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The coefficient of inclination of the diameter is:
$$b_{d\Gamma} = - 0.0019577,$$
and thus a good deal smaller than the coefficients of argon (—0.0026235) and of oxygen (— 0.002265).

The "undisturbed" *critical density* derived from the diameter using as the critical temperature —147°.13[1]) is found to be:
$$\varrho_{kd} = 0.31096.$$

A comparison with the value for the "undisturbed" critical density which might be derived by the aid of the equation $\left(\dfrac{\partial p}{\partial T}\right)_{r} = \left(\dfrac{dp}{dT}\right)_{oex}$ from the vapour-pressure curve and the isotherms near the critical point (as this was carried out for argon) is impossible for nitrogen, as isotherms are not available in the mean time.

The *critical coefficient* is
$$K_{4d} = 3.421,$$
a comparatively small value, as was to be expected in connection with the simple molecular structure of nitrogen, its deviation from the theoretical value $\frac{8}{3}$ is in the same direction and to much the same degree as that of argon (3.424) and that of oxygen (3.419) [2]).

The liquid densities at the lower temperatures are in fairly good agreement with those found by BALY and DONNAN [3]), the differences being of the order of 1°/₀.

Physics. — *Isothermals of di-atomic substances and their binary mixtures.* XVI. *Vapour-pressures of nitrogen between the critical point and the boiling point."* By Dr. C. A. CROMMELIN. (Communication N°. 145d from the Physical Laboratory at Leiden). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of December 30, 1914).

The determination of the density-curves and the diameter of nitrogen [4]) offered a welcome opportunity for determining the vapour-pressures of nitrogen between the critical point and the boiling point, therefore in the region of the higher pressures, and thus making a contribution towards the knowledge of the equation of

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[1]) H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST, This number of the Proc. Comm. 145b.

[2]) Calculated with the critical constants of Comm. 145b.

[3]) l. c.

[4]) E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, This number of the Proc., Comm. N°. 145c.

state of nitrogen at low temperatures. Moreover several of these data were required for the computation of the corrections of the diameter-measurements.

In the region here dealt with so far all experimental data were lacking, at least if we leave out of account two old determinations by v. Wroblewski [1]), which differ considerably from mine. Vapour-pressures have been measured by Baly [2]) between — 196° and — 182°, by Fischer and Alt [3]) between — 195° and — 210° and by von Siemens [4]) between — 192° and — 205°, but, as will be seen, they all refer to regions of low temperatures and pressures.

The nitrogen was liquefied in the same dilatometer and by the same compression-cylinder, which had been used in the diameter-measurements of argon and nitrogen. It should be mentioned, that this dilatometer was not provided with a stirring-arrangement, so that the determinations were made without stirring. It is possibly due to this circumstance, that the vapour-pressures of nitrogen seem to be a trifle less accurate than those of oxygen. [5])

As in the previous measurements the temperature was determined by means of two platinum-thermometers which had been compared with the standard resistance-thermometer Pt'_L. As regards all this we may therefore refer to previous communications [6]). The pressures above 20 atm. were determined by means of the closed hydrogen-manometer [7]), those below 20 atm. with the open standard-manometer [8]).

The calculations do not call for special remarks. The atmosphere at Leiden was taken equivalent to 75.9488 cms. mercury.

The nitrogen with which the experiments were made was, as mentioned in connection with the diameter-measurements, the same as was used for the determinations of the critical constants. By these determinations the purity of the substance had been submitted to a

1) S. v. Wroblewski, C. R. 102. (1886) p. 1010.

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

3) K. T. Fischer and H. Alt, Ann. d. Phys. (4) 9 (1902) p. 1149.

4) H. von Siemens, Ann. d. Phys. 42. (1913) p. 871.

5) H. Kamerlingh Onnes, C. Dorsman and G. Holst, This number, of the Proc. Comm. No. 145b.

6) E. Mathias, H. Kamerlingh Onnes and C. A. Crommelin, Proc. Oct. and Dec. 1912 and Jan. 1913. Comm. No. 131a (argon) and these Proc. above Comm. No. 145c (nitrogen).

7) H. Kamerlingh Onnes and H. H. F. Hyndman, Proc. April 1902. Comm. No. 78 (§ 17) and H Kamerlingh Onnes and C. Braak. Proc. March 1907, Comm. No. 97a (§ 3).

8) H. Kamerlingh Onnes, Proc. Nov. 1898, Comm. No. 44.

severe test. The nitrogen was moreover once more tested for its purity in the apparatus itself. For this purpose the vapour-pressure was measured at a temperature which was kept constant (about − 153°), first when only a drop of liquid was present in the appendix of the dilatometer and immediately afterwards with the dilatometer completely filled with liquid. The vapour-pressure was found in the two cases to be

25.38 and 25.41 atm.

This difference of about one thousandth of the total value is not far removed from the limits of accuracy of the observations and proves (1) that the nitrogen was very pure and (2) that the temperature-difference near the top and near the bottom in the cryostat must have been inappreciable.

In the further observations the liquid-surface was always brought to about the middle of the dilatometerbulb.

Date 1914	Number	θ(centigrade in KELVIN degrees).	$p_{obs.}$ atm. int.	$p_{calc.}$	Obs.-calc. (abs.)	Obs.-calc. (%)
21 Febr.	X	− 148.85	30.364	30.631	− 0.267	− 0.9
„	IX	− 152.11	25.889	26.087	− 0.198	− 0.8
„	VIII	− 155.47	21.820	21.945	− 0.125	− 0.6
20 Febr.	VII	− 161.31	15.949	15.949	0.000	0.0
17 Febr.	V	− 173.58	7.3705	7.3705	0.0000	0.0
„	IV	− 179.18	4.8278	4.8632	− 0.0354	− 0.7
16 Febr.	I	− 182.47	3.7248	3.7117	+ 0.0131	+ 0.4
„	II	− 186.88	2.5067	2.4863	+ 0.0204	+ 0.8
„	III	− 191.88	1.4727	1.4727	0.0000	0.0

In the above table are given the results of the measurements and a comparison with a formula of the form

$$log\,p = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3}$$

where T represents the absolute temperature, the coefficients having the values

$$a = + 5.76381$$
$$b = − 853.522$$
$$c = + 54372.3$$
$$d = − 1783500$$

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which satisfy the following values of the critical constants

$$p_k = 33.49 \text{ atm. and } T_k = 125.°96 \ K \ [1])$$

$$(\theta_k = T_k — T_{0°} \ c = — 147.°13 \ C. \text{ in Kelvin-degrees)}$$

The circumstance, that the observations do not agree very well with the formula, finds its explanation, at least partly, in the fact, that the critical point falls a little outside the extrapolated vapour-pressure curve. The same fact occurs with the vapour-pressure curves of argon (CROMMELIN) [2]), ether (RAMSAY and YOUNG) [3]), isopentane (YOUNG) [4]) normal octane (YOUNG) [5]), carbon disulphide (BATTELLI) [6]) in contrast with what is found with the great majority of vapour-pressure curves of other substances, with regard to the critical point.

A systematic inquiry into the cause of these deviations would be very desirable.

In conclusion I wish to thank Prof. H. KAMERLINGH ONNES most heartily for the continued interest shown in my work.

Chemistry. — *"On the vapour pressure lines of the system phosphorus."* III. By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1914).

I. *Determinations of the vapour pressure of the violet phosphorus.*

In the preliminary investigation about the vapour tension of the violet phosphorus we found a vapour pressure line with a discontinuity at about 450°, which result seemed to confirm the existence of a transition point found by JOLIBOIS [7]) at ± 460.

To get further certainty about the existence or non-existence of this transition point, it had to be examined whether really two branches intersecting each other, could be realized here. For this purpose it would be necessary to determine also a part of the metastable prolongations on either side of the transition point, and keeping this end in view we undertook the definitive investigation.

The preliminary experiments were made with a preparation N°. 1, which was obtained by heating pure white phosphorus with 0.1 % Iodium at ± 300° for 24 hours. This preparation was hard and

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[1]) Comm. 145b.

[2]) C. A. CROMMELIN, Proc. May 1910 and Oct. 1913, Comm. 115 and 138c and Dissertation Leiden 1910.

[3]) W. RAMSAY and S. YOUNG, Phil. Trans A 178, (1887) p. 57.

[4]) S. YOUNG, Proc. phys. Soc. 1894/1895 p. 602.

[5]) S. YOUNG, Journ. Chem. Soc. 77 (1900) p. 1145.

[6]) A. BATTELLI, Mem. d. Ac. di Torino. (2) 41 I (1890) and 42 I (1891).

[7]) C. r 149, 287 (1909); 151, 382 (1910).