

section of c can coincide with one of the first 4, for in that case a line of F^2 would pass through the point of intersection of b_1 and b'_1 , without being situated in the plane through these lines".

p. 1253 l. 2 from bottom, for: "cannot occur"; read: "can only occur".

Physics. — "*The quadrupole moments of the oxygen and nitrogen molecules*". By Prof. W. H. KEESOM. (Communication N°. 6a from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). (Communicated by Prof. KAMERLINGH ONNES).

(Communicated at the meeting of November 27, 1920).

§ 1. *Introduction.* In Suppl. N°. 39a to the communications from the physical laboratory of Leiden ¹⁾ it has been proved, that, as far as the term with the second virial coefficient, the equation of state of hydrogen can be accounted for in the temperature interval between $+100^\circ$ C. and -100° C. (according to Suppl. Nr. 39c down to still lower temperatures) by assuming the molecules to act on each other as electric quadrupoles with constant quadrupole moment ²⁾. Thereto the repulsions which predominate at small distances had to be replaced by the forces that would act when the molecules collided as solid spheres of definite radius. At the same time the quadrupole moment of the hydrogen molecules was determined. This proved a configuration of the two nuclei and the two electrons constituting a H_2 -molecule to be very well possible in such a way that it has the demanded quadrupole moment. By these considerations it was evident that the molecular attractions can be explained for homopolar molecules too by the electric forces exerted by the nuclei and the electrons constituting the molecules. To show this was for the moment the principal purpose of those considerations.

A comparison of the quadrupole moment demanded by the equation of state with that of the BOHR-DEBIJE model for the hydrogen molecule was not made because of the many difficulties that arise against this model, especially with respect to the magnetic properties. ³⁾ Meanwhile BURGERS ⁴⁾ has calculated the quadrupole moment of the hydrogen

¹⁾ These Proceedings, vol. 18, p. 636.

²⁾ The following Communication will treat the influence on the second virial coefficient of the mobility of the electrons within the molecule, which finds its expression in the dielectric constant.

³⁾ Comp. Leiden Comm. N°. 39a, p. 15, note 1. At present this difficulty has perhaps a somewhat smaller weight than was thought then. (Added in the translation).

⁴⁾ J. M. BURGERS, Diss. Leiden 1918, p. 186.

molecule according to BOHR-DEBIJE and he found a remarkable agreement with the value derived from the second virial coefficient (Comm. Leiden, Suppl. N°. 39a):

$$\begin{array}{l} \text{from the equation of state } ^1) \quad 2,03 \times 10^{-26} \text{ (e. st. e. cm}^2\text{)} \\ \text{according to BOHR-DEBIJE} \quad 2,05 \times 10^{-26} \quad , , \end{array}$$

However favourable this result may be for the BOHR-DEBIJE model, still it seems probable that the always increasing objections against this model ²⁾ will compel us to seek for another. The calculation of the quadrupole moment from the equation of state retains however its value. Abstracted from the uncertainty caused by the simplifying assumption on the repulsing forces, it gives namely important data which will have to be taken into consideration in the construction of the definite model of a molecule. In this sense it seemed interesting to calculate the quadrupole moments for other gases too. In § 2 this has been done for oxygen and for nitrogen.

§ 2. In the temperature interval in which the second virial coefficient has been calculated for quadrupole molecules, we possess the data comprised in table I for the second virial coefficients of oxygen and nitrogen ³⁾.

The index Θ indicates here that the volume v in the equation of state

$$pv = RT \left\{ 1 + \frac{B}{v} + \dots \right\}$$

is expressed in the theoretical normal volume as a unit ⁴⁾.

These data do not admit a control of the change of B for these gases with the temperature compared with that of spherical quadrupole molecules. This would require more values of B especially for higher temperatures. Let us assume for the present that this is the case for the considered temperature interval ⁵⁾, then they

¹⁾ When we attend to the circumstance that the molecules are polarized in their mutual electric fields, this value will still undergo a small alteration (comp. Comm. N°. 6b especially § 4).

²⁾ Comp. Miss H. J. VAN LEEUWEN, these Proc. Vol. XVIII, N°. 7, p. 1071. J. M. BURGERS, these Proc. Vol. XIX, 2. p. 480. A. SOMMERFELD, Atombau und Spektrallinien. Braunschweig 1919, p. 288 and 533. Fr. G. LASKI, Physik. Z. S. 20 (1919), p. 550. W. LENZ, Verh. D. Physik. Ges. 21 (1919), p. 632.

³⁾ These numbers are taken from the calculations by Mr. M. DANIELS, phil. nat. doct., where for the observations of AMAGAT were taken the virial coefficients given by KAMERLINGH ONNES in Comm. Leiden N°. 71.

⁴⁾ Comp. H. KAMERLINGH ONNES und W. H. KEESOM, Die Zustandsgleichung. Math. Enz. V. 10, Leiden Suppl. N°. 23, Einheiten b.

⁵⁾ For hydrogen deviations occur in the corresponding interval already.

TABLE I.

| Oxygen | | | Nitrogen | | |
|--------|--------------------------|-----------------|----------|--------------------------|------------|
| T | $B_{\Theta} \times 10^3$ | | T | $B_{\Theta} \times 10^3$ | |
| 472.6 | + 0.273 | AMAGAT | 472.5 | + 0.690 | AMAGAT |
| 372.6 | - 0.088 | " | 372.45 | + 0.324 | " |
| 293.1 | - 0.848 | ONNES & HYNDMAN | 290.6 | - 0.298 | LEDUC 1910 |
| 288.7 | - 0.694 | " | 289.1 | - 0.234 | AMAGAT |
| 288.7 | - 0.739 | AMAGAT | 288.0 | - 0.316 | RAYLEIGH |
| 288.1 | - 0.645 | LEDUC 1910 | 273.1 | 0.372 | AMAGAT |
| 284.3 | - 0.791 | RAYLEIGH | | | |
| 273.1 | - 0.812 | ONNES & HYNDMAN | | | |
| 273.1 | - 0.928 | AMAGAT | | | |

suffice to determine the quadrupole moment, besides the diameter of the molecules when regarded as spheres.

For this purpose we take the values of B/B_{∞} for different values of $T/T_{inv(\rho=0)}$ for spherical quadrupole molecules from Comm. Leiden, Suppl. N°. 39a and c.

Applying the method of the logarithmic diagrams (comp. Comm. Leiden, Suppl. N°. 25) we found successively:

For oxygen:

for the inversion temperature of the Joule-Kelvin-effect for small densities:

$$T_{inv(\rho=0)} = 723 \text{ (450}^\circ\text{C)},$$

for the potential energy of the molecules in contact (with the quadrupole axes mutually perpendicular and perpendicular to the line connecting the centres):

$$v = 5,71 \times 10^{-14},$$

for the diameter of the molecule:

$$\sigma = 2,65 \times 10^{-8},$$

for the quadrupole moment:

$$\mu_2 = 3,55 \times 10^{-26} \text{ [e. st. e.} \times \text{cm}^2\text{]}.$$

For nitrogen:

$$T_{inv(\rho=0)} = 604, \text{ (331}^\circ\text{C.)}$$

$$v = 4,77 \times 10^{-14},$$

$$\sigma = 2,98 \times 10^{-8},$$

$$\mu_2 = 3,86 \times 10^{-26} \text{ [e. st. e.} \times \text{cm}^2\text{]}.$$

§ 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 PICCARD¹⁾ 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 μ^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 σ 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.

¹⁾ 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).

(Communicated at the meeting of November 27, 1920).

§ 1. *Introduction.* DEBIJE¹⁾ 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)²⁾ 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

¹⁾ P. DEBIJE, Physik. Z.S. 21 (1920), p. 178.

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