

Citation:

C.A. Crommelin & H. Kamerlingh Onnes & E. Mathias, On the rectilinear diameter for argon, in: KNAW, Proceedings, 15 II, 1912-1913, Amsterdam, 1913, pp. 960-965

$\rho_N = 20$ the diminution becomes extremely small, pointing to constancy at still lower densities. Argon differs from isopentane, however, in this respect that with argon at higher densities far above $\rho_N = 265$, the increase becomes still more rapid, while the behaviour of isopentane would lead one to expect a diminution in the rate of increase.

From his observations upon isopentane YOUNG¹⁾ deduced the following rule for the behaviour of $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$:

$$\left. \begin{aligned} \left(\frac{\partial^2 p}{\partial T^2}\right)_v < \pm v_k &> 0 \\ \left(\frac{\partial^2 p}{\partial T^2}\right)_v > \pm v_k &< 0 \end{aligned} \right\}$$

This rule has already been confirmed for a variety of substances, and is, as far as its second part is concerned, also obeyed by argon.

For carbon dioxide, ethylene and isopentane, REINGANUM found that the quantity $\alpha_R = \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]v^2$ is a minimum for v about $\frac{3}{4}v_k$ and at temperatures about 10° above t_k . If the law of corresponding states were strictly true this minimum for argon should be at $\rho_N = 380$, and therefore outside the region of experiment. Nothing can be done consequently beyond trying to judge from extrapolation, if, and where, the minimum exists. If for this purpose we graph α_R as a function of ρ_N at -122° and -116° , then extrapolation towards higher densities shows that it is probable that these curves would also exhibit a minimum for argon at $v = \frac{3}{4}v_k$.

Physics. — “*On the rectilinear diameter for argon.*” By E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN. *Comm.* 131*a* from the physical Laboratory at Leiden. (Continued).

(Communicated in the meeting of November 1912).

§ 5. *Results.* The results obtained are given in the following table²⁾ (p. 961):

The calculated values of the ordinates of the diameter given in this table have been obtained from the equation

$$D_{\rho T} = 0.20956 - 0.0026235 t_{(K)}.$$

¹⁾ l. c.

²⁾ For the notations, see Suppl. No. 23.

The diameter has been drawn through the points $-175^{\circ}.39$ C_{in} K.gr and $-131^{\circ}.54$ C_{in} K.degr.

| bath | $t_{(K)} = T - T_0^{\circ}\text{C.}$ Kelvin degrees. | $Q_{liq}\Gamma$ | $Q_{vap}\Gamma$ | $D_{p\Gamma}(O)$ | $D_{t\Gamma}(C)$ | $O-C$ |
|-------------------------------|---|-----------------|-----------------|------------------|------------------|-----------|
| O ₂ | - 183.15 | 1.37396 | 0.00801 | 0.69099 | 0.69006 | + 0.00093 |
| CH ₄ | - 175.39 | 1.32482 | 0.01457 | 0.66970 | 0.66970 | |
| CH ₄ | - 161.23 | 1.22414 | 0.03723 | 0.63069 | 0.63255 | - 0.00186 |
| C ₂ H ₄ | - 150.76 | 1.13851 | 0.06785 | 0.60318 | 0.60508 | - 0.00190 |
| C ₂ H ₄ | - 140.20 | 1.03456 | 0.12552 | 0.58004 | 0.57738 | + 0.00266 |
| C ₂ H ₄ | - 135.51 | 0.97385 | 0.15994 | 0.56690 | 0.56507 | + 0.00183 |
| C ₂ H ₄ | - 131.54 | 0.91499 | 0.19432 | 0.55466 | 0.55466 | |
| C ₂ H ₄ | - 125.17 | 0.77289 | 0.29534 | 0.53412 | 0.53794 | - 0.00382 |

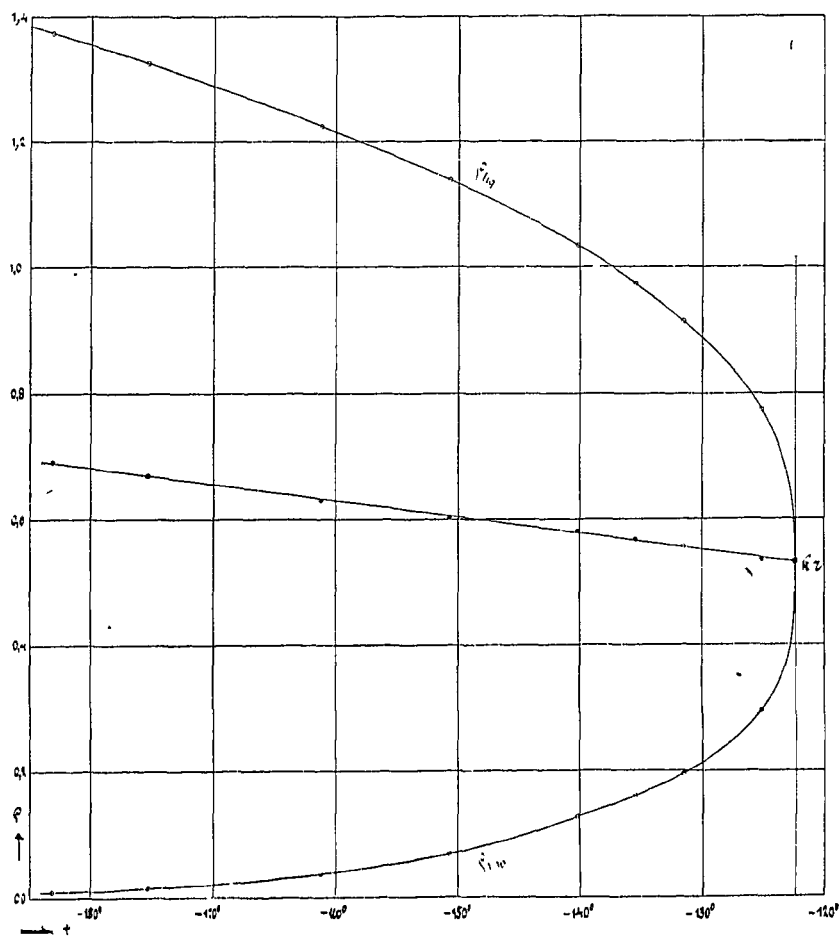


Fig. 2.

§ 6. *Discussion.* The slope of the diameter is given by

$$b_{dr} = -0.0026235.$$

This coefficient is very large, larger than has been found for any other substance yet investigated with the exception of xenon, for which PATTERSON, CRIPPS and WHYTLAW-GRAY¹⁾ have found -0.003055 . Comparison of the values of this constant for the two monatomic substances argon and xenon again reveals the influence exerted upon it by the values of the critical temperature.

With respect to the critical density the following remarks must be made. If we assume that the diameter remains rectilinear right up to the critical point, we then find

$$\varrho_{kd} = 0.53078.$$

Using the equation

$$\left(\frac{\partial p}{\partial T}\right)_{vk} = \left(\frac{dp}{dT}\right)_{\text{coex.k.}}$$

the value

$$\varrho_{k.s.} = 0.509.$$

was previously found from the argon isotherms.²⁾ The difference between these two values is of the same order of magnitude and is in the same direction as the differences found for other substances, carbon dioxide³⁾, methyl chloride⁴⁾, sulphur dioxide⁵⁾ amongst others. The fairly large deviation from rectilinearity of the experimental diameter apparent in the neighbourhood of $-125^{\circ}.17$ C_{in K_{gr.}} agrees well with this behaviour.

3.283 was the value previously⁶⁾ obtained for the critical coefficient on taking $K_{4d} = K_{4s}$; we now find

$$K_{4d} = 3.424$$

which is therefore slightly greater than that for oxygen⁷⁾ (3.346). If, therefore, we leave $K_{4d} = 3.13$ for helium out of account, oxygen, and not argon, is the substance for which K_{4d} lies nearest the theoretical value, 2.67, deduced from VAN DER WAALS's equation.

¹⁾ PATTERSON, CRIPPS and WHYTLAW-GRAY, Proc. R. S. (A.) 86 (1912), p. 579.

²⁾ C. A. CROMMELIN, Proc. Dec. 1910, Comm. No. 118a, and Thesis for the doctorate, Leiden 1910.

³⁾ W. H. KEESOM, Proc. Jan. 1904, Comm. No. 88; H. KAMERLINGH ONNES and W. H. KEESOM, Proc. Febr. 1908, Comm. No. 104a

⁴⁾ C. H. BRINKMAN, Thesis for the doctorate, Amsterdam 1904.

⁵⁾ E. CARDOSO, Arch. sc. phys. et Nat. Genève. (4). 34. (1912) p. 127.

⁶⁾ H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. March 1911 Comm. No. 121a.

⁷⁾ E. MATHIAS and H. KAMERLINGH ONNES, Proc. Febr. 1911, Comm. No. 117.

The density of the liquid at $-183^{\circ}.15$ agrees well with the figures given by BALY and DONNAN¹⁾. The difference is less than 1 %.

Although the deviations of the diameter from rectilinearity are sufficiently small to enable one to say that argon obeys the law of the diameter, they are still too large, and especially too systematic, to be due to experimental errors. As is easily seen from the table and from the accompanying figure, the experimental diameter in the neighbourhood of the critical point exhibits a curvature concave towards the axis of temperature, while at higher temperatures it is convex towards the same axis. The same behaviour has already been observed in other substances, e. g. carbon dioxide²⁾.

In fig. 3 are given the reduced density curves and diameters for ether (RAMSAY and YOUNG³⁾), isopentane (YOUNG⁴⁾), oxygen (MATHIAS and KAMERLINGH ONNES⁵⁾), xenon (PATTERSON, CRIPPS and WHITLAW-GRAY⁶⁾), argon and helium (KAMERLINGH ONNES⁷⁾), the reduction from the experimental data has been made by means of the critical density obtained from the diameter.

On a previous occasion it was shown by KAMERLINGH ONNES and KEESOM⁸⁾ how the equations of state for different substances deviate one from another, and how these differences may find expression in deviation functions. On doing this, it appears that substances may be arranged in order so that the deviations of successive substances gradually increase, while it also appears that substances of widely divergent critical temperatures are then found to be in the order of their critical temperatures. The exemplification of this general property afforded by the behaviour of the diameter was noticed by one of us some time ago⁹⁾ and is brought to light in fig. 3 in which the density curves are seen to enclose one another.

If the law of corresponding states were strictly obeyed, then these curves ought to coincide exactly. From the diagram, however, it is seen that this is not the case. The curves enclose one another¹⁰⁾ in

¹⁾ E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. Trans. 81. (1912). p. 911.

²⁾ H. KAMERLINGH ONNES and W. H. KEESOM. Proc. Febr. 1908, Comm. N^o. 104a. J. P. KUENEN and W. G. ROBSON, Phil. Mag. (6). 3. 1902. p. 624.

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

⁴⁾ S. YOUNG. Proc. phys. soc. London 1894/1895 p. 602.

⁵⁾ l.c.

⁶⁾ l.c.

⁷⁾ H. KAMERLINGH ONNES. Proc. Dec. 1911, Comm. N^o. 124b.

⁸⁾ Enc. Math. Wiss. V. 10. Suppl. N^o. 23.

⁹⁾ E. MATHIAS C. R. 139, (1904), p. 359.

¹⁰⁾ In the diagram of N^o. 36 of Enc. Math. Wiss. V. 10. Suppl. N^o. 23, is clearly shown the surrounding of the boundary curve for helium by that for isopentane.

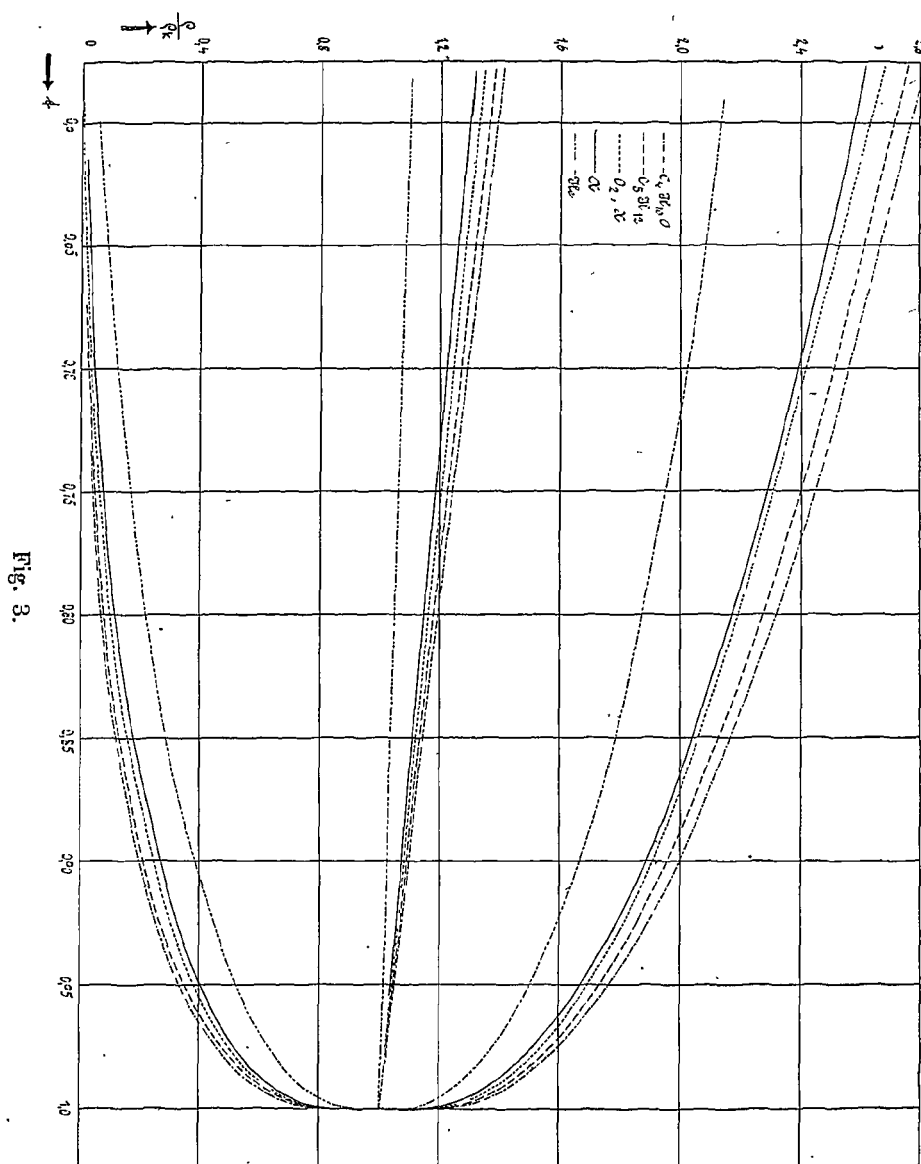


Fig. 3.

such a way that a complex molecular structure and a high critical temperature (circumstances which are usually coexistent) cause divergence between the branches of the curve, while simple molecular structure and a low critical temperature appear to cause them to contract.

Looked at from this point of view, it is of importance to note that the curves for xenon and oxygen so closely correspond that there appears no appreciable difference between the density curves in the diagram, and they have accordingly been represented by a single

curvè. (The observations for xenon, however, extend only to $t = 0.7$). The cause of this correspondence can well be explained on the assumption ¹⁾ that the contracting influence of the simpler molecule and the diverging influence of the comparatively high critical temperature ($+16^{\circ}.6$ C) have, at least in part, cancelled each other.

Physics. — *Magnetic researches, VII. On paramagnetism at low temperatures (continued).* By H. KAMERLINGH ONNES and E. OOSTERHUIS. Communication N^o. 132e from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of December 28, 1912).

§ 9. *Crystallized manganese sulphate.* The salt was procured from MERCK as puriss. pro analysi. The results were ²⁾:

| TABLE VII. | | | | |
|--|-------------------|---------------------------|---------------|------------------|
| Crystallized manganese sulphate $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. (I). | | | | |
| T | $\chi \cdot 10^6$ | $\chi \cdot T \cdot 10^6$ | Limits of H | Bath |
| 288 ^o .7 K. | 66.3 | 19140 | 10000—17000 | Air. |
| 169.6 | 111.5 | 18910 | 8000—17000 | Liquid ethylene. |
| 77.4 | 247 | 19120 | 6000—16000 | Liquid nitrogen. |
| 70.5 | 270 | 19030 | | |
| 64.9 | 292 | 18950 | | |
| 20.1 | 914 | 18370 | 4000—16000 | Liquid hydrogen. |
| 17.8 | 1021 | 18170 | | |
| 14.4 | 1233 | 17760 | | |

Down to and at nitrogen temperatures, this substance follows pretty much the law of CURIE.

¹⁾ See N^o. 34 of Enc. Math. Wiss. V. 10. Suppl. N^o. 23.

²⁾ Prof. WEISS has kindly informed us that in the determination of standards of susceptibility in Zürich, for this substance $\chi = 66.77 \cdot 10^{-6}$ at $14^{\circ} 2$ C. was found.