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**Physics.** — *The second virial coefficient for rigid spherical molecules, whose mutual attraction is equivalent to that of a quadruplet placed at their centre*". By Dr. W. H. KEESOM. Supplement No. 39a to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 25, 1915).

§ 1. This Communication forms a continuation of the investigation started in Suppl. N<sup>o</sup>. 24 (April '12, these Proceedings June '12), the aim of which is to derive, on different suppositions concerning structure and mutual interaction of the molecules, the first terms in the development of the equation of state into ascending powers of  $v^{-1}$  as functions of the temperature, in order to compare them with the available experimental material. It is obvious that in this problem it is indicated to proceed step by step from the simplest to more complicated suppositions.

In Suppl. N<sup>o</sup>. 24b § 6 the second virial coefficient, i. e.  $B$  in the equation of state:

$$pv = A \left( 1 + \frac{B}{v} + \frac{C}{v^2} + \dots \right). \quad \dots \quad (1)$$

was derived for rigid spheres of concentric structure, which carry a doublet at their centre, or whose mutual attraction is equivalent to that of such doublets. In a following paper it will be shown i. a., that the limitation to molecules of concentric structure, observed there, can be omitted as far as concerns the derivation of  $B$ .

In Suppl. N<sup>o</sup>. 25 (Sept. '12) I then showed that the way in which the second virial coefficient of hydrogen between  $-100^{\circ}$  and  $+100^{\circ}$ C. depends on the temperature agrees with that which was derived for doublet-molecules of that structure.

Meanwhile it has, however, become evident especially by DEBIJE's<sup>1)</sup> investigation concerning dielectric constant and refractive index, that the molecules of the diatomic elementary gases do not possess a moment such as that of a doublet. The next step in the theoretical development of the equation of state now seems to be, that the next term of the development of the attractive potential outside the spherical molecule into spherical harmonics, i. e. that of the degree  $-3$ , is considered to be present alone. The corresponding surface harmonic of the second order reduces to the zonal harmonic of the second order for diatomic molecules, which in this paper as in Suppl.

<sup>1)</sup> Cf. P. DEBIJE, Physik. ZS. 13 (1912), p. 97. W. C. MANDERSLOOT, Thesis for the Doctorate, Utrecht 1914, p. 56. N. BOHR, Phil. Mag. (6) 26 (1913), p. 866.

No. 24 we treat as bodies of revolution as regards their fields of force. So we are led to the problem to deduce the second virial coefficient for a system of rigid spheres, whose attraction is equivalent to that of a quadruplet with two coinciding axes, and which is obtained when two doublets are placed along the same line with two homonymous poles towards one another and their distance approaches zero with maintenance of a finite quadruplet-moment<sup>1)</sup>.

We place ourselves in this communication on the standpoint of classical mechanics. The quantum theory only intervenes in so far as the fact that according to that theory the rotations of a diatomic molecule, about one of its principal axes of inertia in consequence of the smallness of the corresponding moment of inertia is not influenced appreciably by the heat motion, is accounted for in our treatment according to the principles of classical mechanics by considering such a molecule as a body of revolution. We do not consider here an influence, as given by the quantum theory, on the rotations about the two other principal axes of inertia nor a possible influence on the translational motion. If perhaps the bearing of the results obtained in this paper is limited by this circumstance, still they are in any case applicable to molecules for which these two principal moments of inertia and eventually the molecular weight in connection with the temperature region which is to be considered are sufficiently large.

§ 2. As we explained in § 1 we will consider here the molecules as rigid spheres of concentric structure<sup>2)</sup>, with at their centre a quadruplet which consists of two doublets whose axes lie in the same line and have opposite directions, and which approach each other indefinitely preserving, however, a finite quadruplet-moment.

For calculating the second virial coefficient we have again to consider, just as in Suppl. N<sup>o</sup>. 24 *a* and *b*, pairs of molecules which at a given moment lie in each other's sphere of action. The mutual position of a pair can be specified in a way corresponding to that followed in Suppl. N<sup>o</sup>. 24b § 6 in discussing the doublets, viz. by the following coordinates (Fig. 1):

1<sup>st</sup>. the distance  $r$  between the centres;

1) J. C. MAXWELL. Electricity and Magnetism. 3rd ed. Vol. I, p. 197.

2) This expression is meant to indicate that the density is uniformly distributed over concentric spherical layers. Yet the following deduction of  $B$  is also valid if the density is distributed symmetrically about an axis, if this axis coincides with the axis of the quadruplet. The result is, as far as regards  $B$ , even more general and is also valid, if the density is distributed arbitrarily.

2<sup>nd</sup>. the angles  $\theta_1$  and  $\theta_2$ , which the axes of the quadruplets make with the line which joins the centres. For a closer definition of these angles we choose in each molecule arbitrarily one of the two equivalent directions on the axis as the positive direction; we choose further as the positive direction on the line which joins the centres the direction from the molecule whose position is determined by the angle considered, towards the other molecule;  $\theta_1$  and  $\theta_2$  are then the angles, from 0 to  $\pi$ , between the positive directions;

3<sup>rd</sup>. the angle  $\varphi$  between two half-planes each of which contains the positive direction of the axis of one of the quadruplets and the line joining the centres. This angle is further specified as in Suppl. N<sup>o</sup>. 24b § 6, and goes from 0 to  $2\pi$ .

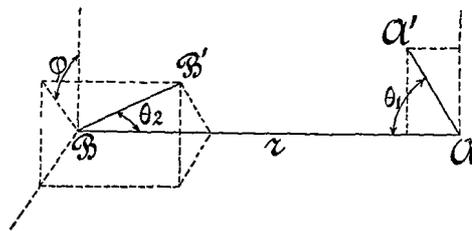


Fig. 1.

The method of Suppl. No. 24b § 6 may then be applied immediately to the problem dealt with here. It gives for the specific heat at constant volume in the AVOGADRO-state, assuming that the spheres are smooth:

$$\gamma_{vA} = \frac{5}{2} R,$$

and for the second virial coefficient:

$$B = \frac{1}{2} n \left( \frac{4}{3} \pi \sigma^3 - P' \right) \dots \dots \dots (2)$$

where:

$n$  = the number of molecules in the quantity of gas for which the equation of state is derived,

$\sigma$  = the diameter of the molecule and

$$P' = \frac{1}{2} \int_{\sigma}^{\infty} \int_0^{\pi} \int_0^{2\pi} (e^{-hu_{b1}} - 1) r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi \dots \dots (3)$$

In this formula

$$h = \frac{1}{kT} \dots \dots \dots (4)$$

$k$  is PLANCK's well known constant, whereas  $u_{b1}$  is the potential energy of the pair of quadruplets indicated by the index 1, when the potential energy is put = 0 for  $r = \infty$ . Its value is given by:

$$u_{b1} = \frac{3}{4} \frac{\mu_2^2}{r^5} \{1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos^2 \theta_1 \cos^2 \theta_2 + \\ + 2 (4 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \varphi)^2\}, \dots \quad (5)$$

if  $\mu_2$  represents the moment of the quadruplet.

We introduce:

$$v = \frac{3}{4} \frac{\mu_2^2}{\sigma^5}, \dots \quad (6)$$

then  $v =$  the potential energy, when two molecules are touching each other, the axes of the quadruplets being at right angles to each other and to the line joining the centres.

We put further

$$\Psi = 1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos^2 \theta_1 \cos^2 \theta_2 + 2 (4 \cos \theta_1 \cos \theta_2 + \\ + \sin \theta_1 \sin \theta_2 \cos \varphi)^2,$$

or:

$$\Psi = A + B \cos \varphi + C \cos 2\varphi, \dots \quad (7)$$

if

$$\left. \begin{aligned} A &= 2 (1 - 3 \cos^2 \theta_1) (1 - 3 \cos^2 \theta_2) \\ B &= 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2 \\ C &= \sin^2 \theta_1 \sin^2 \theta_2 \end{aligned} \right\} \dots \quad (8)$$

so that

$$u_{b1} = v \frac{\sigma^5}{r^5} \Psi.$$

Developing  $e^{-hu_{b1}} - 1$  into a series of ascending powers of  $hu_{b1}$ , and integrating in (3) according to  $r$ , we obtain<sup>1)</sup>:

$$P = \frac{1}{2} \sigma^3 \sum_{n=1}^{n=\infty} (-1)^n \frac{1}{5n-3} \frac{1}{n!} (hv)^n \int_0^\pi \int_0^\pi \int_0^{2\pi} \Psi^n \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\varphi \quad (9)$$

If for the sake of brevity we write  $[\Psi^n]$  for the integral in (9) and correspondingly:

$$\left. \begin{aligned} [A^p B^q C^r] &= \int_0^\pi \int_0^\pi A^p B^q C^r \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 \\ [\cos^r \varphi \cos^s 2\varphi] &= \int_0^{2\pi} \cos^r \varphi \cos^s 2\varphi d\varphi \end{aligned} \right\} \dots \quad (10)$$

observing that  $[\cos^{2l-1} \varphi] = 0$ ,  $[\cos^{2l-1} 2\varphi] = 0$ ,  $[\cos^{2l-1} \varphi \cos^m \varphi] = 0$   $l$  and  $m$  being positive integers, we find:

<sup>1)</sup> The quantities  $n, p, q, r, s$ , which we introduce temporarily in this § have a meaning different from that in the other part of this paper and in Suppl. No. 24.

$$\begin{aligned}
 [\Psi^n] = & 2\pi [A^n] + \\
 & + \binom{n}{2} [A^{n-2} B^2] [\cos^2 \varphi] + \binom{n}{2} [A^{n-2} C^2] [\cos^2 2\varphi] + \\
 & + \binom{n}{3} \binom{3}{1} [A^{n-3} B^2 C] [\cos^2 \varphi \cos 2\varphi] + \\
 & + \binom{n}{4} [A^{n-4} B^4] [\cos^4 \varphi] + \binom{n}{4} \binom{4}{2} [A^{n-4} B^2 C^2] [\cos^2 \varphi \cos^2 2\varphi] + \\
 & \quad + \binom{n}{4} \binom{4}{4} [A^{n-4} C^4] [\cos^4 2\varphi] + \\
 & + \binom{n}{5} \binom{5}{1} [A^{n-5} B^4 C] [\cos^4 \varphi \cos 2\varphi] + \binom{n}{5} \binom{5}{3} [A^{n-5} B^2 C^3] [\cos^2 \varphi \cos^3 2\varphi] \\
 & + \binom{n}{6} [A^{n-6} B^6] [\cos^6 \varphi] + \binom{n}{6} \binom{6}{2} [A^{n-6} B^4 C^2] [\cos^4 \varphi \cos^2 2\varphi] + \\
 & \quad + \binom{n}{6} \binom{6}{4} [A^{n-6} B^2 C^4] [\cos^2 \varphi \cos^4 2\varphi] + \\
 & \quad + \binom{n}{6} \binom{6}{6} [A^{n-6} C^6] [\cos^6 2\varphi] + \\
 & + \dots
 \end{aligned} \tag{11}$$

If we write

$$\left. \begin{aligned}
 A &= 2A_1 A_2, & A_1 &= 1 - 3 \cos^2 \theta_1 \\
 B &= 16 B_1 B_2, & B_1 &= \sin \theta_1 \cos \theta_1 \\
 C &= C_1 C_2, & C_1 &= \sin^2 \theta_1
 \end{aligned} \right\} \dots \tag{12}$$

then

$$[A^\nu B^{2q} C^r] = 2^{\nu+8q} \{ [A_1^\nu B_1^{2q} C_1^r] \}^2 \dots \tag{13}$$

where the square brackets in the second member now refer to  $\theta_1$  only :

$$[\dots] = \int_0^\pi \dots \sin \theta_1 d\theta_1.$$

One finds

$$\left. \begin{aligned}
 [A_1^\nu B_1^{2q} C_1^r] &= 2^{\nu+q+r+1} \frac{(p+q+r)!}{(2p+4q+2r+1)(2p+4q+2r-1)\dots(2q+1)} \\
 & \left\{ 1 - \binom{p}{1} \frac{2q+1}{p+q+r} + \binom{p}{2} \frac{(2q+1)(2q+3)}{(p+q+r)(p+q+r-1)} \dots \right\},
 \end{aligned} \right\} \tag{14}$$

from which formula also the special cases  $[A_1^\nu]$ ,  $[A_1^\nu B_1^{2q}]$  etc., may be derived.

Of these expressions  $[A_1^\nu]$  can be calculated more easily from the following relation :

$$[A_1^\nu] = (-1)^\nu \frac{2^{\nu+1}}{2\nu+1} + \frac{2^\nu}{2\nu+1} [A_1^{\nu-1}] \dots \tag{15}$$

Further:

$$\begin{aligned}
 [\cos^{2q} \varphi] &= [\cos^{2q} 2\rho] = 2\pi \cdot \binom{2q}{q} \cdot \frac{1}{2^{2q}}, \\
 [\cos^{2q} \varphi \cos^{2r} 2\rho] &= 2\pi \cdot \frac{1}{2^{q+2r}} \left\{ \binom{2r}{r} + \binom{q}{2} \cdot \frac{1}{2^2} \binom{2r+2}{r+1} + \binom{q}{4} \cdot \frac{1}{2^4} \binom{2r+4}{r+2} \dots \right\} \cdot (16) \\
 [\cos^{2q} \varphi \cos^{2r-1} 2\rho] &= 2\pi \cdot \frac{1}{2^{q+2r}} \left\{ \binom{q}{1} \binom{2r}{r} + \binom{q}{3} \frac{1}{2^2} \binom{2r+2}{r+1} \dots \right\}
 \end{aligned}$$

These formulae give finally:

$$\begin{aligned}
 P' &= \frac{4}{3} \pi \sigma^3 \left\{ \frac{16}{15} (hv)^2 - \frac{128}{735} (hv)^3 + \frac{18176}{37485} (hv)^4 - \frac{262144}{419265} (hv)^5 + \right. \\
 &\quad \left. + 0,2360 (hv)^6 - 0,1355 (hv)^7 + 0,1019 (hv)^8 \dots \right\}, \quad (17)
 \end{aligned}$$

so that

$$\begin{aligned}
 B &= \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - 1,0667 (hv)^2 + 0,1741 (hv)^3 - 0,4738 (hv)^4 + \right. \\
 &\quad \left. + 0,6252 (hv)^5 - 0,2360 (hv)^6 + 0,1355 (hv)^7 - 0,1019 (hv)^8 \dots \right\} \quad (18)
 \end{aligned}$$

§ 3. For the lower temperatures, e. g. at the BOYLE-point (the temperature at which  $B = 0$ ), this series converges very slowly, so that for them the terms given above are not sufficient.

At the inversion point of the JOULE-KELVIN effect for small densities the term with  $(hv)^8$  in (18) amounts to about  $1/800$  of  $B_\infty (= b_{\infty})$ , the value to which  $B$  would approach for  $T = \infty$ , if the equations found here remained valid. Hence for the inversion point just mentioned and for higher temperatures, the terms given above may be considered to be sufficient, assuming that none of the following terms is unexpectedly large. At  $0.75 T_{inv(\rho=0)}$  the above mentioned term amounts to  $1/80$  of  $B_\infty$ , so that on the same assumption we may reckon upon an accuracy of about 1% (of  $B_\infty$ ).

I have not succeeded in deducing a series which is more suitable for lower temperatures.

Just as for the (spherical) molecules, which bear a doublet at their centre, so also for the quadruplets the term with  $T^{-1}$  is absent in the series for  $B$ . Whereas, however, for the doublets all odd powers are absent, here the higher odd powers appear in the series, although the coefficient of  $T^{-3}$  is still relatively small<sup>1)</sup>.

Above  $3 T_{inv(\rho=0)}$  with an accuracy of  $1/1000$  and above  $1.2 T_{inv(\rho=0)}$  with an accuracy of  $1/100$ , the first two terms in (18) are sufficient. The dependence of  $B$  on temperature then agrees with the suppo-

<sup>1)</sup> The questions under what conditions in general the term with  $T^{-1}$ , as also the higher odd powers disappear from  $B$ , will be dealt with in a following paper (Suppl. No. 39b).

sition that in VAN DER WAALS' equation  $b_W$  is independent of  $T$  and  $a_W$  is proportional to  $T^{-1}$ . The latter assumption was already made by CLAUSIUS, with a view to the vapour pressures of carbon dioxide. A relation agreeing with

$$B = B_\infty \left( 1 + \frac{b_2}{T^2} \right) \dots \dots \dots (19)$$

(with a negative value of  $b_2$ ) was also found by D. BERTHELOT<sup>1)</sup> to be suitable to represent the compressibility at densities near the normal. In these investigations the approximate validity of that relation was extended to much lower temperatures than those indicated above. It will appear in the next §, that equation (18) actually agrees with an equation of the form (19) down to an appreciably lower temperature than those indicated above.

§ 4. For the purpose of a closer comparison between the second virial coefficients of quadruplet-bearing molecules and of doublet-bearing molecules we shall introduce as a reduction temperature a temperature which is specific for each gas<sup>2)</sup>. According to what was said in § 3 about the region in which equation (18) is applicable the inversion temperature of the JOULE-KELVIN-effect at small densities is a suitable one for this purpose. This temperature is found from the relation:

$$B - T \frac{dB}{dT} = 0,$$

or

$$B + hv \frac{dB}{d(hv)} = 0.$$

Equation (18), and Suppl. N<sup>o</sup>. 24b equation (59) give respectively, for quadruplets:

$$hv_{inv(\rho=0)} = 0.576,$$

for doublets:

$$hv_{inv(\rho=0)} = 0.969.$$

If we call  $\frac{T}{T_{inv(\rho=0)}} = t_{(inv)}$ , it follows further, that:

for quadruplets:

$$B = B_\infty \left\{ 1 - 0.3539 t_{(inv)}^{-2} + 0.03327 t_{(inv)}^{-3} - 0.05215 t_{(inv)}^{-4} + \right. \\ \left. + 0.03964 t_{(inv)}^{-5} - 0.00862 t_{(inv)}^{-6} + 0.00285 t_{(inv)}^{-7} - 0.00123 t_{(inv)}^{-8} \dots \right\} \quad (20)$$

<sup>1)</sup> D. BERTHELOT. Trav. et Mém. Bur. Internat. des Poids et Mesures, t. 13 (1907).

<sup>2)</sup> Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandgleichung. Math. Enc. V 10. Leiden Comm. Suppl. No. 23 § 28a.

for doublets:

$$B = B_{\infty} \{1 - 0.3130 t_{(inv)}^{-2} - 0.01175 t_{(inv)}^{-4} - 0.00044 t_{(inv)}^{-6} \dots\} \quad (21)$$

Table I contains some values calculated from (20) and (21) respectively.

TABLE I.

$\frac{T}{T_{inv.} (\rho=0)}$	$B/B_{\infty}$			
	quadr.	doublets	v.D.WAALS	CLAUSIUS-BERTHELOT
0.75	0.413	0.404	0.333	0.407
1	0.660	0.675	0.5	0.667
1.5	0.847	0.859	0.667	0.852
2	0.914	0.921	0.75	0.917
3	0.961	0.965	0.833	0.963
4	0.978	0.980	0.875	0.979

The table also gives some values calculated from the equation

$$B = B_{\infty} \left\{1 - 0.5 t_{(inv)}^{-1}\right\}, \dots \quad (22)$$

which follows from VAN DER WAALS' equation with constant  $a_W$ ,  $b_W$  and  $R_W$ , and some values calculated from the equation

$$B = B_{\infty} \left\{1 - \frac{1}{3} t_{(inv)}^{-2}\right\}, \dots \quad (23)$$

which is obtained from CLAUSIUS' and BERTHELOT's assumption:  $a_W \propto T^{-1}$ .

As appears from table I, the difference between the values of  $B$  for quadruplets and for doublets is small in the temperature region considered here, i. e. above  $0.75 T_{inv.(\rho=0)}$ , viz. smaller than 1% of  $B_{\infty}$ , or 2.3% of  $B$ .

Hence the circumstance of a diatomic molecule possessing or not possessing a doublet, has but a small influence on the dependence of  $B$  on temperature in this temperature region. This leads one to expect that in the considered region of temperature and density the equation of state of diatomic compound gases and that of diatomic elementary gases will not be easily distinguished from each other.

From table I it appears further, that the values of  $B$  for quadruplets and for doublets both deviate very little from equation (23), viz. over the whole region above  $0.75 T_{inv.(\rho=0)}$  less than 0.6% of the value of  $B_{\infty}$ , and less than 1.5% of the value of  $B$ .

§ 5. *Hydrogen.* Values of  $B$  for a diatomic gas in the temperature region for which the terms given in (18) and (20) are sufficient are only known as yet for hydrogen. For this substance in view of its small molecular weight one has to pay particular attention to a possible modification of the molecular translational motion according to the quantum theory. According to it a correction ought to be applied to the values of  $pn$ , before the equation of state in the form (1) would be applicable. As that correction depends on other powers of  $v$  than occur in the second member of (1), a conclusion about that influence might be drawn for the temperature region to be considered here from the agreement or disagreement between the values of  $B$  calculated according to (1) without a quantum-correction from measurements at higher pressures and from such at densities near the normal one. The available experimental material<sup>1)</sup>, however, does not yet enable us to apply this test. Meanwhile as mentioned above we will disregard a possible influence for the temperature region under consideration. We shall also leave out of account the possible influence on the value of the second virial coefficient of those deviations from the equipartition laws, which according to EUCKEN's measurements of the specific heat are shown by the rotations about the axes at right angles to the line joining the atomic centres, at least in the lowest part of the temperature region under consideration.

In Suppl. N<sup>o</sup>. 25 (Sept. '12) it was shown that the dependence of  $B$  on the temperature for temperatures above  $-100^{\circ}$  C. agrees with that which was derived for spherical molecules carrying a doublet. From the agreement found in § 4 between the latter and that for spherical molecules carrying a quadruplet in the temperature region specified there it follows immediately that the values of  $B$  for hydrogen in the temperature region under consideration ought to be found in agreement with the dependence on temperature which we derived for quadruplets.

To test this  $B/B_{inv}$  for hydrogen was represented in a diagram as a function of  $T/T_{inv(\rho=0)}$  and compared with the values calculated from (20) and (21) respectively. The values of  $B$  for hydrogen at  $-140^{\circ}$ ,  $-104^{\circ}$ ,  $0^{\circ}$  and  $100^{\circ}$  C. were taken from KAMERLINGH ONNES and BRAAK<sup>2)</sup>, that for  $B$  at  $20^{\circ}$  C. from SCHALKWIJK<sup>3)</sup> and from KAMERLINGH ONNES, CROMMELIN and Miss SMID<sup>4)</sup>. The temperature of

<sup>1)</sup> Cf. W. J. HAAS, Comm. N<sup>o</sup>. 127a (April '12) § 4.

<sup>2)</sup> H. KAMERLINGH ONNES and C. BRAAK, Comm. N<sup>o</sup>. 100 a and b (Nov. '07).

<sup>3)</sup> J. C. SCHALKWIJK. Thesis Amsterdam 1902. p. 116, also Leiden Comm. N<sup>o</sup>. 78 p. 22.

<sup>4)</sup> H. KAMERLINGH ONNES, C. A. CROMMELIN and Miss E. J. SMID. Comm. N<sup>o</sup>. 146b (June '15).

the inversion point for the JOULE-KELVIN effect at small densities (200.6° K.) was taken from the calculations by J. P. DALTON<sup>1)</sup>.  $B_{inv}$  the value of  $B$  for the just mentioned temperature, was calculated from the special reduced equation of state for hydrogen, communicated in Comm. N°. 109a § 7.

In this manner no sufficient agreement was, however, obtained, neither with the quadruplet-equation, nor with the doublet-equation; the value for 100° C. deviates pretty considerably from the calculated curves.

This is to be ascribed chiefly to the value, which is assumed for  $T_{inv(\rho=)}$ . The special equation of state used for the calculation of  $T_{inv(\rho=0)}$  appears to give a somewhat less perfect agreement with experiment in this region than elsewhere, and this fact has a considerable influence on the result obtained for  $T_{inv(\rho=0)}$  in consequence of the circumstance that for the determination of  $T_{inv(\rho=0)}$ , the value of  $dB/dT$  is of great importance.

A value of  $T_{inv(\rho=0)}$  was therefore subsequently deduced with the aid of an equation which shows a good agreement in this region of temperatures; for this purpose an equation of the form (19) was chosen, and its constants were derived from the experimental data. From the results of KAMERLINGH ONNES and BRAAK we obtained:  $T_{inv(\rho=0)} = 194.5$ ,  $B_{N_{inv}} = 0.000465$ .

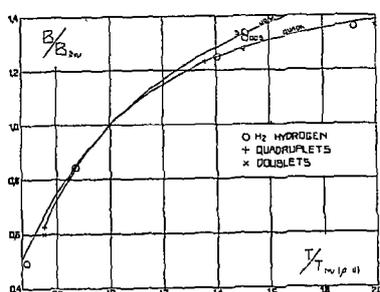


Fig. 2.

Fig. 2 shows what agreement is obtained with these values of the constants<sup>2)</sup>. For comparison the curve following from VAN DER WAALS' equation with constant  $a_W$ ,  $b_W$  and  $R_W$  is also represented.

It appears now that, as expected, for the temperature region under consideration the values of  $B$  for hydrogen can be made to agree with the equation derived for spherical molecules carrying a quadruplet, just as well as with the equation derived for doublets.

From the value found for  $B_{inv}$  we obtain for  $\sigma$ <sup>3)</sup>:

$$\sigma = 2,32 \cdot 10^{-8} \text{ cm.}$$

<sup>1)</sup> J. P. DALTON. Comm. N°. 109a (March 1909).

<sup>2)</sup> The values taken from the measurements by SCHALKWIJK, and by KAMERLINGH ONNES, CROMMELIN and Miss SMID are indicated by S and OCS respectively.

<sup>3)</sup> From  $B_{N_{inv}} = 0.000465$ , and  $B_{inv}/B_{\infty} = 0.660$  (table I), follows  $B_{N_{\infty}} = 0.000705$ .  $AN_{0^{\circ}C.} = 0.99942$  then gives  $B_{\infty} = 0.000705$ .  $B_{M_{\infty}} = 0.000705 \times 22412 = 15.80 = \frac{1}{2} N \cdot \frac{4}{3} \pi \sigma^3$ . With  $N = 6.06 \cdot 10^{23}$  according to MILLIKAN one obtains for the dia.

From  $T_{inv(\rho=0)}$  then follows: <sup>1)</sup>

$$v = 1,53 \cdot 10^{-14}$$

and using this value one obtains from (6) for the moment of the quadruplet:

$$\mu_2 = 2,03 \cdot 10^{-26} \text{ [electrostatic units} \times \text{c.m.}^2\text{].}$$

If the quadruplet is assumed to consist of two positive charges  $e$  at a distance  $d$  from each other, and midway between them a charge  $-2e$ , so that  $\mu_2 = \frac{1}{2} ed^2$ , and if further  $e =$  the charge of an electron  $= 4.77 \cdot 10^{-10}$  (MILLIKAN), one finds

$$d = 0,92 \cdot 10^{-8} \text{ cm.},$$

a value whose order of magnitude agrees properly with what the distance of the positive nuclei of the two hydrogen atoms within the molecule <sup>2)</sup> may be expected to be. It is to be kept in view, however, that, properly speaking, with this distance of the charges it would not be allowable to assume the charges to be situated infinitely near to one and the same point, as is done in this paper. By taking account of this circumstance one would presumably find a smaller value of  $d$ .

#### § 6. *Résumé.*

1. For a system of rigid spherical molecules, whose mutual attraction is equivalent to that of a quadruplet situated at their centres the second virial coefficient is developed in a series of ascending powers of  $T^{-1}$ .

2. Above  $0.75 T_{inv(\rho=0)}$  the dependence of  $B$  on the temperature for spherical molecules carrying a quadruplet nearly coincides with that for molecules carrying a doublet and for both differs but little from the relation

$$B = B_\infty \left\{ 1 - \frac{1}{3} t_{(inv)}^{-2} \right\}.$$

3. The values of  $B$  for hydrogen from  $-100^\circ$  to  $+100^\circ$  C. may be represented with sufficient accuracy by the equation derived for spherical molecules carrying a quadruplet.

meter of the molecule the value mentioned in the text. For the meaning of the indices  $N$ ,  $\vartheta$  and  $M$ , cf. H. KAMERLINGH ONNES and W. H. KEESOM, "Die Zustandsgleichung", Math. 'Enz. V 10, Leiden Comm. Suppl. N<sup>o</sup>. 23, Einheiten  $b$ .

<sup>1)</sup> Calculated from  $T_{inv(\rho=0)} = 194.5$ ,  $h_{inv} = 0.576$  (§ 4), equation (4), and  $k = 1,37 \cdot 10^{-16}$ .

<sup>2)</sup> According to P. DEBIJE, München Sitz. Ber. 1915, p. 1, that distance amounts to  $0.604 \cdot 10^{-8}$  cm. DEBIJE's hydrogen molecule is, however, strongly paramagnetic (its magnetic moment corresponds to 10 WEISS magnetons) so that the magnetic properties of hydrogen are not represented accurately by this model, unless one would assume with SOMMERFELD, ELSTER- and GETTEL jubilee volume 1915, p. 549, that the electrons in the hydrogen molecule in circulating in circular orbits do not exert a magnetic action, and hence behave quite differently from the electrons which in the experiment of EINSTEIN and DE HAAS cause the magnetic moment of the iron molecules.