

Citation:

W.H. Keesom, On the second virial coefficient for di-atomic gases, in:
KNAW, Proceedings, 15 I, 1912, 1912, pp. 417-431

Physics. — “On the second virial coefficient for di-atomic gases”.

By Dr. W. H. KEESOM. Supplement N°. 25 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction. Synopsis of the more important results.* In Supplements N°. 24a (§ 1) and b (§ 6), in which the second virial coefficient was deduced from different particular assumptions concerning the structure and action of the molecule, a comparison was contemplated between the results then obtained and such experimental data as are at present available. The present paper will discuss some results obtained by carrying out such a comparison in the case of di-atomic gases. The importance of such a comparison, as well as of a comparison of the second virial coefficients for various gases, especially for di- and mon-atomic gases, from the point of view of the law of corresponding states, was emphasized in Comm. N°. 127c, § 1 (these Proceedings p. 405). That such a comparison can now be made with any fruitful result is due to the extensive series of accurate isotherm determinations made by KAMERLINGH ONNES and his collaborators, BRAAK, CROMMELIN, and W. J. DE HAAS.

In the present investigation a beginning is made with the di-atomic gases, especially with hydrogen, for these reasons: In the first place the most immediately indicated simplified hypothesis that can be made concerning the genesis of molecular attraction and can give any hope of agreement with experimental results¹⁾ is that first introduced by REINGANUM, which represents it as originating in the mutual electrostatic action of doublets of constant moment immovably attached to the molecules at their centres; this, together with the assumption that the molecules collide as if they were rigid spheres of central symmetry, leads to a value of the specific heat which agrees most closely with that of the di-atomic gases dissociating with difficulty at ordinary temperature; for these gases a law of dependence of B upon the temperature quite definite, and therefore ready to be tested, was deduced in Suppl. N°. 24b § 6 from the above assumptions. In the second place, values of B for hydrogen are known over a much more extensive temperature range than for any other gas with the

¹⁾ See M. REINGANUM, Ann. d. Phys. (4) 38 (1912), p. 649 for the rejection of the explanation of molecular attraction by gravitation, or (at least of the total molecular attraction, cf. p. 429 note 2) by the magnetic action of series of magnets assumed to be present in the molecules of paramagnetic and ferromagnetic substances.

exception of helium, but for helium values of B for temperatures below the BOYLE point are still comparatively uncertain.

The most important results yielded by the present investigation can be summarised as follows. The experimental results concerning the second virial coefficient for hydrogen above -100°C . (the observations reaching $+100^\circ\text{C}$.) are consistent with the above assumptions of Suppl. N^o. 24b § 6 (rigid spheres with constant doublets). Below -100°C . hydrogen exhibits deviations from this behaviour which finally become considerable. Below the BOYLE point (the corresponding region of observation is from -180°C . to -230°C . for H_2) hydrogen is found to correspond with argon, and also with helium in so far as the experimental data for helium at present available allow of any definite conclusion. It appears therefore that between -100°C . and -230°C ., as far as B is concerned *the thermal behaviour of hydrogen also approaches that of a monatomic substance and eventually becomes the same, as was found by EUCKEN*¹⁾ to be the case with its caloric behaviour. This conclusion is supported by the results for the coefficient of viscosity.

It was also found that, as far as the second virial coefficient is concerned, the thermal behaviour of oxygen between 0° and 200°C ., as deduced from AMAGAT's observations²⁾ corresponds with that of a system of rigid spheres of central symmetry, each with a doublet of constant moment at its centre.

For nitrogen, on the other hand, within the same temperature region (0° to 200°C ., AMAGAT's observations) important deviations were found from the behaviour of rigid spheres of central structure each with an electric doublet of constant moment at its centre. With nitrogen in that temperature region, the dependence of B upon the temperature corresponds to that deduced from the assumption that the VAN DER WAALS quantities a_W and b_W are constant (Suppl. N^o. 24a § 3); but then, however, the values given by BESTELMEYER and VALENTINER for B from 81° to 85°K . differ greatly from this.

§ 2. *Method.* Logarithmic diagrams were employed for the comparison of the experimental values of B with those deduced in Suppl. N^o. 24 from various assumptions (cf. Suppl. N^o. 23, Math. Enc. V 10, Nr. 33a). For this purpose $\log B_N$ was plotted as a function of $\log T$ upon transparent squared paper to a scale of $1\text{ mm.} = 0,005$. Here, following Suppl. N^o. 23, B_N represents the

¹⁾ A. EUCKEN. Berlin Sitz.-Ber., Febr. 1912, p. 141.

²⁾ Cf. p. 428 note 1.

second virial coefficient when the empirical equation of state is written in the form:

$$pv_N = A_N \left\{ 1 + \frac{B_N}{v_N} + \frac{C_N}{v_N^2} + \frac{D_N}{v_N^3} + \frac{E_N}{v_N^4} + \frac{F_N}{v_N^5} \right\}, \dots \quad (1)$$

while the subscript N indicates that the volume is expressed in terms of the normal volume as unit (cf. Suppl. N^o. 23, Chapter on "Units"). Values of B_N were taken from the corresponding individual values of B_A which were given in previous communications by KAMERLINGH ONNES, and by him in collaboration with BRAAK, with CROMMELIN, and with W. J. DE HAAS. As we must remember that the latter coefficients B_A , belong to the empirical equation when written in the form of equation (II) of Comm. N^o. 71 (June '01), and that the subscript A has there a meaning quite different from that attached to it in Suppl. N^o. 23, they will be in the sequel distinguished as $A_{(71)}$. The reduction is then made by means of the relationship

$$B_N = \frac{B_{A(71)}}{A_{A(71)}} \dots \dots \dots \quad (2)$$

It was first examined for each of the different gases if the temperature variation of B is in agreement with that deduced on the assumption of rigid molecules (cf. Suppl. N^o. 24a § 3 for spheres of central structure, § 4 for ellipsoids, cf. also p. 255 note 1 of that Suppl.) and VAN DER WAALS attractive forces. This assumption gives

$$B_N = b_{WN} \left\{ 1 - \frac{a_{WN}}{b_{WN}R_N T} \right\} \dots \dots \dots \quad (3)$$

(cf. Suppl. N^o. 24a § 3 equation (14)), where a_{WN} , b_{WN} and R_N are constants. For this investigation $\mathcal{F}_1 = \log(1-\tau)$, in which $\tau = \frac{a_{WN}}{b_{WN}R_N T}$ is now plotted as a function of $\log \tau$ on transparent squared paper to the same scale as before. But $\log \tau$ is now taken as increasing in the opposite direction to that in which $\log T$ increases in the previous diagrams.

For comparison with the assumption that the molecules of a gas behave as if they were rigid molecules of central structure each with an electric doublet of constant moment at its centre, equation (59) of Suppl. N^o. 24b § 6 was written in the form:

$$B_N = b_{WN\infty} \left\{ 1 - \frac{1}{3} (hv)^2 - \frac{1}{75} (hv)^4 - \frac{29}{55125} (hv)^6 \dots \right\} \dots \quad (4)$$

Here h and v have the same significance as in Suppl. N^o. 24b § 6, and $b_{WN\infty}$ is the factor which, for the units now employed, must replace the factor $\frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^2$ of Suppl. N^o. 24b § 6.

$$\mathcal{F}_2 = \log \left\{ 1 - \frac{1}{3} (hv)^2 - \frac{1}{75} (hv)^4 - \frac{29}{55125} (hv)^6 \dots \right\} \quad (5)$$

is now plotted as a function of $\log hv$, where again $\log hv$ is taken increasing in the direction opposite to that in which $\log T$ increases in the $\log B_N$, $\log T$ -graph. Where necessary in (5) terms up to and including $(hv)^6$ were used in the calculation.

As in Suppl. N^o. 23 Nr. 38 (cf. note 399 of that Suppl.) where the argument of the logarithm is negative, the absolute value of the logarithm is plotted, and the corresponding portion of the curve is marked by (n).

To ascertain if the experimental values of B_N correspond to one or other of the equations (3) and (4), is now the same as trying if the corresponding $\log B_N$, $\log T$ -curve can be made to coincide as a whole or in part with the corresponding \mathcal{F}_1 , $\log \tau$, or \mathcal{F}_2 , $\log hv$ -curve by moving it over the other, keeping the coordinate axes of the two graphs constantly parallel ¹⁾.

§ 3. *Hydrogen. a.* The individual virial coefficients for hydrogen were taken from Comm. N^o. 100a (Dec. '07) table XXII and from Comm. N^o. 100b (Dec. '07) by KAMERLINGH ONNES and BRAAK (cf. Comm. N^o. 101b (Dec. '07) table XXV for the reduction of the temperatures to the AVOGADRO scale), and from Comm. N^o. 127c (these Proceedings) table IV by KAMERLINGH ONNES and W. J. DE HAAS ²⁾.

b. On moving the $\log B_N$, $\log T$ -diagram for hydrogen over the $\log \mathcal{F}_1$, $\log \tau$ -diagram, which I shall call in what follows the diagram for a_W and b_W constant, it was evident that it was not possible to get them to coincide over any extensive temperature region (see fig. 1). From this it is again (cf. Suppl. N^o. 23 Nr. 44 for the general case) evident that constant values of a_W and b_W cannot be used to represent even the planetary gas state (which, cf. Comm. N^o. 127c, these Proceedings, § 1 by KAMERLINGH ONNES and W. J. DE HAAS, can be more closely defined as that state in which only the B -term is still of influence in the equation of state) for hydrogen, over a temperature region of any appreciable extent.

One could now try to determine values of a_W and b_W which on the assumption that a_W and b_W are constant over any limited region

¹⁾ This method corresponds to the $\log B$, $d \log B / d \log T$ -method of Suppl. N^o. 23 note 399.

²⁾ The individual virial coefficients for hydrogen calculated from the observations of AMAGAT, and given in Comm. N^o. 71, June '01, p. 143, do not agree sufficiently with those given by the Leiden measurements and are therefore unsuitable for extending the temperature variation of B_N to higher temperatures.

of temperature for these regions would give by equation (3) values of B in sufficiently good agreement with the experimental values; this is done by so moving the curves with respect to each other that the curve joining the experimental points touches the $F_1, \log \tau$ -curve within the limits of each particular region¹⁾. In fig. 1 the one curve is moved over the other so as to give agreement at the BOYLE-point²⁾.

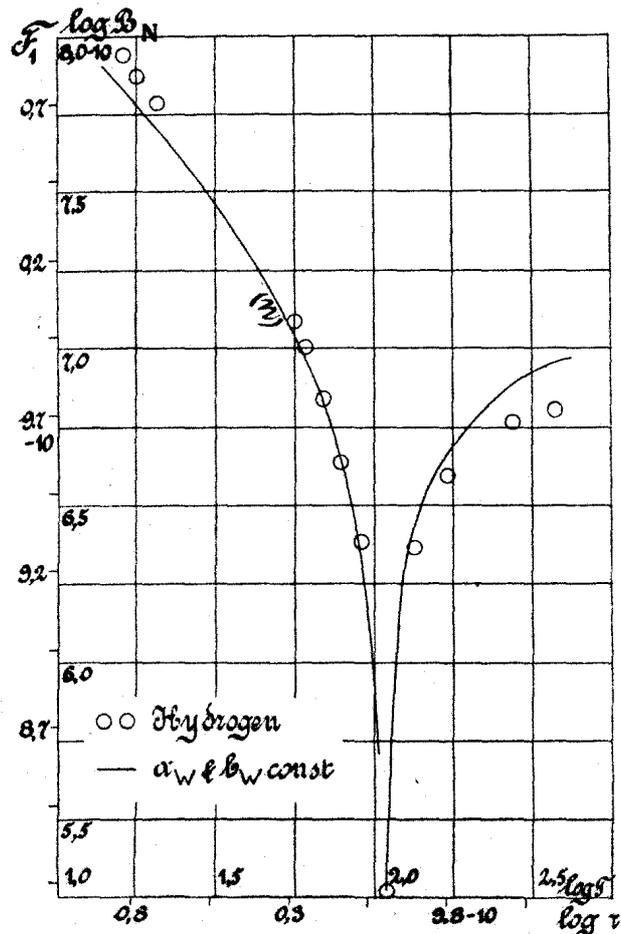


Fig. 1.

In this the point $\log T = 2,0$, $\log B_N = 6,5-10$ coincided with the point $\log \tau = 0,024$, $F_1 = 9,412-10$. From this in conjunction with $A_{N_0^{\circ}C} = A_{A_0(71)} = 0,99942$ ³⁾ we find $a_{WN} = 0,473 \cdot 10^{-3}$ and $b_{WN} =$

¹⁾ With these values of a_W and b_W we could, as in Suppl. No. 28 Nr. 38, for each temperature determine values of the critical reduction quantities for the planetary gas state of the substance under investigation, if we choose as standard for comparison a fictitious substance whose a_W and b_W are assumed to be constant

²⁾ One can easily see how the criterion of contact must be modified for this case.

³⁾ In Comm. No. 100b, Dec. '07, 0.99924 is printed by mistake (as is at once seen from the value of $B_{A_0(71)}$).

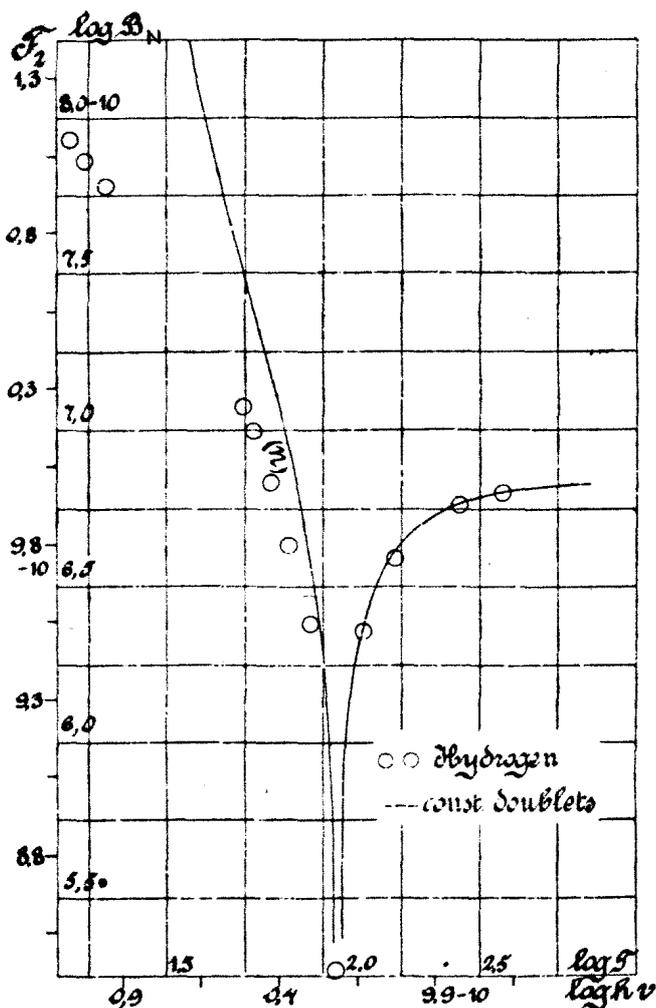


Fig. 2.

$1,224 \cdot 10^{-3}$; these values, therefore, on the assumption that these magnitudes are constant, will give the closest possible agreement with the experimental thermal equation of state, at least for the planetary gas state, at the particular temperature under consideration, which is here found to be $106^\circ \text{K.}^1)$ 2).

1) The values of a_{wN} and b_{wN} given by BRAAK, Diss. Leiden 1908, p. 82 were obtained by a method of calculation which is essentially the same as the $\log B$, $\lg C$ -method of Suppl. No. 23, Nr. 38, applied to the comparison of hydrogen with a fictitious standard with constant a_w and b_w . The difference between these and the results obtained by the $\log B$, $d \log B / d \log T$ -method here, show that complete correspondence does not exist between hydrogen and the fictitious standard with constant a_w and b_w even over a limited temperature region, if one is not confined to the planetary state.

2) The deduction of similar values of a_w and b_w for other temperatures which might be followed by the development of deviation functions as for instance indicated in Suppl. No. 23, Nr. 38, was not made.

c. On moving the $\log B_N$, $\log T$ -diagram for H_2 over the F_2 , $\log hv$ -diagram, which I shall refer to henceforth as the diagram for constant doublets, it was found that comparatively good coincidence was obtained at temperatures above the BOYLE point, see Fig. 2. At temperatures below the BOYLE point, differences, which begin to be noticeable even at the point $-164^\circ C.$ still above the BOYLE point, become very marked, so that below a certain temperature not even local coincidence (contact between the two curves) can be obtained.

If we look upon these differences at the lower temperatures as a consequence of a deviation, which increases regularly towards those temperatures, of the behaviour of the H_2 -molecules from that which is assumed in the hypotheses from which the constant doublets diagram is constructed, there is then reason for superposing the diagrams in a manner slightly different from that shown in Fig. 2, viz. so that the points indicating the highest observed temperatures should lie upon the curve of constant doublets. The $\log B_N$, $\log T$ -diagram does then, in fact, exhibit a deviation from the constant doublets diagram, increasing regularly towards the lower temperatures, and already appreciable at $-139^\circ C.$ At higher temperatures as far as the observations extend, that is, up to $100^\circ C.$, and taking into account the accuracy with which B can be deduced from the observations, we may say that as far as B is concerned *the thermal behaviour of hydrogen in the planetary gas state may be represented by that of a system of rigid spheres of central structure, each with an electric doublet of constant moment at its centre.* The caloric behaviour of H_2 , in which differences clearly occur earlier, is, to a first approximation, consistent with this at the higher temperatures of the region under consideration.

From this method of superposing the diagrams we may easily deduce values of σ , the diameter of a molecule, and of v , the potential energy (v being 0 for $r = \infty$) of two molecules in contact, when the axes of the doublets are respectively parallel and perpendicular to the line joining the centres of the molecules (cf. Suppl. N^o. 24b § 6). On superposing them so that the H_2 -points for the highest three temperatures fell upon the line for constant doublets, then the point $\log hv = 0,2$, $F_2 = 9,7-10$ coincided with the point $\log T = 2,075$, $\log B_N = 6,540-10$. From this, together with the value $k_P = 1,21 \cdot 10^{-16}$ (Suppl. N^o. 23, note 174) taken from PERRIN'S observations we obtain

$$v = 2,28 \cdot 10^{-14} \text{ [erg].}$$

From this too, we get for four times the molecules own volume

on the assumptions here made, expressed in terms of the normal volume as unit, $b_{WN\infty} = 0.692 \cdot 10^{-3}$. This value, which can also be regarded as to be obtained by extrapolation to very high temperatures, is markedly smaller than the value obtained above on the assumption that a_W and b_W may be regarded as constant over a small region of temperature, and it is also much smaller than that given by BRAAK, Diss. p. 82 and 83. We shall return to the variation of b_W with the temperature when we come to consider the viscosity.

From $b_{WN\infty}$ we obtain the diameter of the molecule using the relation

$$b_{WN\infty} A_{N_0} \Theta_M = \frac{1}{2} N \cdot \frac{4}{3} \pi \sigma^3. \quad (6)$$

In this $\Theta_M = 22413$ [cm³.]¹⁾ is the theoretical normal volume of the gram molecule, and $N = 6,85 \cdot 10^{23}$ ²⁾ is the AVOGADRO number. We find

$$\sigma = 2,21 \cdot 10^{-8} \text{ [cm.]}$$

From the values of r and σ we further obtain the moment of the doublet

$$m_e = 4,96 \cdot 10^{-19} \text{ [electrostatic unit. cm.]}$$

Assuming that each pole bears a charge equal to that of a single electron, the distance between the poles should be $1,17 \cdot 10^{-9}$ cm.³⁾, that is, about one twentieth of the diameter of a molecule; within the interior of a molecule there is therefore plenty of room for such a doublet. At the temperatures here considered the mean speeds of rotation assumed by the molecules are such that the electromagnetic force exerted by the molecules upon each other need not be taken into account, and this confirms the assumption previously made

1) Cf. Suppl. N^o. 23, note 23, and "Einheiten" a.

2) Taken from PERRIN's researches; cf. Suppl. N^o. 23, note 173.

3) From the energy required to ionise the gas RUTHERFORD and Mc KLING, Physik. ZS. 2 (1900), p. 53, obtained the same order of magnitude. So, too, did REINGANUM, Physik. ZS. 2 (1900), p. 241, Ann. d. Phys. (4) 10 (1903), p. 334, and loc. cit. p. 417 note 1, from the dependence of viscosity upon temperature (cf. § 6), from the tensile strength of metals, and from the latent heats of vaporisation of liquids, while the same order of magnitude for the moment of the molecule was obtained by DEBIJE, Physik. ZS. 13 (1912), p. 97, from the variation with temperature of the dielectric constants of certain liquids.

(Suppl. N^o. 246 § 6), that we need only allow for electrostatic forces.¹⁾

Consideration of the viscosity lends some support to the result obtained above that hydrogen behaves at higher temperatures in the planetary gas state as a system of hard spheres of central symmetry, each with an electric doublet at its centre, but deviating considerably therefrom at lower temperatures. On this point we may refer to § 6.

d. Comparison of the $\log B$, $\log T$ -diagram for hydrogen with that for argon affords an important insight into the behaviour of H_2 below the BOYLE point which is closely related to the deviation found in c for the H_2 diagram from that for constant doublets²⁾. The

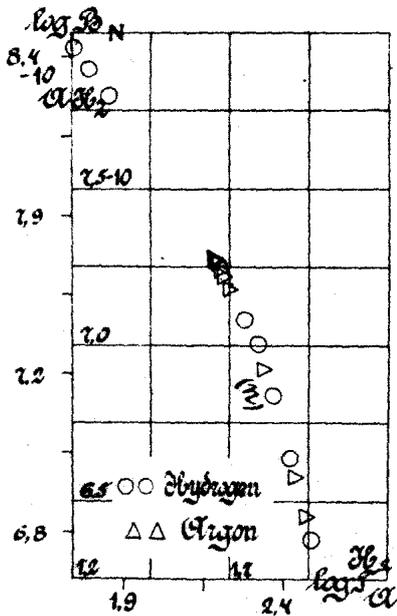


Fig. 3.

individual virial coefficients for argon were taken from Comm. N^o. 1186 (Dec. 1910) by KAMERLINGH ONNES and CROMMELIN. From their measurements a portion of the branch (n) of the $\log B$, $\log T$ -curve lying below the BOYLE point is accurately known.

On superposing the $\log B_N$, $\log T$ -curve for hydrogen on that for argon it is evident that the latter quite well fits the corresponding part of the hydrogen curve, see Fig. 3³⁾.

From this it follows that, in so far as the second virial coefficient of the thermal equation of state is concerned, the thermal behaviour of hydrogen from -180°C. to at least -230°C. (the temperature for hydrogen which corre-

¹⁾ The length of the axis of a doublet may also be neglected in a first approximation, as has always been done here. In a more accurate calculation, however, this would have to be allowed for.

²⁾ The deviations from the law of corresponding states occurring in B and C for hydrogen when compared with their values for other substances, such as oxygen, nitrogen, carbon dioxide, ether and isopentane, for which, as well as for hydrogen at very high reduced temperatures, the mean reduced equation VII.1 (Suppl. N^o. 19, p. 18) holds, first found definite expression in the special equation VII. H_2 . 3 (Comm. N^o. 109a equ. (16)), which was introduced for this purpose; marked differences occur between the \mathfrak{B} and \mathfrak{C} of this special equation and those of the mean equation VII.1. The continuation of the investigation of the nature of these differences which was commenced in Suppl. N^o. 23, Nr. 38, was left to me by Prof. KAMERLINGH ONNES.

³⁾ Then the point $\log T = 2.4$, $\log B_N = 7.2-10$ for argon coincided with the point $\log T = 1.869$, $\log B_N = 6.908$ for hydrogen.

sponds to the lowest observed argon temperature) *corresponds to that of a monatomic substance*^{1) 2)}.

e. In Nr. 38 of Suppl. N°. 23 hydrogen is compared with helium. From fig. 15 of that Suppl. it is evident that from the BOYLE point downwards good correspondence is obtained between He and H₂ in so far as any conclusion is possible from the small number of helium points which were available for the construction of that particular branch of the log *B*, log *T*-curve³⁾. To the figure just quoted we may now add the helium point 4°,29 K. from Comm. N°. 119 (March 1911) § 5, which, in that figure, comes above the argon-hydrogen line. A suitable displacement⁴⁾, however, of the helium diagram brings this point (whose degree of accuracy, however, is not so high as that of the points forming the H₂-A-curve), too, on to the hydrogen-argon curve.

From fig. 16 of Suppl. N°. 23 one can see further that, when superposing the hydrogen and helium curves so that the branches below the BOYLE point coincide, those above the BOYLE point deviate markedly from each other, from the figure quoted and from the table referring to it in note 399, that coincidence between the branches above the BOYLE point can be obtained only over a very limited region⁵⁾. So that at these higher temperatures appreciable deviations from correspondence between He and H₂ exist.

¹⁾ The preliminary values of B_N obtained for helium in the corresponding region do not conflict with the suspicion that this is the case down to much lower temperatures (see e).

²⁾ From the data given on p. 425 note 3 for the displacement necessary to obtain coincidence between the A-curve and the H₂-curve, and from the value $T_k = 150.65$ for argon (C. A. CROMMELIN, Comm. N°. 115, May 1910), we can calculate $T_{kr(H_2:A)} = 25.25$ for the critical reduction temperature for hydrogen with respect to argon as standard for comparison (cf. Suppl. No. 23, Nr. 386). Comparison with the critical temperature for hydrogen on the one side, with $T_{kr(H_2:N_2,O_2)} = 43$ (Suppl. No. 23 note 399) on the other side leads to the conclusion that the virial coefficients for hydrogen and argon higher than the second do not correspond perfectly, though the deviation from correspondence between the two substances within the region of temperature under consideration is much smaller than that between H₂ and N₂ or O₂.

³⁾ The third virial coefficient, *C*, then corresponds as well (see fig. quoted). In good agreement with this is the finding of a constant value for $T_{kr(He:H_2)}$, at the points $t_{He} = -253^\circ$ and -259° , which does not differ much from $T_k He$ (Suppl. No. 23 note 399).

⁴⁾ In this there is no longer any notice taken of the correspondence between the *C* coefficients, as is also the case in the other diagrams discussed in the present paper.

⁵⁾ Comparison with fig. 15 shows that the third virial coefficient, *C*, would then exhibit wide deviations from correspondence.

f. If we combine the results obtained in *d* and *e* with those given in *c* we reach the conclusion that, as far as *B* is concerned, *between* -100°C. and -180°C. the thermal behaviour of hydrogen, which, between -100°C. and $+100^{\circ}\text{C.}$ is that of a system of rigid spheres of central structure each with an electric doublet of constant moment at its centre, and acting upon each other according to the ordinary laws of mechanics and of the electromagnetic field, now changes to that which characterises a monatomic substance, and that between -180°C. to at least -230°C. this behaviour is completely followed ¹⁾. On this account we shall postpone further considerations of the second virial coefficient for hydrogen in this region until monatomic gases are discussed in a subsequent communication.

From the above it is accordingly evident that the thermal behaviour of hydrogen exhibits a strict parallelism with its caloric behaviour as deduced from EUCKEN's measurements of the specific heat at constant volume. As we suspect, in accordance with the theories of NERNST ²⁾ and EINSTEIN ³⁾, that the decrease in the specific heat at lower temperatures will find an explanation in the application of the hypothesis of finite elements of action to the rotations of the molecule, the parallelism here observed at once leads to the question as to whether the explanation of the peculiarities of the thermal equation of state for hydrogen obtained in the present paper may not profitably be sought in the same direction. For instance, one can imagine that the hypothesis in question would lead to the assumption that, on approaching one another, the molecules have not such orientations and are not so distributed with respect to their mutual distances, as is required by the laws of statistical mechanics according to ordinary dynamics and electrodynamics, and that therefore the mean attraction would be smaller at lower temperatures ⁴⁾ than would be the case if these laws were obeyed at these temperatures as well.

From the fact that *B* is negative at those temperatures at which the di-atomic hydrogen begins to behave as a monatomic substance, and that there is consequently some attraction still left which does not decrease much more even with the temperature (cf. *b*), it follows that the quantum hypothesis applied to this region would not have

¹⁾ The temperature regions here given are not to be regarded as sharply bounded, still less are they to be considered as sharply defined by the observations at present available.

²⁾ W. NERNST. ZS. f. Elektrochem. 17 (1911), p. 265.

³⁾ A. EINSTEIN. Discussions of the SOLVAY Congress, Nov. 1911.

⁴⁾ A similar diminution of the attraction was assumed in Comm. No. 119 in order to explain the maximum observed in the density of helium.

to lead to a large decrease of the whole of the attraction, but only to that of a part of it. This, then, would again lead to the hypothesis that at higher temperatures only part of the attraction is to be ascribed to the mutual action of the doublets of constant moment, another part being ascribed to a mutual action of the molecules corresponding to the mutual attraction of monatomic molecules (cf. Suppl. N°. 23 Nr. 34*d*). The answer to the question as to whether treatment on these lines would lead to a still better agreement with observation than that obtained in *c* must, in the meantime, be postponed till a later Communication.

§ 4. *Oxygen*¹⁾ The individual virial coefficients for oxygen were taken from Comm. N°. 71, p. 143.

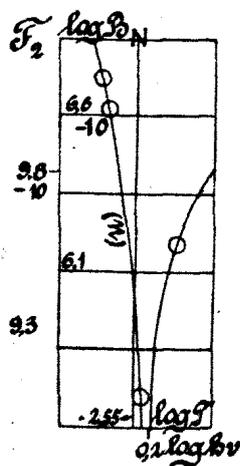


Fig. 4.

From Fig. 4 it is evident that the oxygen points (∞) lie well upon the curve (—) for constant doublets, so that in this particular region (0° — 200° C.), as far as B is concerned, and subject to the reserve of note 1, the behaviour of oxygen may be regarded as that of a system of rigid spheres of central structure each with a doublet of constant moment at its centre. From the following data concerning the superposition of the diagrams (cf § 3*c*) we obtain the accompanying results: the point $\log T = 2,6$, $\log B_N = 6,5 - 10$ for oxygen coincides with the point $\log h v = 0,204$, $F_2 = 9,628 - 10$ on the curve for constant doublets, hence:

$$v = 7,71 \cdot 10^{-14}, b_{WN\infty} = 0,745 \cdot 10^{-3}, \sigma = 2,27 \cdot 10^{-8}, m_e = 9,47 \cdot 10^{-19}.$$

On the assumption that each of the poles of the doublet bears a charge equal to that carried by a single electron, the length of its axis should consequently be one tenth of the diameter of the molecule. The oxygen molecule should accordingly be about as large as the hydrogen molecule, but the moment of its doublet should be about twice as great as that of the hydrogen doublet.

§ 5. *Nitrogen*¹⁾. The individual virial coefficients deduced from

¹⁾ The lack of agreement between the observations of KAMERLINGH ONNES and BRAAK upon hydrogen and those of AMAGAT (cf. p. 420, note 2) shows how desirable it is that new observations should extend our experimental data over a wider range of temperature and give a control upon the values of B deduced from AMAGAT's data for oxygen and nitrogen as well as for hydrogen. In the meantime

AMAGAT's observations covering the region 0° tot 200° C. were taken from Comm. No. 71, p. 143. From the observations of BESTELMEYER and VALENTINER ¹⁾ it is possible to obtain still another value for B_N . At $T = 51,01$ we get $B_{A(71)} = -3,411 \cdot 10^{-3}$, from which with (2) B_N follows.

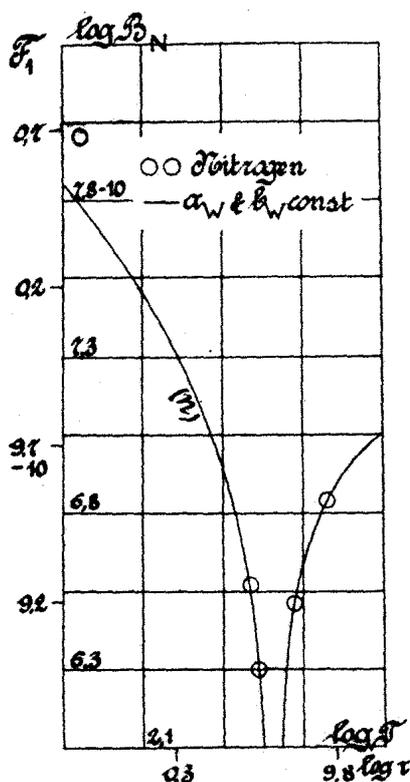


Fig. 5.

Comparison of the nitrogen diagram with the curve for constant doublets and with the hydrogen diagram shows that nitrogen deviates markedly from the other two especially in the neighbourhood of the BOYLE-point ²⁾. Comparison with the curve for a_w and b_w constant shows that the four points taken from AMAGAT's observations can be brought into pretty close agreement with the curve, while the point given by BESTELMEYER and VALENTINER lies then pretty far above it (see Fig. 5).

In Fig. 5 the point

$\log \tau = 0,004$, $\mathcal{F}_1 = 9,731-10$
coincides with the point

$\log T = 2,5$, $\log B_N = 7,05$,
from which we get, for the region covered by AMAGAT's observations:
 $a_{WN} = 2,44 \cdot 10^{-3}$, $b_{WN} = 2,08 \cdot 10^{-3}$.

§ 6. *Coefficient of viscosity* ³⁾. It seemed of importance to investigate whether the results obtained in § 3 find confirmation or not in the manner in which the coefficient of viscosity varies with the temperature. The second column of the following Table, which, on

it appeared not quite devoid of interest to utilise the data at present available for these two gases subject to such reserve as may be necessitated by future control and extension, for comparing with the results of Suppl. N^o. 24.

¹⁾ A. BESTELMEYER and S. VALENTINER. Ann. d. Phys. (4) 15 (1904), p. 72.

²⁾ The different behaviours of N_2 and O_2 from the point of view of the law of corresponding states was illustrated by the two corresponding Tables of Comm. No. 71. The influence of the magnetic properties of oxygen will be investigated later.

³⁾ An investigation of viscosity at low temperatures has been in progress at Leiden for some time. Papers by KAMERLINGH ONNES and DORSMAN on the viscosity of hydrogen and by KAMERLINGH ONNES and S. WEBER on helium will soon be published.

the theory of rigid spheres without attraction, should show the figure 1,000 at each temperature, gives results taken from the observations of MARKOWSKI¹⁾ and of KOPSCH²⁾; in column 3, b_W is the quantity which, multiplied by the factor $\frac{3}{2} \frac{RT}{v}$, gives the collision virial; in accordance with the splitting indicated in Suppl. N°. 24b § 6 of the whole virial of the mutual forces between the molecules into the collision virial and the attraction virial, $b_{W0°C}/b_W$ is calculated from³⁾

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 + \frac{1}{3!} q_1 (hv)^2 + \frac{1}{5!} q_2 (hv)^4 + \frac{1}{7!} q_3 (hv)^6 \dots \right\} \quad (7)$$

(for $q_1, q_2 \dots$ see Suppl. N°. 24b § 6), or

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 + \frac{1}{3} (hv)^2 + \frac{1}{25} (hv)^4 + \frac{29}{11025} (hv)^6 \dots \right\} \quad (8)$$

Although the theory of viscosity, and, in particular, of the influence of molecular attraction upon it, is not yet sufficiently worked out to draw quite certain conclusions therefrom, yet comparison of these two columns seems to show that the behaviour of hydrogen above 0° C. is in pretty good agreement with that of a system of rigid spheres of central structure each with an electric doublet of

t	$\frac{\eta}{\eta_{0°C}} \sqrt{\frac{T_{0°C}}{T}}$ hydrogen	$\frac{b_{W0°C}}{b_W}$ const. doublets
184.2	1.108	1.104
100.5	1.058	1.074
0	1.000	1.000
- 78.73	0.940	0.865
- 194.9	0.827	0.236

constant moment at its centre, but that below 0° C. it deviates considerably therefrom. Comparison of hydrogen and argon shows that

¹⁾ H. MARKOWSKI. Ann. d. Phys. (4) 14 (1904), p. 742,

²⁾ W. KOPSCH. Diss. Halle 1909.

³⁾ For the corresponding α_W we obtain a series with only odd powers of hv beginning with the first; the first term is consequently proportional to T^{-1} (cf. Suppl. No. 23, Nr. 48c) while the subsequent terms become small with comparative rapidity.

the viscosity of hydrogen at $-192^{\circ}.7$ C. and that of argon at 0° C. deviate from correspondence by only 6% (taking the coefficients of similarity from § 3 *d*), but that the viscosity of hydrogen from -193° C. upwards increases much more slowly with the temperature (corresponding to a more rapid increase in the attraction in the case of hydrogen within the region of transition) than corresponds to the increase in the viscosity of argon. This confirms in some degree the conclusions reached in § 3.

Confirmation would have been attained in a higher degree if corresponding to § 4 agreement had been obtained between the temperature variation of the viscosity of oxygen and $b_{w\ 0^{\circ}\text{C.}}/b_w$ as given by (8), using the value of v obtained in § 4. This, however, is not at all the case. That temperature variation can, indeed, as far as observations¹⁾ go, be represented with the aid of b_w^{-1} of (8) but then we find $v = 2,79 \cdot 10^{-14}$ instead of the $7,71 \cdot 10^{-14}$ deduced in § 4 from the coefficient B . Unless the agreement obtained in § 4 is wholly fortuitous we must conclude from this that a deviation from the temperature variation of the viscosity of oxygen as deduced upon the assumption of rigid spheres each with a constant doublet at its centre is occasioned by some circumstance whose influence upon B vanishes, or is at least extremely small. As such, for instance, one could regard deviations from sphericity in the molecular shape.

¹⁾ By H. MARKOWSKI. p. 430, note 1. (The observations by E. VÖLKER, Diss. Halle 1910, on the coefficient of viscosity of O_2 down to $-152^{\circ}.52$ C., which came to my notice only after the Dutch original of this paper was printed, join those observations at 0° — $14^{\circ}.65$ C. Below 0° C. they show a deviation from b_w^{-1} for constant doublets in the same sense as that exhibited by H_2 . At -40° C. this deviation is already distinct and it finally becomes very marked. (Added in the English translation).

E R R A T A.

In the Proceedings of the meeting of June 29, 1912.

- p. 258 l. 9 from the top: for micro-complexion read macro-complexion,
 p. 261 l. 1 „ „ bottom: for $u_{w_1} - h\{\frac{1}{2}\varphi(r_1)\}$ read $h\{u_{w_1} - \frac{1}{2}\varphi(r_1)\}$.
 p. 266 l. 5 „ „ top: for ∞ read τ .
 p. 271 l. 13 „ „ bottom: for EBD read EBB' .

(October 24, 1912).