Physics. — *"Isotherms of diatomic gases and of their binary mixtures. X. Control measurements with the volumenometer of the compressibility of hydrogen at 20° C.* By **W. J. de Haas**. Communication N°. 127a from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of April 26, 1912).

X. *The compressibility of hydrogen at 20° C.*

§ 1. *Introduction.* In Communication IX. "Control measurements with the volumenometer", (Comm. N°. 121a, Proc. May 1911) a discussion based upon experimental data was given of the degree of accuracy attainable in determinations with the volumenometer. A determination of the compressibility of hydrogen at ordinary temperature has now given an additional desirable test of the accuracy with which the various experimental conditions in their mutual relationships have been fulfilled.

The investigation is based upon the Leiden measurements of the compressibility of hydrogen at pressures up to 60 atm. The accurate piezometers (Comm. N°. 50) and the sectional open manometer (Comm. N°. 44) specially designed by Kamerlingh Onnes for that investigation rendered a very high accuracy attainable in those measurements. Considering this degree of accuracy, we may therefore take Schalkwijk's measurements with those apparatus at 20° C. to be quite accurate, and ascribe the small difference between his formula and that deduced from Amagat's results to a lower degree of accuracy in one or other of Amagat's measurements (perhaps in his determination of the normal volume, which can be done more accurately by Kamerlingh Onnes's method). This conclusion is also supported by the fact that Schalkwijk's formula is confirmed by the results obtained by Kamerlingh Onnes and Hyndman (Comm. N°. 78).

We may therefore write at 20° C.

$$pv_A = 1.07258 + 0{,}000667\, d_A + 0{,}00000099\, d_A{}^2$$

in which p is the pressure, v_A the volume in terms of the normal volume and d_A is the reciprocal of v_A. On account of the small densities which occur in measurements made with the volumenometer (in which d_A is at the most 1.1) the $d_A{}^2$ term may be neglected. The compressibility at 20° C. is then given by

$$pv_A = A_A + B_A\, d_A$$

in which
$$A_A = 1.07258$$
$$B_A = 0.000667$$

. . . . . (I)

Again, on account of the small densities at which the volumeno-meter is used, the second of the terms on the right of the sign of equality plays but a small part in the result; it varies from 7.10^{-4} of pv_A at density 1.1 to 1.10^{-4} of pv_A at density 0.15. The question to be investigated in the proposed test was if compressibility determinations with the volumenometer could give values of pv_A to within 2.10^{-4}.

As appears from the table at the end of § 3 giving pv_A as obtained from experiment and d_A as calculated, the accuracy attained in the compressibility determinations is as a rule somewhat greater than that which we desired. (Comm. No. 121, § 1). To show more clearly the nature of the remaining deviations, values of B_A determined by formula (I) have also been calculated from the volumenometer results by themselves; in doing this, of course, a sufficiently good approximation can be obtained only at the highest densities.

§ 2. *Summary of the experimental methods.* To get as good an idea as possible of the reliability of the volumenometer determinations of compressibility at temperatures between $-252°$ C. and $-259°$ C. the compressibility was first measured at ordinary temperature within the same pressure limits as would be chosen or were to be expected at the lower temperatures. Measurements were made with two distinct quantities of distilled hydrogen. For the first series a pressure of half an atmosphere was chosen as the starting point, and it was desired to ascend to a pressure of 1.1 atm. while in the second series the limits chosen were 0.16 atm. to 0.5 atm. The apparatus was filled in the usual way (cf. Comm. No. 94f) after repeated evacuations and washings with hydrogen.

For the determination at higher pressures measurements were made in the neck m_3 (see Plate I, Comm. No. 117) and pressures were obtained from the manometer $\Theta_B - \Theta_s$ and the barometer $\theta_C - \theta_D$. In this an artificial constant pressure practically equal to the barometric pressure was maintained in the manner usually adopted in the Leiden Laboratory by means of the ice pot R. To eliminate changes due to temperature fluctuations the four menisci to be observed were read twice in reverse order. Measurements were then made in the necks m_4 and m_5 (Pl. I loc. cit.). To do this the tap l_7 was closed, and, keeping k_4 closed, communication was established with a mercury pump through k_{41}, k_{43}. After careful evacu-

ation the pressures of the volumes close to the necks m_4 and m_5 were measured, using the manometer as an indicator. For this two of the telescopes of the large Société Genevoise cathetometer were focussed upon the menisci in the volumenometer and manometer, and the heights were read each time from the standard metre S.

In an identical fashion measurements were made with a smaller quantity of gas in the necks m_3, m_4, and m_5.

For further experimental conditions and precautions reference may be made to Comm. No. 121, § 4 and 5 and also to my dissertation, which is to be published shortly.

§ 3. *Calculation and values of pv_A.*

The final value of the gas density for each of the two series of measurements, each with its own definite quantity of gas, was obtained by means of equation (I) from the observed final pressure after the application of the correction necessary for the small difference between 20° C. and the temperature at which the measurements were made. The pressure coefficient used was 0,0036627 (Comm. N°. 60). On account of the smallness of the temperature difference for which a correction has to be applied no correction is needed for the dependence of this pressure coefficient upon the pressure. The observed volumes v_A for each measurement follow from the v_A's obtained from the final density and from the ratio of the volumes in each series measured at 20° C. to the final volume. Table I gives

TABLE I. H_2. Values of pv_A					
No.	t	p	d_A calc.	pv_A obs.	O—C
1	20° C.	0.46780	0.43603	1.07278	— 0.00009
2	»	0.58113	0.54162	1.07295	+ 0.00001
3	»	1.12867	1.05161	1.07328	
1	20° C.	0.16310	0.15205	1.07247	— 0.00021
2	»	0.20258	0.18885	1.07248	— 0.00022
3	»	0.39313	0.36645	1.07282	

the values of pv_A, and those of d_A as calculated from p by means of equation (I).

From this it is evident that an accuracy of one in four thousand to one in five thousand is attained at the lower pressures, while in the series of measurements made at higher pressures the accuracy reached is greater than one in ten thousand.

§ 4. *Calculation of* B_A. From the former of the two series contained in Table I (pressures varying from 1.1 to 0.46) B_A can be calculated. Instead of $B_{A20^\circ} = 0,00067$ it gives

$$B_{A20^\circ} = 0,00074 \text{ so that } O-C = 0,00007,$$

in which only the fourth decimal is significant. In the second series the percentage error expected in B_A is too great to allow of a calculation of B_A itself. Only under more favourable circumstances could one count upon an accuracy of one in ten thousand or more in the values of pv_A; the error in pv_A becomes greater at smaller pressures; in B_A it is magnified four or five times and at small densities the utmost value of the whole term $B_A d_A$ for that series is 0,00026. In the meantime it may be remarked that a comparison of the positive differences found here between observation and calculation ($+0,0013$) with the corresponding positive difference in the first series seems to indicate a possible systematic error which makes its presence specially felt at the lower pressures [1]).

In order to be able to compare the results obtained with others which just had in view the determination of the compressibility at ordinary temperature we must reduce the results to a common basis.

Take first the measurements made by LEDUC [2]) at 16° C. and at pressures varying from 1 to 1.5 atmospheres. From the numbers which he obtains from his experiments after the incorporation of other data for the compressibility at 0° C. we find to correspond with his result

$$B_{A20^\circ} = 0,0007 \text{ and therefore } O-C = 0,0000.$$

The figure last given does not necessarily lead to the conclusion that the Leiden determinations with the volumenometer are the less accurate. The degree of accuracy of LEDUC's results is indicated by the fact that he goes only to the fourth decimal place (for CO_2 CHAPPUIS [1]) and LEDUC differ by 0,0002). And the pressures used by LEDUC in this determination, which is accurate to 1 in 10000 were very much more favourable (the smallest density was twice as great as that of the first series of Table I) than those which are expe-

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[1]) Possibly a small constant error arising from a change in the correction for the capillary depression since the control measurement of Comm. N^0. 121a.

[2]) A. LEDUC, Recherches sur les gaz. 1898.

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).

§ 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-

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[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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