rienced in experiments at liquid hydrogen temperatures and at which my measurements had to be made.

Determinations made by CHAPPUIS[1]) and by RAYLEIGH, in each case with apparatus designed to attain a higher degree of accuracy than that of the Leiden volumenometer, also afford a basis of comparison. CHAPPUIS measured compressibilities at $0°$ C. between 1.4 and 1.8 atmospheres. His results give $B_{A0} = 0,00058$, from which, using the figure given by KAMERLINGH ONNES and BRAAK[2]) for the difference between $B_{A100°}$ and $B_{A0°}$ we get

$$B_{A20°} = 0,00064 \text{ and } O—C = —0,00003.$$

The values deduced from the two single observations distant by about half the pressure difference from each other, in which the errors are increased, differ by $0,0001$.

Finally, Lord RAYLEIGH's[3]) measurements were made with an apparatus specially designed to give an accurate comparison between pv_A at half an atmosphere and its value at double that pressure. From them we get $B_{A10.7} = 0,00054$ from which, using again the KAMERLINGH ONNES—BRAAK result just given, we obtain

$$B_{A20°} = 0,00057 \text{ and } O—C = —0,00010.$$

So that comparison between the results now given with those yielded by these different researches shows a satisfactory agreement.

In the proposed determination of B_A at hydrogen temperatures circumstances will' be much more favourable than at ordinary temperature, for $B_A d_A$ will then be 15 to 20 times greater at the same pressure. We may regard the value obtained for B_A in this way at $—252°$ C. as accurate to within $2°/_0$, and to within $10 °/_0$ at $—259°$ C.

Physics. — *"Isotherms of diatomic gases and of their binary mixtures. XI. On determinations with the volumenometer of the compressibility of gases under small pressures and at low temperatures."* By W. J. DE HAAS. Communication N°. 127[b] from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of May 25, 1912).

§ 1. *Criticism of the pressure equilibrium between the piezometer and the volumenometer.* In the investigation of the compressibility of hydrogen vapour with which a subsequent paper by Prof. KAMER-

[1]) P. CHAPPUIS, Nouvelles études sur le thermomètre à gaz.

[2]) Comm. no. 100b, These Proceedings Dec. '07.

[3]) Lord RAYLEIGH, Proc. Roy. Soc. 73 (1904). Ztsch. phys. Chem. 52 (1905).

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ᴛᴛɴɢʜ Oɴɴᴇs and myself will deal, the volumenometer described in the previous Communication was used to measure the quantity of hydrogen contained under different pressures in a reservoir — the piezometer reservoir — which was immersed in liquid hydrogen and connected with the volumenometer by a capillary and tap. The pressure of the gas in the piezometer reservoir was then given for each measurement by the pressure of the gas in the volumenometer in pressure equilibrium with it. It was shown in Communications N°. 121^a (Proc. May 1911) and N°. 127^a (These Proc. p. 295) that the accuracy with which the pressure, volume and temperature of the quantity of gas contained in the volumenometer could be determined was sufficient to allow of the evaluation of the virial coefficients B at low temperatures for hydrogen vapour from determinations of the compressibility of that vapour. More particular attention must now be bestowed upon the question of pressure equilibrium between the volumenometer and the piezometer.

In the course of the above experiments it was repeatedly necessary to adjust the mercury in the volumenometer to one of the lower necks (for instance, m_1, m_2, or m_4. Cf. Comm. N°. 117, Pl. I, Proc. Febr. 1911). The quantity of gas contained in the volumenometer was in those cases always less (though not many times) than that in the piezometer of 110 cc. capacity and at a temperature of —252° to — 258° C., so that the gas in the piezometer was of a density from 12 to 20 times greater than that in the volumenometer. On each side of the capillary, therefore, which had to be long on account of the construction of the cryostat and narrow on account of the uncertainty of the volume correction to be applied for it, there are relatively large quantities of gas. On account of friction in the capillary, pressure equilibrium will be but slowly attained. A preliminary experiment had shown the desirability of a means to decide from the measurements themselves when exactly this pressure equilibrium had been attained. In order therefore to obtain the necessary data for this, the behaviour of the pressure in the volumenometer was systematically observed during the final experiments upon the compressibility of hydrogen vapour at low temperatures (June 23 and 24, July 8, 14, and 18, 1911) on each occasion on which the meniscus was adjusted to one of the necks m_1, m_2, m_3, m_4 — this of course only after satisfying the experimental conditions to be fulfilled for equilibrium (regulation of cryostat and of volumenometer thermostat, constancy of room temperature). At intervals, as a rule every 5 minutes, the difference between the levels of the mercury in the manometer and in the volumenometer was read and corrected, from

tables prepared beforehand, for changes occurring during the measurement in the quantities determining the corrections (such as change in the temperatures of the volumenometer, the piezometer, the deadspace, change in the capillary depression, etc.).

In this way the actual change in the difference between the pressure and the equilibrium pressure was known at all stages of the measurement. During the measurements a curve was drawn with this pressure difference as ordinate and time as abscissa, and the observation was regarded as at an end as soon as the plotted points began to fluctuate about a line drawn parallel to the abscissa axis. The accompanying diagram (unit ordinate representing 0.1 mm. mercury) is taken from the above investigation and refers to the adjustment of the pressure equilibrium on July 18, 1911, an occasion on which circumstances were particularly unfavourable. The observed pressure differences, increased by a certain fixed quantity, are represented by circles. At the end of § 3 we shall return to this diagram.
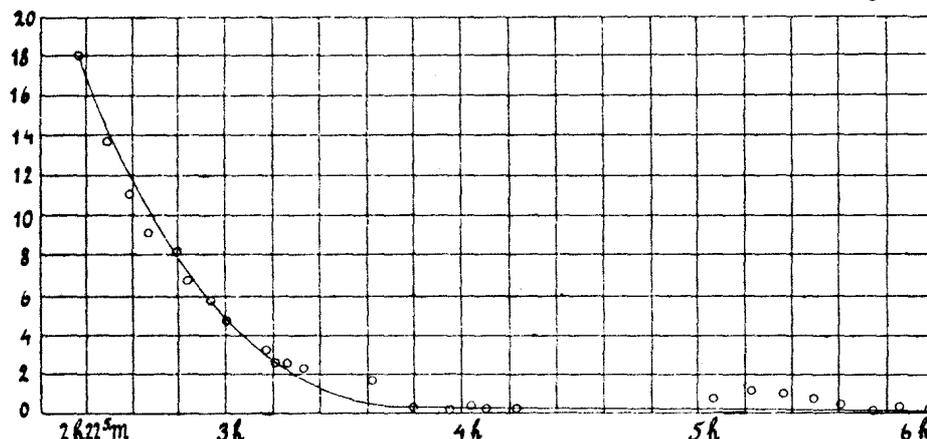

Fig. 1.

§ 2. *Calculation of the pressure change from the experimental data.*

The curve giving the change in the pressure difference between the two communicating vessels as a function of the time was now calculated from the dimensions of the apparatus and from data determining the temperature distribution along the glass capillary. As will be seen from the end of § 3, calculation is in complete agreement with observation, and is therefore suitable for checking the smallest pressure difference experimentally determined by the above method in the case discussed in § 3. The reduction of the theoretical calculation to formulae has the result that it not only covers this particular case, but it can also be applied to gauge the degree of pressure equilibrium in similar cases in which capillary connections occur in experiments at low temperatures.

The influence of gravity upon the gas is left out of account in the calculation, as is also the pressure difference which KNUDSEN's researches show must exist. If necessary both corrections may be applied to the observed pressure at which equilibrium is attained [1]. The influence of slipping along the walls of the capillary is also left out of account, while the volume of the capillary has been regarded as negligible compared with that of the reservoir and of the volumenometer. It is also assumed that the speed may be regarded as to remain the same over a short period of time, and that the speed is small (far below the critical); further that the temperature, T, and the pressure, p, may be regarded as uniform over any cross-section, so that if x is the length and y and z two axes at right angles to it and to each other, p is independent of y and z; and, finally, that the speeds v and w in the directions of y and z may be taken to be zero. A flow is therefore assumed such that in a tube at constant temperature throughout and for a substance whose density is independent of the pressure POISEUILLE's law should hold, and such as may be regarded as subject to this law over any element of length, dx, of the capillary when the values of the pressure gradient, the density ϱ and the viscosity η at that particular place are inserted. Working out the equations of motion subject to the given assumptions [2] at once leads to the result

$$\frac{dm}{dt} = \frac{\pi}{8} R^4 \frac{\varrho}{\eta} \frac{dp}{dx} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where m is the mass of the gas contained in the reservoir, and hence $\dfrac{dm}{dt}$ the mass which flows per unit time across any section of the capillary.

We assume η to be independent of the pressure so that $\eta = f(T)$, and for $f(T)$ we take SUTHERLAND's formula

$$\eta = \eta_0 \frac{1 + \dfrac{C}{273}}{1 + \dfrac{C}{T}} \sqrt{\frac{T}{273}}$$

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[1] As a general rule, however, both corrections may be neglected. For the lowest pressure occurring in the course of the experiments for which this calculation was made the KNUDSEN correction just reached that limit at which the calculations by KAMERLINGH ONNES for the capillaries of his hydrogen and helium thermometers show it would begin to be appreciable.

[2] Cf. O. E. MEYER, Pogg. Ann. 127. p. 253, 353.

in which C is a constant. As an approximation for vapours we may write $p = a\varrho + b\varrho^2$ in which a and b are functions of T. These and all other quantities occurring in the present calculation were expressed in absolute measure (the C. G. S. system was chosen). If T be given as a function of x, equation (1) can at once be integrated.

As a further simplification for this integration we shall regard b as negligible on account of the smallness of $b\varrho^2$ compared with $a\varrho$. If the pressure difference between the ends of the capillary is small, deviations from BOYLE's law may, to the same extent, be allowed for. For further information on this point I may refer to my dissertation.

It may be further remarked that we may differentiate between three different portions of the capillary. The first part projects above the cryostat, and has throughout its whole length the same temperature, that of its surroundings (room temperature); for the pressure at the upper end of this portion we shall write p_4 and for the pressure at the lower end p_3. In the second part of the capillary the temperature changes from the room temperature to that of the cryostat bath. The pressure at the upper end of this part is p_3, and for the pressure at the lower end we shall write p_2. The third portion of the capillary is wholly within the cryostat bath, and over its whole length has the temperature of the bath. p_2 is the pressure at the upper end, and we shall write p_1 for the pressure at the lower end.

With the object above indicated of not only calculating for the particular case discussed in § 3, but also of obtaining simple formulae applicable to analogous cases I have endeavoured to find a simple form for the function expressing the temperature of the middle portion in terms of the length; in order that four terms in this would suffice I have imagined a sudden change in the temperature at the junction of the second and third portions of the capillary, in other words I assume that at that point the temperature changes rapidly over a length which is large compared with the diameter of the capillary but is still small compared with its length.

The calculation is therefore made for a temperature distribution other than that which actually exists, but, as will be seen, the difference between the two cases does not affect the result.

The temperature distribution over that portion of the capillary in which the temperature is variable is thus represented by

$$x = q + l_x T + m_x T^2 + n_x T^3. \qquad \ldots \quad \ldots \quad (2)$$

In the experiment further discussed in § 3 the temperature change

at the surface of the bath would be one of from $T_3 = 26°$ K. to $T_1 = 15°$K. With $a = a_1 T$,

$$k = \frac{1 + \dfrac{C}{273}}{\sqrt{273}} \quad \text{and} \quad A = \frac{8}{\pi R^4} \frac{dm}{dt}, \quad \cdots \cdots \quad (3)$$

(1) now gives

for the first portion $\qquad A = \dfrac{1}{2\lambda_4 \eta_4 T_4} (p_4{}^2 - p_3{}^2), \quad \cdots \cdots \quad (4)$

and for the third portion $\quad A = \dfrac{1}{2\lambda_1 \eta_1 T_1} (p_2{}^2 - p_1{}^2), \quad \cdots \cdots \quad (5)$

while the substitution of

$$T = C \, tg^2 \, a \quad \cdots \cdots \cdots \cdots \quad (6)$$

gives

$$p_2{}^2 - p_3{}^2 = 4 A a_1 \, k\eta_0 \, C^{5/2} [(F_T)_3 - (F_T)_2] \quad \cdots \cdots \quad (7)$$

in which

$$F_T = \left[\frac{nC^2}{3} tg^9 a + \frac{C(2m - 3nC)}{7} tg^7 a + (l - 2mC + 3nC^2) \right.$$

$$\left. \left(\frac{tg^5 a}{5} - \frac{tg^3 a}{3} + \frac{tg \, a}{1} - a \right) \right], \quad \cdots \quad (8)$$

so that p_2 and p_3 can be expressed in terms of p_1 and p_4. From (4), (5), (7) it is seen that for a case such as that discussed in § 3 for which $T_1 = 15°$K. and $T_4 = 295°$K, p_1 does not differ appreciably from p_2, so that one need not be very particular about the lower limit in the integral of (7) and (8), and the small jump in the temperature is of no influence within the limits of accuracy desired; this indeed is obvious if one considers that the gas flows about 20 times more slowly in the cold portion while the viscosity is also about as many times smaller.

With the temperature function now obtained for the interchange of pressure in a gas of known C, η_0 and a, through a capillary of radius R, and for a given temperature distribution, we obtain

$$\frac{dm_2}{dt} = \frac{\pi R^4}{8 K a_1} (p_1{}^2 - p_4{}^2) \quad \cdots \cdots \quad (9)$$

in which m_2 is the mass of gas in the volumenometer, and

$$K = L\eta_0 (F_{T_2} - F_{T_3}) + M\eta_1 \lambda_1 T_1 + N\eta_4 \lambda_4 T_4$$

where the quantities L, M and N follow at once from (4), (5) and (7). The first member of the expression for K refers to the portion of the capillary in which the fall of temperature occurs, and the second

and third members to those portions in which the temperature is uniform.

If we further write

$$p_1 = a_1 T_1 \frac{m - m_2}{v_1} \qquad p_4 = a_1 T_4 \frac{m_2}{v_2} \quad . \quad . \quad . \quad . \quad (10)$$

in which v_1 represents the volume at the lower temperature, v_2 that at ordinary temperature, and m the total mass, and then integrate (9) we obtain, with the omission of an integration constant

$$\frac{v_1 v_2}{T_1 T_4 m} \, log \, \frac{(m - m_2) + \dfrac{T_4 v_1}{T_1 v_2} m_2}{(m - m_2) - \dfrac{T_4 v_1}{T_1 v_2} m_2} = \frac{\pi R^4 a_1}{4 K} t \quad . \quad . \quad (11)^1)$$

The case discussed in § 3 and graphed in fig. 1 gives an example of the curves given by this equation.

§ 3. *Application to a special case. Deductions.*

From measurements made during the experiment of 18th July 1911 temperatures were to be taken as

$\qquad$ —258° C. for 10 cm. in the liquid bath

$\qquad$ —228° $\quad$,, $\quad$ 7 cm.

$\qquad$ —115° $\quad$,, $\quad$ 7 cm.

$\qquad$ — 25° $\quad$,, $\quad$ 14 cm.

Room temp. at + 22° $\quad$,, $\quad$ 22 cm. projecting outside the cryostat.

For the calculation of (2) the temperature of each portion is regarded as the temperature at its centre.

We therefore get $\lambda_1 = 10$, $\lambda_4 = 11$, $T_1 = 15$, $T_4 = T_2 = 295$; and from $x = 10$ to $x = 49$ equation (2) holds with the values

$$q = 1.66 \quad l_x = 0.389 \quad m_x = -0,00278 \quad n_x = 0,00000682;$$

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[1]) In the simple case in which $p_1 + p_2$ may be regarded as constant, and $T_1 = T_4$, $m = v_1 \, d + v_2 \, d$ in which d is the common density in both vessels, substitution of (10) in (11) gives

$$\frac{v_1 v_2}{C_1 (v_1 + v_2)} \, log \, \frac{C_2}{p_1 - p_2} = C_3 t \, .$$

The subscript 4 is here replaced by 2.

This is the formula given by RAYLEIGH Scientif. papers Vol. IV 1892—1901 p. 53. This formula does not hold for instance for the evacuation of a vessel by a pump through a capillary, to which (11) is applicable as long as the pressure is not so small that the mean free path becomes comparable with the diameter of the capillary.

while, as was already remarked, the temperature jump assumed to take place at the surface of the liquid has no influence upon the result. We also find

$$m = 0{,}017, \quad v_1 = 110, \quad v_2 = 1035.$$

The line drawn in fig. 1 has been calculated from these data. The observed pressures, indicated by circles, agree well with the results of calculation.

Between half-past four and five more liquid gas was admitted into the cryostat. The readings during which the resulting pressure interchange was stopped by means of a valve are not marked in the figure. A slight temperature fluctuation occasioned by the refilling is clearly seen in the diagram. A small pressure increase at 5^h5^m dies down about six o'clock quite in accordance with the calculated curve. (See 3^h27^m. At this point the temperature also increased).

As can be seen, it took more than an hour for the last 1.8 m.m. pressure difference to die down to 0.02 m.m. (the whole pressure was 5 cm.).

The calculations show that the assumed distribution of temperature along the capillary is, in the main, correct. It gives a very welcome estimate of the time requisite for the last appreciable interchange of gas.

To establish pressure equilibrium as rapidly as possible in such experiments it is necessary that:

1. as little of the capillary as possible should project above the cryostat, and that the stem within the cryostat should be kept as cold as possible;

2. the upper part of the capillary should be wider than the lower, as is the case, for instance, in the helium thermometer of KAMERLINGH ONNES, or better still, the connecting capillary should be gradually narrowed. (In fig. 5 Comm. Suppl. N°. 21*b* [1]) compare the tube which, in the experiments by KAMERLINGH ONNES on the attainment of the lowest possible temperatures, had to carry off helium vaporised under a pressure of 0.2 mm. with the least possible reduction of pressure; the dimensions of this tube were calculated according to the principles of § 2).

(To be continued).

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[1]) Bericht über den II. Internationalen Kältekongres, Wien, October 1910, Bd. II.