Physics. — "*On the rectilinear diameter for argon.* By E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm. N°. 131*a* from the phys. Lab. at Leiden.

§ 1. *Introduction.* The present paper forms a continuation of the investigation of the diameter for substances of low critical temperature with which a beginning was made with oxygen. [1]) The importance of this and of similar investigations was indicated in the introduction to the Communication referred to, so that we need not discuss the point further here.

We chose argon for the present investigation since the isotherms for that gas had already been determined to within the neighbourhood of the critical point, while the critical pont itself, the vapour pressures and even preliminary values of the densities of the coexisting vapour and liquid phases were already known [2]) the monatomic nature of the gas, moreover, will undoubtedly enhance the value of the results.

§ 2. *Apparatus.* The apparatus was essentially the same as that employed in the investigation of oxygen. The arrangement for compressing the argon and also the volumenometer have, however, undergone some modification since that time, so that it seemed desirable to take this opportunity of publishing a new diagram of the whole apparatus (Fig. 1).

The modifications of the volumenometer and of the auxiliary apparatus belonging to it have already been described in full detail [3]).

The use of such a costly gas as pure argon necessitated, however, a completely new arrangement of the pressure connections. The copper tubes of which all the connections were made were chosen as narrow as possible so as to reduce the quantity of gas in the dead space to a minimum. The argon was contained in the steel cylinder A which was completely immersed in oil; so too were all the taps and coupling pieces which contained compressed gas. [4])

Through the taps C_{16} and C_{18}, the gas passes to the spiral Sp;

[1]) Proc. Febr. 1911. Comm. No. 117. C. R. 151, 213 and 477, 1910.

[2]) Proc. May 1910. Comm. No. 115, Proc. Dec. 1910, Comm. No. 118, C. A. CROMMELIN, Thesis for the doctorate, Leiden. 1910.

[3]) Proc. May 1911 Comm. No. 121*a*, Proc. Sept. 1912 Comm. No. 127*c* and W. J. DE HAAS, Thesis for the Doctorate, Leiden 1912, in which diagrams of the modified volumenometer are also given. Certain small errors in these diagrams make it desirable to publish a diagram here in which these errors are corrected.

[4]) Proc. June 1905 Comm. No. 94*b*. The value of this device for the detection of leaks has already been repeatedly emphasized

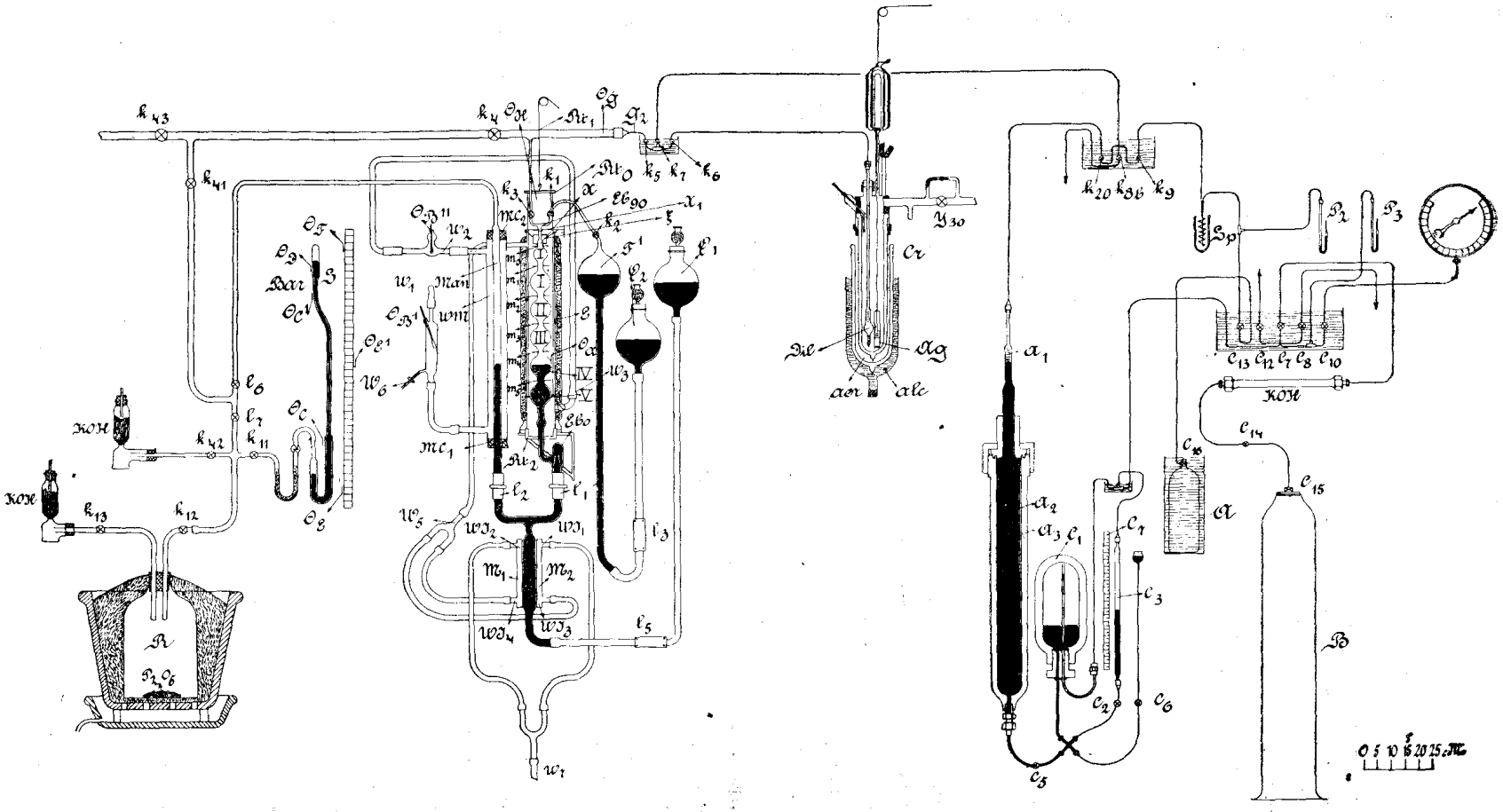

Fig. 1.

here the argon is dried by immersing this spiral in alcohol and cooling it down to its melting point by means of liquid air. Through k_9 and k_{10} the gas then reaches the compression tube A_2 within the compression cylinder A_3 [1]). In this compression tube the mercury is forced by means of compressed air from the steel cylinder B; by this the required amount of argon is compressed into the dilatometer on closing the tap k_9 and opening k_7 and k_6. This arrangement for compressing pure gases has already been fully described in previous Communications [2]); moreover, its mode of operation is easily seen from the accompanying diagram.

Through the tap C_{12} it was possible to establish communication between the air compressor and our accurate closed hydrogen manometer [3]), and by this means we were able during the actual measurements to obtain a few further determinations of the vapour pressure, which will be published shortly.

The cryostat Cr was the same as that used in the investigation of oxygen, the sole modification being the introduction of a different type of stirrer, Ag, provided with valves. [4]).

As the appendix of the dilatometer formerly used was found to be too narrow, another dilatometer Dil, very accurately calibrated, was employed with an appendix sufficiently wide to allow of the suitable measurement of the small volume of the liquid coexisting with the vapour.

A GAEDE vacuum pump was used, and we found it of the greatest utility, particularly during the actual measurements, in ensuring the continued absence of leaks.

Two platinum resistance thermometers were introduced into the cryostat to serve for the regulation und measurement of the temperature.

The argon used for the present measurements was taken from the same supply as that employed in the previous investigations already quoted. The impurity in this argon is certainly less than 0.1 % [5]).

§ 3. *Experiments.* We may now give a short description of the sequence of operations involved in the measurements:

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[1]) At the cylinder A is connected the glass manometer P_2 for high pressures and of small volume, especially constructed for the use of such cylinders as reservoirs for the rare gases.

[2]) Proc. April 1901 Comm. No. 69, Proc. March 1907 Comm. 97*a*.

[3]) April 1902 Comm. no. 78, Proc. March 1907 Comm. no. 97a.

[4]) Proc. June 1911. Comm. no. 123.

[5]) For a detailed description of the preparation and of the analysis of this argon see C. A. CROMMELIN, Thesis for the Doctorate, Leiden, 1910.

1. All the apparatus and connections were reduced to a high vacuum and then washed out with argon.

2. The cryostat was filled with the liquid gas desired (O_2, CH_4, or C_2H_4).

3. The argon was admitted to the compression tube A_2 and then pumped into the dilatometer.

4. The argon meniscus was adjusted to the upper part of the stem of the dilatometer, and the tap k_6 was closed.

5. When the temperature is constant the position of the argon meniscus is read, the temperature is measured, and also when required, the pressure registered by the hydrogen manometer.

6. By reducing the pressure in the cryostat transition is made to a lower temperature, the same measurements are repeated; a lower temperature is then installed and so on until the meniscus has sunk below the subdivided portion of the stem.

7. Sufficient argon is then allowed to escape into the volumenometer to bring the meniscus to the lower part of the appendix below the dilatometer; the temperature, pressure and volume of the escaped gas are measured.

8. The measurements of 5° and 6° are repeated in the reversed order of temperature until the meniscus reaches the upper part of the appendix.

9. The argon still remaining in the dilatometer is transferred to the volumenometer, and the measurements of 7° are repeated.

It is clear that these measurements yielded the data requisite for the calculation of the liquid and vapour densities at all the experimental temperatures. To these calculations we shall return in the succeeding section.

The dimensions of the dilatometer were so calculated that one could finish off the temperature range for any particular substance by successive measurements; in this way only two measurements with the volumenometer were required to give both the liquid and vapour densities.

§ 4. *Calculations.* In many respects the calculations were made in the same way as those of Comm. No. 117. It was of great advantage to us that so many data are already available for argon, and that we could already make use of the reduced equation of state, VII. A. 3. [1]). We shall, however, here give a short summary of the method adopted in the calculations.

Working from the very accurate calibration of the dilatometer,

[1]) Proc. June 1912, Comm. no. 128.

the *liquid volumes* were first calculated directly from the positions of the meniscus top in the stem and in the appendix, without applying any correction. To the numbers so obtained the following corrections were then applied:

1. A fairly large correction for the diminution of the volume at low temperature, seeing that the calibration of the dilatometer had been reduced to + 20° C.; the correction was obtained by means of a formula from a former Communication [1]).

2. A correction for the increase of volume due to the pressure. For this correction, which was so small as to be negligible in almost every case, approximate values were calculated from data contained in two previous Communications [2]).

3. A correction for the volume of the argon meniscus. KELVIN's graphical method [3]) was employed for the evaluation of this by no means negligible correction. To obtain the volume of the menisci it was usually sufficient for our purpose to regard the surface of the liquid as half of an oblate ellipsoid of revolution. Only at the higher temperatures was it necessary to apply GULDIN's theorem to the KELVIN diagram in order to determine the body of revolution.

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[1]) Proc. Sept. 1906, Comm. no. 95b.

[2]) Proc. April 1902, Comm. no. 78, Proc. March 1907, Comm. no. 97a.

[3]) The capillary constant for argon and its variation with temperature must be known for the construction of these diagrams. Now BALY and DONNAN (Journ. of the Chem. Soc. Trans. 81. 907. 1902) have determined capillary constants for liquid argon but only between — 189 C°. and — 183° C. so that the question now arose as to how to interpolate in the most rational manner possible from — 183°. C. to the critical temperature. A comparison between the results giving the reduced capillary constant $\frac{\psi_\sigma}{T_k^{1/3} p_k^{2/3}}$ (see J. D. VAN DER WAALS, Cont. I. p. 176) as a function of the reduced temperature by BALY and DONNAN (l.c.), for argon, by DE VRIES (Zittingsversl. Febr. 1893, Comm. no. 6, and Thesis for the doctorate, Leiden 1893) for ether, by VERSCHAFFELT (Zittingsversl. Juni 1895, Comm no. 18) for carbon dioxide and nitrous oxide was fruitless, seeing that the last three correspond well, while argon deviates strongly from them. A suitable rational method is given by the assumption of the validity of the EÖTVÖS formula (Ann. d. Phys. und Chem. 27 (1886) p. 448) according to which the quantity $\psi_\sigma \left(\frac{M}{\varrho_{liq}}\right)^{\frac{2}{3}}$ is a linear function of the temperature. According to BALY and DONNAN we get for argon $\psi_\tau \left(\frac{M}{\varrho_{liq}}\right)^{\frac{2}{3}} = 2.020\ (145.44 - T)$; from this formula our estimates have been made except that for the highest temperature, $\pm$ — 125° C., at which one is so close to the critical temperature that the EÖTVÖS formula no longer holds, and for which interpolation was resorted to in correspondence with the curves given by other substances.

Having thus calculated all the liquid volumes, we were able, taking the first two of the above corrections into account, to obtain *the volumes of the saturated vapour*. In this it was assumed that the temperature of the bath extended to a distance of 2 cms. above the surface of the liquid.

The following method was adopted of *reducing the gaseous argon* in the glass and steel capillaries from the point of the capillary just mentioned up to the tap k_4 *to terms of the normal volume*. The portion of the glass capillary within the cryostat was divided into different parts for each of which the mean temperature was known from previous papers [1]). The temperatures of the part of the glass capillary outside the cryostat and of the steel capillary up to the tap k_4 were obtained from thermometers during the measurements. The volumes of all these portions were known from the calibrations and the pressures from the vapour pressures already published [2]) together with those added by the present measurements.

In order now to obtain the normal volume of all these portions at different temperatures we again make use of the modified series

$$pv_N = A_N \{1 + B^{(p)} p + C^{(p)} p^2 + \ldots .\}$$

Since $v_N = \frac{V}{N}$ and $A_N = A_{NO°C.}\ (1 + \alpha_A t)$, it follows that

$$N = \frac{pV}{A_{NO°C}\,(1 + \alpha_A t)\,[1 + B^{(p)} p + C^{(p)} p^2]}\ [3])$$

The virial coefficients necessary for the employment of this equation were taken from the equation VII. A. 3. In all these calculations the coefficient $C^{(p)}$ could be neglected.

We may again refer to previous papers [4]) for the corrections which have to be applied to the volumenometric determinations.

For the normal specific mass of argon we used the value given by RAMSAY and TRAVERS [5]) 0.001782.

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[1]) C. BRAAK, Thesis for the doctorate, Leiden. 1908. p. 16.

[2]) Proc. May 1910, Comm. N°. 115.

[3]) In these formulae p is the pressure in atmospheres, v_N the volume expressed in terms of the normal volume as unit, N the normal volume, V the actual experimental volume and α_A, the coefficient of expansion in the AVOGADRO state, 0.0036618. For the notation see also Suppl. No. 23.

[4]) Proc. May 1911, Comm N°. 121a. Proc. Sept. 1912 Comm. N°. 127c and W. J. DE HAAS. Thesis for the doctorate, 1912.

[5]) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

We may further state that at the lowest three temperatures the vapour densities were not measured but calculated; in view of the degree of accuracy desired this is quite permissible. The calculation was made by means of the above series in which, however, $C^{(p)}$ is now no longer negligible. *(To be continued).*

ERRATUM.

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p. 415 l. 10 from the top: for 0.507834 read 0.057834.

(November 28, 1912).