instance did not simply disappear, but automatically disappeared and reappeared again a few times in succession with a period of about one second. Evidently by the upward motion of the stirrer, the air under it becomes slightly expanded and thus cooled, while at the same time some gas is driven into the higher, warmer part of the capillary. The increase of pressure produced thereby assists in driving the gas back into the observation-tube, by which motion the mist becomes dissolved. The conditions must have been such this time, that the phenomenon repeated itself a few times in succession. The slow periodic time makes it probable, that a movement up and down of the mercury-surface in the wide compression-tube was at the bottom of the phenomenon.¹⁾

It is worth mentioning, that more than once a blue opalescence

¹⁾ A vibration of the air in the small tube under the influence of its own elasticity would take place much faster and is, moreover, improbable, because the air is cooled during the compression and warmed during the expansion, whereas the condition for a vibration being sustained by supply and withdrawal of heat is exactly opposite. The closed reservoir at the end of the tube should be the warm part of it, as in the case of the well-known singing which sometimes takes place in blowing a bulb at the end of a tube.

was noticed, when the pressure was somewhat lower than that required to produce the cloudy condensation, and sometimes persisted during the stirring. By a rapid movement of the stirrer the opalescence could as a rule be changed into a mist. Pure oxygen and argon do not seem to show opalescence.¹⁾

Condensation-constants. Our results as regards temperature and pressure are given in Table I and in Figure I.

TABLE I.

t	p_b	p_e
-140.63	37.17	37.17 P. of C.
-140.64	37.12	37.24
-140.69	37.02	37.26
-140.73		37.25 P. P.
-140.74	36.99	37.42
-140.75	36.86	
-140.80	36.65	37.20
-140.80	36.70	
-140.83 ⁵	36.68	
-140.85	36.75	37.18
-140.89	36.57	
-140.99	35.35	
-141.35	35.24	36.49
-141.99	34.58	
-142.35	33.91	35.31
-143.14	32.06	
-143.34	31.85	33.79
-144.12	31.06	33.12
-144.35		32.52
-146.32		29.83
-150.12	23.68	25.04

¹⁾ See Comm. 145b.

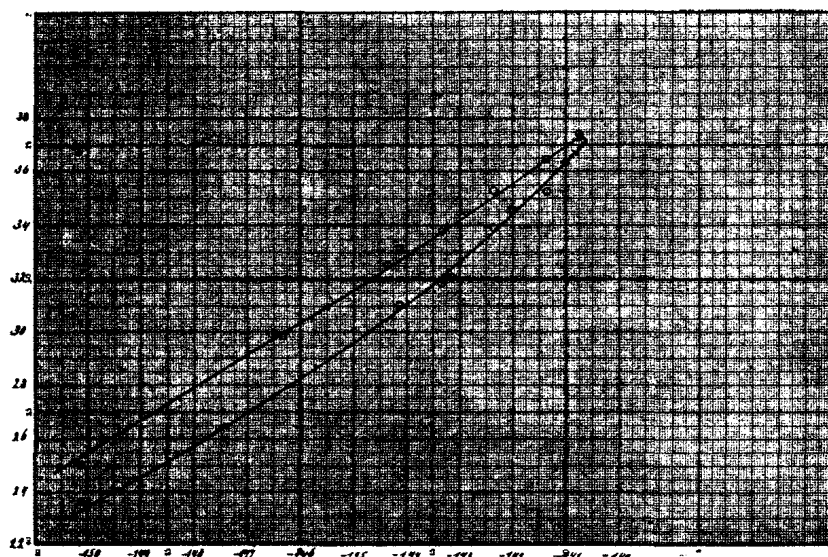


Fig. 1.
TABLE 2.
Densities.

Temperature	Vapour	Liquid
-140.63	0.31	0.31 P. of C.
-140.69		0.323
-140.70		0.328
-140.73		0.35 P. P.
-140.75	0.277	
-140.80	0.265	0.365
-140.84	0.269	
-140.85		0.359
-140.89	0.262	
-140.99	0.253	
-141.34		0.439
-141.99	0.217	
-142.35		0.461
-143.34	0.188	
-143.35		0.488
-144.35		0.503
-146.32		0.523

The points of beginning and of completed condensation which are contained in the Table were all determined with compression, as explained before; for the sake of accuracy the change of volume was conducted as slowly as possible. All the same the results show very distinct irregularities, which must find their explanation in the various grounds mentioned.

The densities especially must be accepted with some reserve: they are given in Table 2 (p. 1095) and Figure 2. The densities at the plaitpoint and the point of contact were read from the figure.

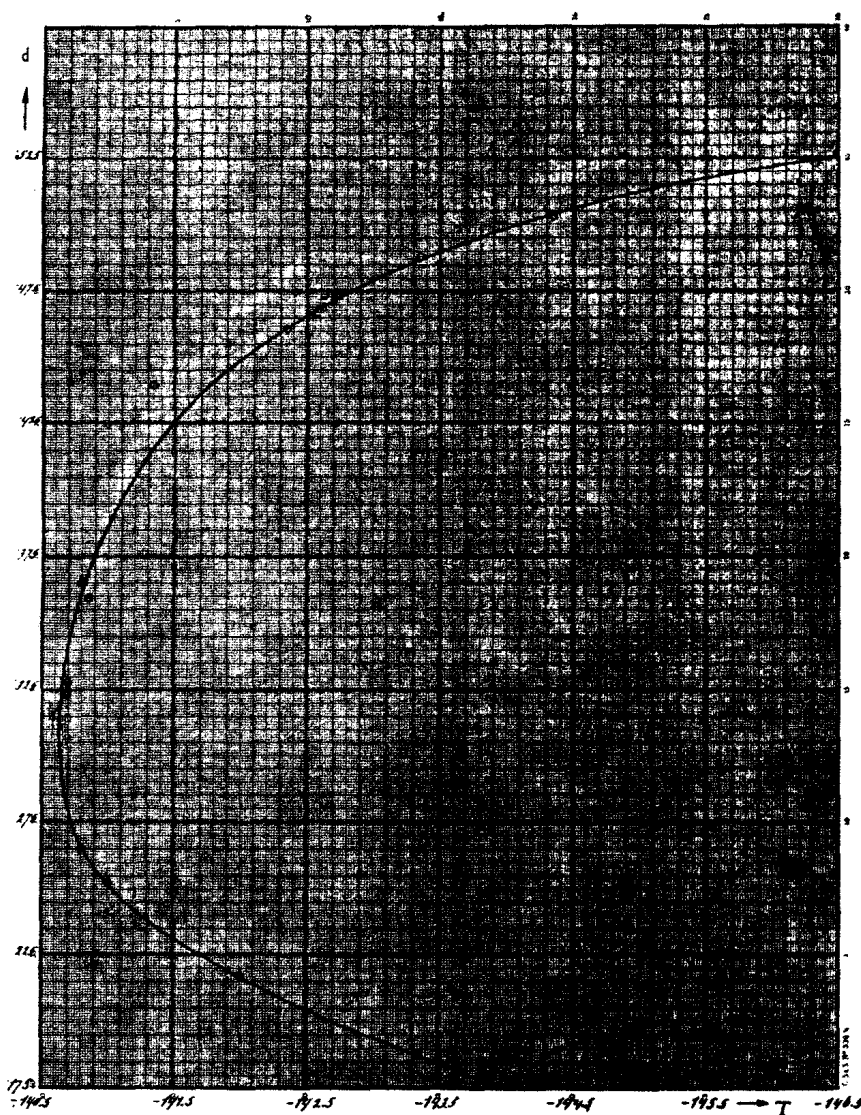


Fig. 2.

In comparing the plait-point of air with the critical points of its constituents (Comm. 145*b*), viz. $-118^{\circ}.82$, 49.73 atm. for oxygen

and $-147^{\circ}.13$, 33.49 atm. for nitrogen, it appears, that the critical curve for the oxygen-nitrogen mixtures differs very little from a straight line. On a straight line a temperature of $-140^{\circ}.73$ would correspond to a pressure of 37.16 atm. whereas the plait-point pressure is 37.25 atm. The critical point appears to change approximately proportionally to the composition in weight: t_k calculated according to the composition would be $-140^{\circ}.56$. PAWLEWSKI's rule thus holds approximately for mixtures of oxygen and nitrogen.

In connection with the very small distance between plait-point and point of contact, already referred to, a further conclusion may be drawn from this result. The latter fact involves that the critical temperature which air would have, if it condensed without change of composition, deviates very little from the two other critical points and that this temperature — the so-called critical temperature of the undivided mixtures — thus also changes proportionally to the composition, with a certain degree of approximation. If this proportionality held for the molar composition, we might, as the theory of mixtures shows, infer from this, that at low temperatures the vapour-pressure of these mixtures would change about linearly with the composition of the liquid ¹⁾. Evidently with mixtures of oxygen and nitrogen this is not the case and in agreement with this BALY's experiments ²⁾ gave a vapour-pressure line which is very distinctly curved.

The critical density of air calculated from those of oxygen and nitrogen, 0.43 and 0.31 respectively, according to the simple rule of mixtures by weight, is 0.34, a value which as the table shows is intermediate between the density at the critical point of contact 0.31 and that of the plait-point 0.36. Assuming that the rule of mixtures would hold approximately for the mixtures of constant composition and that therefore the critical density of undivided air would be 0.34, a somewhat higher density might actually be expected at the plait-point. For the connodal curve lies entirely outside the saturation-curve for the mixtures of constant composition and on that curve the plaitpoint lies in this case on the side towards the smaller volumes or higher densities. The somewhat smaller density at the critical point of contact is also as might be expected.

To Professor H. KAMERLINGH ONNES our sincere thanks are due for his continual interest in our research, many helpful suggestions

¹⁾ Comp. e.g. J. P. KUENEN, Handb. ang. Phys. Ch. IV p. 126 1906.

²⁾ E. C. C. BALY, Phil. Mag. (5) 49 p. 517 1900.

and for the way in which he enabled us to complete our investigation in the short time at our disposal.

We also wish to thank Mr. J. M. BURGERS for looking after the temperature readings, Mr. A. T. VAN URK for assistance during the whole work and finally him and Mr. CH. NICAISE for help in the calculations.

Chemistry. — "*On the distinction between methylated nitro-anilines and their nitrosamines by means of refractometric determinations*". (II). By Dr. J. D. JANSEN (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of February 24, 1917).

In a former communication¹⁾ I called attention to the difference in optical properties between coloured nitro-compounds, as nitro-anilines and nearly colourless ones as dinitro-benzenes. In the first mentioned substances, the molecular-refractions of the isomerides showed great differences, whereas the molecular-refractions of the isomerides of the colourless compounds were nearly the same.

This phenomenon proved to be closely related to the light absorption. The first group of compounds (the coloured) showed absorption-bands in the neighbourhood of the kind of light chosen for the determination of the refraction. The refractive-indices and in connection therewith, the molecular-refractions of those substances were raised. This rise is not the same for the different nitro-compounds, because it depends on the place and the depth of the absorption-bands (anomalous dispersion). The colourless substances, the absorption-bands of which are situated far outside the visible part of the spectrum, showed no rise at all of the molecular-refractions or only a very slight one.

By stating this fact we directed the attention to the molecular-refractions of the 2.5- and 2.3-dinitro-dimethyl-p-toluidines and the respective nitrosamines.

	Spec. Refr.	M.-R.	Δ
2.5-dinitro-dimethyl-p-toluidine	0,2730	61,4	1,8
2.3- " " " "	0,2649	59,6	
2.5-dinitro-tolyl-methyl-nitrosamine	0,2391	57,4	0,5
2.3- " " " "	0,2370	56,9	

¹⁾ Proc. Roy. Akad. Amst. 564 (1916).