Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Physics. — *"Two theorems concerning the second virial coefficient for rigid spherical molecules which besides collisional forces only exert* Coulomb-*forces and for which the total charge of the active agent is zero".* By Dr. W. H. Keesom. Supplement No. 39 b to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of October 29).

§ 1. In calculating the second virial coefficient B in the equation of state written in the form:

$$pv = RT \left(1 + \frac{B}{v} + \frac{C}{v^2} + \ldots \right) \quad \ldots \ldots \quad (1)$$

for a system of rigid spherical molecules, which carry a doublet at the centre (Suppl. No. 24b, June 1912), the second term in the development according to inverse powers of the temperature:

$$B = B_\infty \left(1 + \frac{b_1}{T} + \frac{b_2}{T^2} \ldots \right) \ldots \ldots \ldots \quad (2)$$

did not occur. This was also the case as regards all the higher odd powers.

In treating rigid spherical molecules which carry a quadruplet of revolution-type in Suppl. No. 39a (see p. 636), the second term in (2) was again found to be absent, but in this case the higher terms with b_3 etc. were present.

The question now arises whether general conditions can be given for the structure of the molecules under which the second term in (2) does not occur.

If, as will appear to be the case, such conditions can be given, the next question is: can still further conditions be given under which, if also satisfied by the molecules, no one of the odd powers of T^{-1} occurs in (2)?

In discussing these questions we shall place ourselves completely on the basis of classical mechanics.

In that case the following theorems can be proved:

1. In the development of B the term with T^{-1} does not occur if the following conditions are fulfilled:

(A). a. the molecules behave at their collisions as rigid spheres,

b. the attractive or repulsive forces[1]), which the molecules exert on each other, originate from fixed points in the molecule, and can be derived from a Coulomb law of force (inversely proportional to

---

[1]) Not including the collisional forces.

the second power of the distance between the attracting or repulsing points), so that these forces might be ascribed to an electric agent, [1] possibly with multiple points [2]),

c. the total quantity of the agent in each molecule $= 0$ (the molecules behave as electrically neutral).|

2. No odd power of T^{-1} occurs, if the following conditions are fulfilled:

(B): a, b and c as above, and besides:

d. the molecule possesses, as regards its attractive and repulsive forces, at least one axis of "inverse symmetry", by which expression we mean, that each volume element contains a quantity of the agent (as indicated under b) equal and opposite to that of the volume element with which it coincides after a revolution about that axis through an angle of $2\pi/k$, k being a whole and necessarily even number [3]).

In this case B is an even function of the temperature.

The proof of these two theorems follows below in § 3 and 4.

If in the development of B according to (2) the second term does not occur, the series for B reduces for high temperatures to:

$$B = B_\infty \left(1 + \frac{b_2}{T^2} \right) \quad \ldots \ldots \ldots (3)$$

This dependence of B on the temperature is the same as that which follows - from VAN DER WAALS' equation by putting $b_W =$ constant, and assuming for a_W with CLAUSIUS and D. BERTHELOT: $a_W \backsim T^{-1}$ (cf. Suppl. N°. 39a). Hence if the molecules satisfy the conditions (A), then for high temperatures and at densities for which only encounters of two molecules at a time have to be considered, the equation of state in the form accepted by D. BERTHELOT would hold.

If the conditions (B) are fulfilled the agreement with BERTHELOT's equation of state is still closer in consequence of the absence of the term b_3/T^3.

---

[1] On the supposition that electrodynamic forces (other than magnetic) need not be considered.

[2] In this, if need be, a magnetic agent may be included.

[3] As examples of this we mention the cases, that a molecule contains two positive and two negative charges situated at the corners of a square, the centre of which coincides with that of the molecule. If the homonymous charges lie diametrically opposite to each other, the molecule has one quadruple and two double axes of inverse symmetry, in the other case it has two double axes of inverse symmetry. We have another example, where the charges form a figure of revolution about an axis through the centre of the molecule, and the part on one side of the equatorial plane is the "inverse image" of the part on the other side.

§ 2. The second virial coefficient for a gas the molecules of which fulfil the conditions (A) can be deduced by the method given in Suppl. N°. 24, for which method Boltzmann's entropy principle serves as basis. This deduction follows more particularly the lines of the treatment in § § 4 and 6 of that paper; it differs, however, from that treatment in the following points:

1st. The three principal moments of inertia are now supposed to be unequal. In this case also in determining micro-elements of equal probability the expression $d\varphi d\theta d\chi d\bar\varphi d\bar\theta d\bar\chi$, φ, θ and χ being the angles which determine the position of the principal axes of inertia relative to a fixed system of coordinates, and $\bar\varphi$, $\bar\theta$ and $\bar\chi$ being the corresponding moments of momentum, may be replaced by $do d\chi dp_2 dq_2 dr_2$, where do represents a surface element of the sphere of unit radius, which serves for marking the position of one of the principal axes of inertia, and p_2, q_2 and r_2 represent the velocities of rotation about the principal axes of inertia.

2nd. For determining the relative position of the two members of a pair of molecules, we now need, besides the coordinates r, θ_1, θ_2, φ, which as in Suppl. N°. 24b § 6 and recently N°. 39a fix the distance of the centres and the relative orientation of a definite arbitrarily chosen principal axis of inertia of one molecule relative to the corresponding axis of inertia of the other molecule, two more angles, which for each molecule specify the azimuth of the plane going through the principal axis of inertia mentioned above and a second principal axis of inertia. As such we may choose the angle χ_1 between that plane and the plane which contains the first principal axis of inertia and the line joining the centres . χ_1, and similarly χ_2, for the second molecule, are counted from 0 to 2π.

Quite analagously to Suppl. N°. 24b §.6 the following result is obtained:

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

where now [1]:

$$P' = \frac{1}{8\pi^2}\int_\sigma^\infty\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi}(e^{-hu_{b1}}-1)\, r^2 \sin\theta_1 \sin\theta_2 dr d\theta_1 d\theta_2 d\chi_1 d\chi_2 d\varphi . \quad (5)$$

In this formula u_{b1} is again the potential energy of a pair of molecules in the position indicated by definite values of $r \ldots \varphi$, the

[1] As in P' the manner in which the density is distributed over the spherical molecule does not occur, it appears that the limitation to molecules of spherical symmetry observed in Suppl. N°. 24b § 6, can be omitted (cf Suppl. N°. 39a § 2 note).

potential energy for $r = \infty$ being chosen as zero. Further $h = \dfrac{1}{kT}$, k being PLANCK's constant. Finally the attraction is supposed 'to decrease sufficiently rapidly with increasing r, for the integral in (5) to be convergent.

§ 3. For the proof of the first of the theorems mentioned in § 1 we develop P' according to ascending powers of h. The first term becomes:

$$- \frac{1}{8\pi^2} \, h \int_0^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} u_{b1} r^2 \, \sin \theta_1 \, \sin \theta_2 \, dr d\theta_1 d\theta_2 d\chi_1 d\chi_2 d\varphi. \quad . \quad (6)$$

The integration according to θ_2, χ_2 and φ, the coordinates r_1, θ_1 and χ_1 being kept constant, must necessarily give 0, if the conditions (A) are fulfilled. In fact the result of this integration can be represented as the potential energy of a molecule 1 relative to a great number of superposed molecules 2, all with the same centre, but further as regards their orientations uniformly distributed over all the possible positions. By this superposition at the limit a sphere is obtained in which the agent is uniformly distributed over concentric shells. According to a well known theorem of the theory of potential, the potential outside such a sphere is constant if the total quantity of the agent acting according to COULOMB's law of the inverse square of the distance equals 0; from this, together with the assumption mentioned above about u_{b1} becoming 0 for $r = \infty$, follows the above result; the theorem in question is hereby proved.

§ 4. The odd powers of h in the development of P' (§ 3) occur in the following form:

$$- \frac{1}{8\pi^2} \cdot \frac{1}{(2q+1)!} \cdot h^{2q+1} \int_\sigma^\infty \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} u_{b1}^{2q+1} r^2 \, \sin \theta_1 \, \sin \theta_2 \, dr d\theta_1 d\theta_2 d\chi_1 d\chi_2 d\varphi \quad (7)$$

q is here a whole positive number.

If the conditions (B) are fulfilled, the integration of this integral according to θ_2, χ_2 and φ, the coordinates r, θ_1 and χ_1 being kept constant, will again necessarily give 0. This results from the fact that each contribution to the integral, obtained from positions of the second molecule indicated by definite values of θ_2, χ_2 and φ, with the ranges $d\theta_2$, $d\chi_2$, $d\varphi$, is neutralized by the contribution obtained from positions, which can be derived from the first by a revolution through an angle of $2\pi/k$ about one of the axes of inverse symmetry. With this the second theorem mentioned in § 1 is proved also.

56

Proceedings Royal Acad. Amsterdam, Vol. XVIII.