Physics. — *"On the calculation of the molecular quadrupole-moments from the equation of state."* By Prof. **W. H. Keesom**. (Communication N°. 9 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). (Communicated by Prof. H. Kamerlingh Onnes).

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§ 1. *Introduction.* When the potential in the field of the electric charges in a rotational symmetric homopolar molecule is developed in a series of powers of r^{-1}, the first term may be regarded as being due to a zonal quadrupole.

As far as is evident from the investigation of the equation of state especially for hydrogen, the molecular attraction in diatomic homopolar gases may be regarded to a first approximation as due to such a quadrupolar term in the field of force of the molecule, at least for a high temperature and in a diluted gaseous state. That finally an attraction results must be ascribed to two causes: 1st that two molecules when approaching each other will try to direct each other in such a way that attracting forces arise between them, and 2nd that in two approaching molecules the charges are displaced by their mutual influence thus that this gives rise to an attraction.

As far as this Debije[1]) and the author[2]) agree. Their opinions

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[1]) P. Debije. Physik. ZS. **22**, p. 302, 1921. Very interesting is the application made by Debije of these considerations to monatomic gases, where the mutually directing influence of the molecules mentioned under 1st becomes zero, so that only the attraction due to the polarisation of the molecules mentioned under 2nd remains. See for this also F. Zwicky, Physik. ZS. **22**, p. 449, 1921. As to this, we may remark however the following. The application of the above to a quadrupole term in the field of the monatomic molecules gives us a mean value of the potential energy of two such molecules proportional with r^{-8} (a dipole term would give r^{-6}), while on the contrary the observations for argon are more in favour of r^{-4} or r^{-5} (hydrogen below the Boyle-point r^{-4}), see Leiden Suppl. N°. 26 § 3, these Proceedings October 1912, p. 643.

[2]) Comm. N°. 6*b*, these Proc. Vol. XXIII, N°. 6, 1920. Physik. ZS. **22**, p. 129, 1921.

differ however on the magnitudes of the quadrupole moments [1]) that are to be ascribed to the molecules of the gases in question (hydrogen, oxygen and nitrogen) on account of the data of the equation of state.

The author has deduced these quadrupole moments [2]) from the experimentally found second virial coefficients for the above mentioned gases at selected temperatures by comparing them with the dependency of the second virial coefficient on the temperature as deduced for fixed quadrupoles and thus without attending to the displacement of the charges mentioned under 2nd. Afterwards [3]) he has proved that at those temperatures the influence of the displacibility of the charges is only small compared with that of the attraction due t the fixed quadrupoles. From this it is evident, that the values for the quadrupole moments derived from the experimental data do not undergo considerable changes by the displacibility of the charges.

Following another way of calculation however DEBIJE finds considerably higher values for the quadrupole moments and on several grounds he prefers these higher values.

In this communication will be shown that the author cannot adhere to this opinion and by further calculation he will investigate the influence of the polarisability of the molecules on the value found for the quadrupole moment. Then, as might be expected, this influence will be found to be small.

§ 2. *Rectification.* In the first place it may be mentioned here, that at the last moment a calculation error has been made in my former calculation of the quadrupole moment of hydrogen. From the values for σ and v given in Leiden Suppl. N$^\circ$. 39a § 5 we find for the quadrupole moment of the hydrogen molecule:

$$\mu_2 = 1{,}17 \times 10^{-26} \quad [\text{e.s.e.} \times \text{cm.}^3],$$

instead of the value that was given there [4]).

As by his calculation of the quadrupole moment of hydrogen DEBIJE found the value

$$\mu_2 = 2{,}14 \times 10^{-26},$$

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[1]) For a molecule which is not rotationally symmetric (and which has no dipole-moment) this is replaced by a mean quadrupole moment, comp. DEBIJE l. c.

[2]) Leiden Suppl. N^0. 39a. These Proc. Vol. XVIII, p. 636. These Comm. N^0. 6a, these Proc. Vol. XXIII N^0. 6 p. 939.

[3]) l.c. p. 162, note 2.

[4]) In note 1 p. 15 l.c. we must read therefore $0{,}70 \times 10^{-8}$ instead of $0{,}92 \times 10^{-8}$. As to the remark in § 1 of Comm. N^0. 6a, these Proc Vol. XXIII p. 940 on the agreement between the values of the quadrupole moment deduced from the equation of state and from the model of BOHR-DEBIJE, this loses its sense.

the two methods of calculation are evidently leading to considerably different results for hydrogen too.

§ 3. His opinion that the polarisation of the molecules caused by their mutual influence, is of great importance, is based by Debije principally on the values of the coefficients of the *mean* reduced equation of state. This mean equation of state has been given by Kamerlingh Onnes for a systematic summary and discussion of the material of observations and of the deviations from the law of corresponding states. At the same time, however, he declared emphatically [1]) that for no substance this mean reduced equation of state will coincide with the real reduced equation of state. It would only do so, when the substances the data of which have been used in the derivation of the mean reduced equation of state, strictly obeyed the law of corresponding states. Now this is by no means the case, especially not for hydrogen compared with nitrogen and oxygen, which gases gave the data for the higher reduced temperatures, which are of most interest for our question. This is a. o. evident from the following fact. When for the great volumes and for the dominion of reduced temperatures corresponding to the temperature interval in which Amagat has made measurements on O_2 and N_2 we want to make the reduced equations of state of H_2 correspond with those of O_2 and N_2, we must choose as critical reduction temperature for H_2 [2]) 43, whereas however the critical temperature of H_2 is 33. Now in the mean reduced equation of state the reduced second virial coefficient $\mathfrak{B}$ is represented as a function of the reduced temperature t that is obtained by combining the values taken from H_2 with those of O_2 and N_2, etc. and reduced as well for H_2 as for O_2 and N_2 by means of the experimental values of T_k. And it is evident that this function can show a quite different character from that which corresponds to the behaviour of each of the substances.

For the discussion of questions as those considered here, we do better not to use the mean reduced equation of state.

It would be preferable to start from the *special* reduced equation of state of hydrogen [3]). In the above question however the special equation of state would lead to trustworthy results only then, when it was fitted to high temperatures. But this is not the case.

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[1]) See e.g. Leiden Comm. N⁰. 74 § 4, 1901.

[2]) H. Kamerlingh Onnes and C. Braak. Leiden Comm. N⁰. 97b, p. 39.
H. Kamerlingh Onnes and W. H. Keesom. Die Zustandsgleichung. Math. Enz. V 10. Leiden Suppl. N⁰. 23, note 399.

[3]) See Leiden Comm. N⁰. 109a, § 7, 1909.

The special equation of state deduced from measurements of KAMER-LINGH ONNES and BRAAK gives e.g.

$$B_\infty = 0,000893,$$

a value higher than might be expected from direct graphical extrapolation of the individual values of B from the measurements of KAMERLINGH ONNES and BRAAK. Therefore this special equation of state too would also give a too high value for the quadrupole moment when the method of calculation of DEBIJE was used.

It seems to me preferable to proceed as was done in my preceding communications viz. to work out the theoretically deduced development of B until [1]) it extends over a sufficiently wide dominion, to compare then this development with the experimental data and to deduce in this way e.g. the value of the quadrupole moment.

§ 4. *Further development of the second virial coefficient for spherical polarisable quadrupole molecules.* In order to take into consideration the influence of the polarisability of the molecules in the deduction of the quadrupole moment, the development started in Comm. N°. 6b § 3 has been extended by a few terms. Thereto the formulae given in Leiden Suppl. N°. 39a may be of use. By multiplying equation (11) from the paper by

$$\chi = \sin^4 \theta_1 + \sin^4 \theta_2 + 4 \cos^4 \theta_1 + 4 \cos^4 \theta_2 . \quad . \quad . \quad (1)$$

(Comm. N°. 6a equation (10)), we find, following the notations of Leiden Suppl. N°. 39a:

$$[\psi^n \chi] = 2\pi [A^n \chi] + \binom{n}{2} [A^{n-2} B^2 \chi] [\cos^2 \varphi] + \binom{n}{2} [A^{n-2} C^2 \chi] [\cos^2 2\varphi] +$$

$$+ \binom{n}{3} \binom{3}{1} [A^{n-3} B^2 C \chi] [\cos^2 \varphi \cos 2\varphi] \text{ etc.} . \quad . \quad . \quad (2)$$

With

$$\sin^4 \theta_1 + 4 \cos^4 \theta_1 = A_1{}^2 + 4 B_1{}^2 \quad . \quad . \quad . \quad . \quad (3)$$

(see Leiden Suppl. N°. 39a equation (9)) we find:

$$[A^p B^{2q} C^r \chi] = 2^{p+8q+1} [A_1{}^p B_1{}^{2q} C_1{}^r] \{ [A_1{}^{p+2} B_1{}^{2q} C_1{}^r] +$$

$$+ 4 [A_1{}^p B_1{}^{2q+2} C_1{}^r] \} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

[1]) Of course I acknowledge the objections made by DEBIJE in § 5 of his cited paper. They show that the results obtained in the above mentioned way can only be accepted with some reserve as has been specially stated in Comm. N°. 6a § 4. On account of all this accurate measurements on the second virial coefficient at higher temperatures are very necessary. In the meantime however it seems to me of some importance that such a good agreement with the experimental data that are at our disposition is obtained by using the mentioned simplifying suppositions (quadrupolar action, no quantum deviations as yet, collisions as of solid spheres).

Applying then equations (14), (15) and (16) of Leiden Suppl. N°. 39a and substituting in equation (16) of Comm. N°. 6b, we finally obtain:

$$B = \tfrac{1}{2}\, n \cdot \tfrac{4}{3}\, \pi\sigma^3 \Big\{ 1 - 1.0667\,(hv)^2 + 0.1741\,(hv)^3 - 0.4738\,(hv)^4 + 0.6252\,(hv)^5 \ldots$$

$$-2{,}4\,\frac{a}{\sigma^3}\, hv\, [1 + 1.0667\,(hv)^2 - 0.3641\,(hv)^3 + 0.2267\,(hv)^4 \ldots] \Big\} \quad . \ . \ (5)$$

§ 5. *Hydrogen*. Substituting for hydrogen $\dfrac{a}{\sigma^3} = 0{,}0640$ (Comm. N°. 6b § 4) we find:

$$B = \tfrac{1}{2}\, n \cdot \tfrac{4}{3}\, \pi\sigma^3 \Big\{ 1 - 0.1536\, hv - 1.0667\,(hv)^2 + 0.0103\,(hv)^3 -$$
$$- 0.4179\,(hv)^4 + 0.5904\,(hv)^5 - 0.2360\,(hv)^6 +$$
$$+ 0.1355\,(hv)^7 - 0.1079\,(hv)^8 + 0.0593\,(hv)^9 \ldots \Big\} \quad . \ . \ . \ . \ (6)$$

This gives for the JOULE-KELVIN point of inversion for small densities (comp. Leiden Suppl. N°. 39a § 4):

$$hv_{inv\,(\rho=0)} = 0.503 \ . \quad . \ . \ . \ . \ . \ . \ . \ (7)$$

From this we derive for B expressed in terms of $\dfrac{T}{T_{inv(\rho=0)}} = t_{(inv)}$:

$$B = B_\infty \Big\{ 1 - 0.0773\, t_{(inv)}^{-1} - 0.2699\, t_{(inv)}^{-2} + 0.01311\, t_{(inv)}^{-3} -$$
$$- 0.02675\, t_{(inv)}^{-4} - 0.01901\, t_{(inv)}^{-5} - 0.00382\, t_{(inv)}^{-6} +$$
$$+ 0.00110\, t_{(inv)}^{-7} - 0.00042\, t_{(inv)}^{-8} + 0.00011\, t_{(inv)}^{-9} \ldots \Big\} \quad . \ . \ . \ (8)$$

$\dfrac{T}{T_{inv\,(\rho=0)}}$	$\dfrac{B}{B_\infty}$	$\dfrac{B}{B_{inv}}$
0.6	0.160	0.246
0.75	0.426	0.650
1	0.655	1
1.5	0.829	1.266
2	0.895	1.366
3	0.944	1.411
4	0.963	1.470

In this way we reach an accuracy of about $1\,°/_0$ (of B_∞ at $T = 0{,}6\ T_{inv\,(\rho=0)}$). The preceding table gives some of the calculated values.

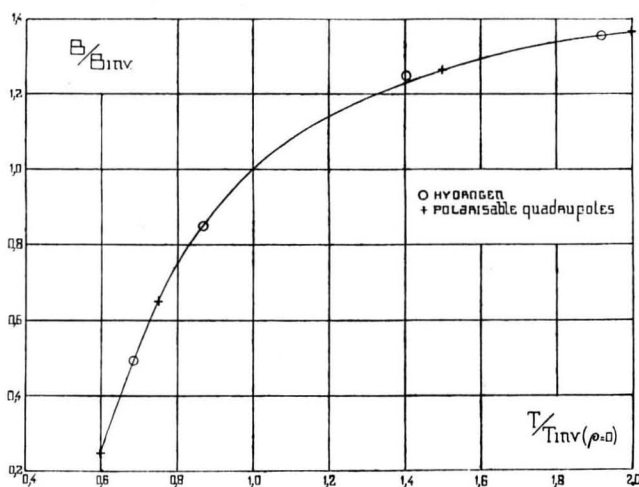In fig. 1 these values have been plotted together with the

Fig. 1.

experimental data according to KAMERLINGH ONNES and BRAAK. Over the whole range of temperature that is considered, the agreement proves to be very good.

As in Leiden Suppl. N°. 39a § 5 we find further:

for σ the same value as was given there, but

$$v = 1.34 \times 10^{-14}$$

and the quadrupole moment ·

$$\mu_2 = 1.10 \times 10^{-26} \quad [\text{e.s.e.} \times \text{cm.}^2].$$

As to the quadrupole moment of H_2 we thus really find, as was expected in Comm. N°. 6b § 4, a value deviating only little from that deduced by the calculations of Leiden Suppl. N°. 39a (see this Comm. § 2).

Further we deduce still easily for μ_2 the following relation

$$\mu_2{}^2 = 9.19 \times 10^{-17} . \sigma^5 \, T_{inv\,(\rho=0)} \quad . \quad . \quad . \quad . \quad (9)$$

For the reasons discussed in § 3 this equation seems to me preferable to equation (6) of DEBIJE l.c.

§ 6. *Oxygen and nitrogen.* For oxygen we may also apply equation (8). For nitrogen the coefficient will be a little different.

For the moment however we omit a more detailed calculation of the quadrupole moments of these gases as these may only be deduced with little accuracy because of the relatively small temperature interval in which for these gases data on B are at our disposal (Comm. N°. 6a § 2). For this reason the small alteration introduced by attending to the polarisability of the molecules would be of no importance.