

§ 3. In order to form a better judgment of the value found for the quadrupole moment of oxygen we must still investigate whether the magnetic attraction between the paramagnetic oxygen molecules contributes considerably to  $B$ . In this case the quadrupole moment ought to be smaller than the value found above with neglect of this attraction. Calculation proves however that this is not the case.

According to WEISS and PICCARD<sup>1)</sup> oxygen should possess 14 magnetons per molecule. This involves a magnetic moment of the  $O_2$ -molecule

$$\mu = 2,6 \times 10^{-20}.$$

In Comm. Leiden Suppl. n°. 25 § 4 has been shown that  $\mu = 9,47 \times 10^{-19}$  should be required in order to explain the molecular attraction. The real magnetic moment has only  $\frac{1}{35}$  of this value. Taking into consideration, that the statistically remaining molecular attraction is proportional to  $\mu^4$ , we see that the contribution of the magnetic moment to the molecular attraction does not come into consideration here.

§ 4. We must expressly point out that the calculations of this communication (as well as those for  $H_2$ , Leiden Suppl. n°. 39) are based on the supposition that the molecules collide as solid spheres with constant diameter. If this were not the case and if the behaviour at a collision should correspond to a value of  $\sigma$  depending on the temperature, this would become manifest in  $B$  by terms also depending on  $T$ . The dependency of  $B$  on  $T$  would then no longer be due to molecular attraction exclusively as in this Comm. For the same reason the values of the quadrupole moments would possibly have to be altered considerably.

<sup>1)</sup> P. WEISS and A. PICCARD. C. R. 155 (1912), p. 1934.

**Physics.** — “*The cohesion forces in the theory of VAN DER WAALS*”.

By Prof. W. H. KEESOM. (Communication N°. 6b from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). Communicated by Prof. KAMERLINGH ONNES).

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§ 1. *Introduction.* DEBIJE<sup>1)</sup> has recently shown in an important paper on the cohesion forces in the theory of VAN DER WAALS that these may be explained in this way that one molecule in the field of neighbouring molecules obtains a bipole moment, and that because of this bipole moment it is attracted by the inducing molecule. DEBIJE considered especially those gases the molecules of which possess no spontaneous bipole moment. In the calculation he assumed that the field of the molecules could be treated in first approximation as that of a quadrupole. Evidently neighbouring molecules will influence their mutual direction in such a way that the cases of attraction are more frequent than those of repulsion. In a preliminary orientating calculation the mean mutual attraction of the molecules due to their own quadrupole moment was neglected. In fact, this will be allowed, as was already remarked by DEBIJE, for sufficiently high temperatures. Then this mean attraction vanishes namely as the heat movement hinders the directing influences of the molecules mutually.

On the other hand we have shown (Comm. Leiden Suppl. N°. 39a)<sup>2)</sup> that the molecular attraction in hydrogen, at least as far as to the second virial coefficient, may be explained by the circumstance that those molecules possess a quadrupole moment, while a contribution to the attraction due to the mobility of the electrons in the molecules was neglected. In fact, DEBIJE remarks rightly that in the calculation of the molecular attraction we shall have to attend to the attraction of the molecules mutually because of their quadrupole moments as well as to that especially treated by DEBIJE and due to the polarisability of the molecules in an electric field.

In this paper we shall discuss principally the influence of the

<sup>1)</sup> P. DEBIJE, Physik. Z.S. 21 (1920), p. 178.

<sup>2)</sup> These Proceedings, vol. 18, p. 636. See also W. H. KEESOM and Miss C. VAN LEEUWEN, these Proceedings, Vol. XVIII, N°. p. 1568.

molecular attraction on the equation of state, confining ourselves to the second virial coefficient.

Now we may ask which of the two mentioned contributions to the attraction will have the greatest influence on the second virial coefficient at the temperatures for which the measurements on the equation of state were made. It will appear that for these temperatures the influence of the molecular attraction in  $B$  is principally due to the spontaneous quadrupole moments of the molecules.

§ 2. *Preliminary orientation.* For shortness sake we shall denote by the name "quadrupole attraction" the contribution to the attraction due to the spontaneous quadrupole moments and by the name "induced attraction" the part due to the forces exerted by the quadrupoles on the bipoles that are induced in the molecules. In the same way we shall speak of "quadrupole terms" for the terms in the second virial coefficient due to the quadrupole attraction and of "induced terms" for those caused by the induced attraction.

Between them this important difference exists, that at high temperatures the quadrupole terms become proportional to  $T^{-2}$ , while the induced terms become proportional to  $T^{-1}$ .

This comes to the same as saying that the VAN DER WAALS attraction force in the case of quadrupole attraction becomes proportional to  $T^{-1}$ , whereas in the case of induced attraction they become constant.

Now it has been shown already (Leiden Suppl. N°. 39a. See Fig. 2 there and comp. also Leiden Suppl. N°. 39c § 3) that for hydrogen the second virial coefficient behaves more in agreement with the hypothesis of quadrupole attraction than with that  $a_w = \text{const.}$ , as would be demanded for high temperatures because of the induced attraction. Therefore we may evidently expect that at least for hydrogen, the quadrupole terms prevail.

We may compare the values derived by DEBIJE for the quadrupole moment under the assumption that for high temperatures the induced attraction has only to be considered, with the quadrupole moment found in Leiden Suppl. N°. 39a for hydrogen. This comparison is in agreement with the above conclusion. For hydrogen DEBIJE finds (table I l.c.)  $3,20 \times 10^{-26}$ , while in the Leiden Suppl. N°. 39a a quadrupole moment of  $2,03 \times 10^{-26}$  has been shown to give already a quadrupole attraction sufficient to explain the experimentally found equation of state. The first of the quadrupole terms being proportional to the fourth power of the quadrupole moment, the quadrupole moments of DEBIJE would therefore give a quadrupole attraction that would be far too great.

The same conclusion is reached for oxygen and nitrogen, the quadrupole moments of which have been calculated in the preceding paper (Comm. n°. 6a) with neglect of the induced attraction:

$O_2$ :	DEBIJE: $11,2 \times 10^{-26}$ ,	Comm. N°. 6a: $3,55 \times 10^{-26}$
$N_2$ :	$13,3 \times$ „	$3,86$ „

The conclusion that the quadrupole attraction for these gases exceeds the induced attraction is confirmed when in the calculation of the second virial coefficient the induced attraction is also attended to. This has been done in § 3.

§ 3. *The second virial coefficient for spherical polarisable quadrupole molecules.* We suppose the state of polarisation of the molecules (displacements of the electrons from their positions or paths of equilibrium) to be at each moment in correspondence with the field that surrounds the molecule at that moment. Further the molecule to be isotropically polarisable, so that the induced bipole moment has the direction of the electric field  $E$  and is equal to

$$i\mu_1 = aE. \dots \dots \dots (1)$$

The index 1 indicates here that we have to do with a bipole moment, while both here and further on quantities with the index  $i$  are due to the electrostatic induction.

The energy of the induced bipole in the field  $E$  (compare DEBIJE l.c.) is:

$$-\frac{1}{2} aE^2. \dots \dots \dots (2)$$

When the induced bipole is placed at a point  $P$  of the field of a zonal quadrupole  $A$  with quadrupole moment  $\mu_2$  (Fig. 1), in such a way that  $PA$  makes the angle  $\theta$  with the axis of the quadrupole, we find for the energy of the induced bipole

$$-\frac{9}{2} \frac{a\mu_2^2}{r^3} \{ \sin^4 \theta + 4 \cos^4 \theta \}. \dots \dots (3)$$

The calculation of the second virial coefficient may be analogous to that of Leiden Suppl. N°. 39a § 2. A pair of molecules that may

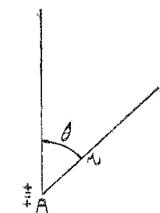


Fig. 1.

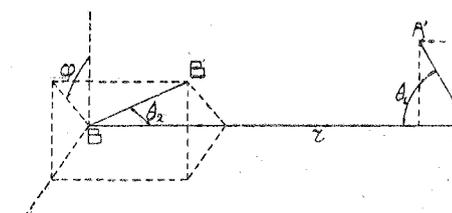


Fig. 2.

be considered as lying in their mutual spheres of action will be characterized again by the distance  $r$  of their centres, the angles  $\theta_1$  and  $\theta_2$  of the quadrupole axes with the line connecting the centres and by the angle  $\varphi$  (see Fig. 2). The energy of this pair will be obtained by adding to the quadrupole term given in the cited paper:

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

the induced term:

$$i u_{b1} = -\frac{9}{8} \frac{a \mu_2^2}{r^5} \{ \sin^4 \theta_1 + \sin^4 \theta_2 + 4 \cos^4 \theta_1 + 4 \cos^4 \theta_2 \} \quad (5)$$

Still a term might be added, due to the forces exerted by the two induced bipoles on each other. This term would contain  $\alpha^2$ . For the moment we shall however omit terms with  $\alpha^2$ .

From Leiden Suppl. N<sup>o</sup>. 39a we take the notations

$$v = \frac{3}{4} \frac{\mu_2^2}{\sigma^5}, \quad \sigma = \text{diameter of the molecule}, \quad (6)$$

where for shortness sake  $v$  will be written for  ${}_q v$ , this being the potential energy of the pair of molecules when in contact with the mentioned (l.c.) directions of the quadrupole axes for the case that only the quadrupole attraction is taken into consideration.

Further

$${}_q u_{b1} = v \frac{\sigma^5}{r^5} \Psi, \quad (7)$$

where

$$\Psi = A + B \cos \varphi + C \cos 2 \varphi. \quad (8)$$

when

$$\left. \begin{aligned} A &= 2 (1 - 3 \cos^2 \theta_1) (1 - 3 \cos^2 \theta_2) \\ B &= 16 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \theta_2 \\ C &= \sin^2 \theta_1 \sin^2 \theta_2. \end{aligned} \right\} \quad (9)$$

We now introduce

$$X = \sin^4 \theta_1 + \sin^4 \theta_2 + 4 \cos^4 \theta_1 + 4 \cos^4 \theta_2. \quad (10)$$

Then we have

$$i u_{b1} = -\frac{3}{2} v \frac{a \sigma^5}{r^5} X. \quad (11)$$

The second virial coefficient becomes

$$B = \frac{1}{2} n \left( \frac{4}{3} \pi \sigma^3 - P' \right) \quad (12)$$

with

$$P' = \int_0^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \left( e^{-h} q u_{b1} - h i u_{b1} - 1 \right) r^2 \sin \theta_1 \sin \theta_2 dr d\theta_1 d\theta_2 d\varphi. \quad (13)$$

Developing into a series of ascending powers of  $h$ , with neglect of terms with  $\alpha^2$  etc., we find  $P'$  to be split up into:

$$P' = {}_q P' + i P', \quad (14)$$

where  ${}_q P'$  may be taken from Leiden Suppl. N<sup>o</sup>. 39a. After integration with respect to  $r$  we find:

$$P' = \frac{3}{20} a h v \int_0^\pi \int_0^\pi \int_0^{2\pi} X \left\{ 1 - \frac{1}{2!} h v \Psi + \frac{1}{3!} (h v)^2 \Psi^2 \right\} \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\varphi. \quad (15)$$

Performing this integration we obtain

$$i P' = \frac{16}{5} \pi \sigma^3 \cdot \frac{\alpha}{\sigma^3} \cdot h v \left\{ 1 + \frac{16}{15} (h v)^2 \dots \right\} \quad (16)$$

and then<sup>1)</sup>

$${}_q B = -\frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \cdot \frac{12}{5} \frac{\alpha}{\sigma^3} \cdot h v \left\{ 1 + \frac{16}{15} (h v)^2 \dots \right\} \quad (17)$$

These terms added to  ${}_q B$  of the Leiden Suppl. N<sup>o</sup>. 39a finally give:

$$B = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - 1,0667 (h v)^2 + 0,1741 (h v)^3 \dots - 2,4 \frac{\alpha}{\sigma^3} h v [1 + 1,067 (h v)^2 \dots] \right\} \quad (18)$$

§ 4. *Conclusions.* In the first place we may remark, that for a strong validity of the law of corresponding states the same value of  $\frac{\alpha}{\sigma^3}$  would be required for different gases.

With DEBIJE we derive the value of  $\alpha$  from the molecular refraction ( $P_0$ ) for  $\lambda = \infty$ , while the values of  $\sigma$  are taken from the Leiden Suppl. N<sup>o</sup>. 39a for H<sub>2</sub>, from the preceding Communication (N<sup>o</sup>. 6a) for O<sub>2</sub> and for N<sub>2</sub>. In this way we obtain:

	$P_0$	$\sigma$	$\frac{\alpha}{\sigma^3}$
hydrogen	2,03	$2,32 \times 10^{-8}$	0,0640
oxygen	3,98	2,65 "	0,0842
nitrogen	4,34	2,98 "	0,0646

<sup>1)</sup> The first term of this result corresponds to a value for the VAN DER WAALS attraction constant  $\alpha$  that perfectly agrees with that given by DEBIJE (l. c. equation (18)).

For hydrogen we have then:

$$B = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \left\{ 1 - 1,0667 (hv)^2 + 0,1741 (hv)^4 \dots - \right. \\ \left. - 0,1536 hv - 0,1638 (hv)^3 \dots \right\} \dots \dots \dots (19)$$

For nitrogen the last row of terms is only slightly different, for oxygen somewhat more.

The values of  $\sigma$  used here being derived from calculations in which the induced attraction has not been attended to, this expression for  $B$  may be regarded as a first step only in a series of succeeding approximations. In the Leiden Supplement N<sup>o</sup>. 39a, the value of  $hv$  in the JOULE-KELVIN point of inversion has been calculated starting from equation (19). When we wished to do this here, we should first have to derive still some terms for the "induced part" of  $B$ . After this the experimental values of  $T_{inv(\rho=0)}$  and  $B_{inv}$  would give us corrected values for  $v$  and  $\sigma$ . We may expect the alteration of  $\sigma$  in consequence of this correction to be rather small, so that also the change of equation (19) due to it will be not considerable.

In this communication we will however confine ourselves to the following statement: A comparison of the terms in question shows that at least for the mentioned gases, unless the temperature be very high, the "quadrupole attraction" has considerably more influence in  $B$  than the "induced attraction". For gases as the above the cohesion forces introduced by VAN DER WAALS into the equation of state may therefore be ascribed principally to the forces exerted by the molecules on each other because of their quadrupole moments

**Mathematics.** — "Intuitionistische Mengenlehre" <sup>1)</sup>. By Prof. L. E. J. BROUWER.

(Communicated at the meeting of December 18, 1920.)

Im folgenden gebe ich eine referierende Einleitung zu den beiden Teilen der Abhandlung: „Begründung der Mengenlehre unabhängig vom logischen Satz vom ausgeschlossenen Dritten“, welche ich im November 1917 bzw. Oktober 1918 der Akademie vorgelegt habe.

Seit 1907 habe ich in mehreren Schriften <sup>2)</sup> die beiden folgenden Thesen verteidigt:

I. dass das *Komprehensionsaxiom*, auf Grund dessen alle Dinge, welche eine bestimmte Eigenschaft besitzen, zu einer Menge vereinigt werden (auch in der ihm später von ZERMELO gegebenen beschränkteren Form <sup>3)</sup>) zur Begründung der Mengenlehre unzulässig bzw. unbrauchbar sei und nur in einer *konstruktiven* Mengendefinition eine zuverlässige Basis der Mathematik gefunden werden könne;

II. dass das von HILBERT 1900 formulierte *Axiom von der Lösbarkeit jedes Problems* <sup>4)</sup> mit dem *logischen Satz vom ausgeschlossenen Dritten* äquivalent sei, mithin, weil für das genannte Axiom kein

<sup>1)</sup> Unter demselben Titel ist ein im wesentlichen gleichlautender Aufsatz im Bd. 28 (1920) des Jahresberichtes der Deutschen Mathematiker-Vereinigung erschienen.

<sup>2)</sup> Vgl. „Over de grondslagen der wiskunde“, Inauguraldissertation Amsterdam 1907, besonders auch die beigefügten Thesen; „De onbetrouwbaarheid der logische principes“, Tijdschrift voor wijsbegeerte 2 (1908), abgedruckt in „Wiskunde, waarheid, werkelijkheid“, Groningen 1919; „Over de grondslagen der wiskunde“, N. Archief v. Wisk. (2) 8 (1908); Besprechung von MANNOURY, „Methodologisches und Philosophisches zur Elementarmathematik“, N. Archief v. Wisk. (2) 9 (1910); „Intuitionisme en formalisme“, Antrittsrede Amsterdam 1912, abgedruckt in „Wiskunde, waarheid, werkelijkheid“, obengenannt; „Intuitionism and formalism“, Amer. Bull. 20 (1913); Besprechung von SCHOENFLIES-HAHN, „Die Entwicklung der Mengenlehre und ihrer Anwendungen“, Jahresber. d. D. M. V. 23 (1914); „Addenda en corrigenda over de grondslagen der wiskunde“, Versl. Kon. Akad. v. Wetensch. Amsterdam 25 (1917), abgedruckt in N. Archief v. Wisk. (2) 12 (1918).

<sup>3)</sup> Vgl. Math. Ann. 65, S. 263.

<sup>4)</sup> Vgl. z. B. Archiv d. Math. u. Phys. (3) 1, S. 52. Nach der hier geäußerten Ansicht HILBERTS entspricht das Axiom einer von jedem Mathematiker geteilten Ueberzeugung. In seinem neulich in Math. Ann. 78 abgedruckten Vortrag „Axiomatisches Denken“ stellt er jedoch auf S. 412 die Frage nach der Lösbarkeit