

Citation:

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a deep impression is made by the very striking realisation which it gives of the mechanism imagined by MAXWELL completed by the conception of electrons.

It is obvious that the subject will lead to further discussions¹⁾ and plans, but in this paper I may be allowed to confine myself to the simple description of the experiment carried out.

Physics. — “*The chemical constant and the application of the quantum-theory by the method of the natural vibrations to the equation of state of an ideal monatomic gas.*” By Dr. W. H. KEESOM. Supplement N°. 36b to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of March 28, 1914).

§ 1. In Suppl. N°. 33 (Dec. 1913) the expression for the entropy, S , of a gas was discussed, as it follows from the application of the quantum-theory to the molecular translatory motion by the method of the natural vibrations. Molecular rotations and intramolecular motions were not taken into account there. As was observed, the chemical constant is connected with the additive constant which occurs in the development of S for high temperatures. The object of this paper is to show that the value of the chemical constant, which in that manner is deduced from the expression for the entropy (an expression which had already been given by TETRODE), is in satisfactory agreement with values of this constant which correspond to the experimental data concerning vapour pressures of monatomic gases.

§ 2. We shall confine ourselves in this paper to the consideration of monatomic gases. If for the energy distribution one of the temperature functions is assumed which occur in the quantum-theory, one may suppose that the molecular rotatory motion, particularly for the molecules of a monatomic gas, is in thermal equilibrium with the translatory motion. If in particular that temperature function (given by PLANCK) is assumed which implies a zero point energy, the molecular rotations in a monatomic gas also, at the temperatures at which they have been investigated, represent a considerable amount of energy in proportion to the molecular trans-

¹⁾ Compare also MAXWELL, Electricity and Magnetism II, Ch. VI.

latory motions. The characteristic temperatures (Θ , cf. Suppl. N^o. 32a), which according to that hypothesis govern the rotatory energy, are, however, owing to the small moment of inertia of the monatomic molecules, so high, that at the temperatures mentioned the energy of rotation of the molecules does not yet deviate appreciably from the corresponding zero point energy. The same applies to the motions within the atom. The contributions to the entropy due to these rotations of and motions within the atom may then be counted as zero. We limit ourselves to the temperature range within which this is the case¹⁾.

We shall further assume that we are dealing with an *ideal* monatomic gas, so that terms due to the influence of the real volume or of the mutual attraction of the molecules need not to be considered.

The entropy of such a gas is then, on the basis of the hypotheses of Suppl. N^o. 30a, determined by the expressions given in Suppl. N^o. 33 § 2a.

§ 3. In the first place, as was already observed in Suppl. N^o. 33 § 2a β , the introduction of the zero point energy makes no change in the value which is found for the chemical constant. Hence a comparison of the value calculated for this constant, e.g. with the value which was found by SACKUR to agree with experimental data, cannot furnish a test between PLANCK's formula with or without zero point energy²⁾.

§ 4. If the development of S for high temperatures: equation (14) Suppl. N^o. 33, is written in the form

$$\left. \begin{aligned} S = C_s + Nk \ln v + \frac{3}{2} Nk \ln T + \\ + \text{terms of smaller order of magnitude} \end{aligned} \right\}, \quad \dots \quad (1)$$

then

$$C_s = Nk \left(4 + \frac{3}{2} \ln \beta M \right). \quad \dots \quad (2)$$

¹⁾ According to measurements by PIER of the specific heat of argon, this temperature range extends for this gas to at least 2300° C. As Prof. EINSTEIN pointed out in a discussion, the investigation at high temperatures of the specific heat of a monatomic gas with high atomic weight, such as mercury, would be of great interest.

²⁾ Prof. SOMMERFELD asks me to say, that he wishes the sentence: "Nebenbei sei bemerkt etc. on p. 139 of: Vorträge über die kinetische Theorie der Materie und der Elektrizität," Leipzig und Berlin 1913, to be omitted.

From equation (13) of Suppl. N^o. 33 with equation (18a) of Suppl. N^o. 30a it follows that

$$\beta = \frac{3}{5Nk} \frac{k^2}{h^2} \left(\frac{4\pi}{9N} \right)^{2/3} \dots \dots \dots (3)$$

From these formulae follows for the entropy constant

$$C_s = Nk \left\{ 4 + \ln \frac{4\pi}{9} \frac{k^2}{Nh^2} \left(\frac{3M}{5Nk} \right)^{3/2} \right\} \dots \dots \dots (4)$$

With the values $N = 6.85 \cdot 10^{23}$ (according to PERRIN), $k = 1.21 \cdot 10^{-16}$, $\frac{h}{k} = 4.86 \cdot 10^{-11}$, which were accepted in Suppl. N^o. 30a, equation (4) with $Nk = R$ passes into

$$C_s = R \left\{ \frac{3}{2} \ln M - 7.43 \right\} \dots \dots \dots (5a)$$

If we take MILLIKAN's¹⁾ values $N = 6.06 \cdot 10^{23}$, $k = 1.37 \cdot 10^{-16}$, $\frac{h}{k} = 4.83 \cdot 10^{-11}$, we find

$$C_s = R \left\{ \frac{3}{2} \ln M - 7.285 \right\} \dots \dots \dots (5b)$$

For the chemical constant C_{NE} , which is derived from C , by means of the relation²⁾

$$C_{NE} = \frac{C_s - 2.5R + R \ln Nk}{R \ln 10}$$

we find

$$C_{NE} = \frac{3}{2} \log M + 3.60 \left\{ \dots \dots \dots (6a) \right.$$

and

$$C_{NE} = \frac{3}{2} \log M + 3.67 \left\{ \dots \dots \dots (6b) \right.$$

respectively.

These values differ from those which SACKUR has compared with the vapour pressures of mercury and argon and which he found fairly well confirmed, only by 0.35 and 0.28 respectively. This agreement may be called very satisfactory considering the uncertainty which yet exists with regard to several of the quantities used in that comparison on the one hand, and the approximate character of some of the hypotheses on which the deduction of the expression for the entropy was founded on the other hand.

¹⁾ R. A. MILLIKAN, Physik. ZS. 14 (1913), p. 796.

²⁾ Cf. O. SACKUR, Ann. d. Phys. (4) 40 (1913), p. 79.

§ 5. The relation (4) also follows from equation (19a) of the paper by SOMMERFELD (p. 134), quoted in note 2 p. 21, if α occurring there is put equal to $\frac{10}{9}$, as has been supposed in the relations (3) and (4) given above, and if in SOMMERFELD's expression h is replaced by $\frac{1}{2} h$ ¹⁾. The latter change is connected with the fact, that in deriving the expressions given here the supposition was made that in considering the molecular translatory motion in an ideal monatomic gas we have to deal with energy elements of a magnitude $\frac{1}{2} h\nu$, as we tried to make probable in Suppl. N^o, 30a § 2.

The fact that in § 4 a satisfactory agreement with experimental data was obtained, may, if the validity of the other hypotheses is admitted as sufficiently approximate, be regarded as a confirmation of the above supposition concerning the magnitude of the energy elements.

Astronomy. — “On SEEELIGER's hypothesis about the anomalies in the motion of the inner planets.” By J. WOLTJER JR. (Communicated by Prof. W. DE SITTER).

(Communicated in the meeting of April 24, 1914).

To explain the differences between observation and calculation in the secular perturbations of the elements of the four inner planets, SEEELIGER²⁾ worked out the hypothesis that these are caused by masses of matter, which by reflection of sunlight offer the aspect of the zodiacal light. He imagines these masses to have the form of a flat disc surrounding the sun and extending nearly in the direction of the orbital planes of the planets and reaching outside the orbit of the earth; the density of the matter within the disc has its greatest value in the proximity of the sun, though it is very small even there. For the calculation of the attraction of the mass of matter special hypotheses on its constitution are introduced; we imagine a number of very flattened ellipsoids of revolution with the sun at the centre, the inclinations of the equatorial planes to the orbital planes of the planets being small. It is evident that by the superposition of a number of such ellipsoids we get a flat disc within which the density varies

¹⁾ This confirms at the same time the fact, that the introduction of the zero point energy does not produce a change in the value of the entropy constant.

²⁾ Das Zodiakallicht und die empirischen Glieder in der Bewegung der innern Planeten. Sitzungsberichte der Bayerischen Akademie, XXXVI 1906.