too, as the water, running in torrents from their sides, carried down much gravel. It was evidently a landformation not very apt to lodge a freshwater fauna of any importance. It is difficult to ascertain whether elements of this fauna still survive in the present fauna. This might possibly be the case with *Aplocheilus celebensis* M. WEB. and *Anabas scandens* DALD., which form a special element in the present fauna. One of these, *Aplocheilus* belongs to the family *Poecilidae*, several genera of which are known from the early tertiary; and *Anabas scandens* has a very wide range of distribution, from the continent of Asia to the eastern part of the indo australian archipelago.

The recent fishfauna only came to full development when Timor was raised to its present level in post pleistoceen times. This very young land developed a system of rivers, which could only be populated by such fishes, as are not hindered by salt water in their distribution. Timor, when rising, was surrounded by sea. The ichthyological material tends to prove that this was originally a shallow sea, possibly surrounding other greater or smaller islands in the neighbourhood, as, for several elements of the freshwaterfauna of Timor, a deep sea with a high salinity would form an unsurmountable barrier. Such a sea could only have been formed after the immigration in the freshwater was accomplished for the greater part.

We are of opinion that this is in accordance with the views of MOLENGRAAFF, who thinks that the formation of the deep seas along the north and south coast of Timor took place in connection with the final upheaval of the island, and that this has been the latest event.

Physics. — "*On the Deduction of the Equation of State from* BOLTZ-MANN'*s Entropy Principle.*" By Dr. W. H. KEESOM. Supplement No. 24*a* to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 26, 1912).

§ 1. *Introduction.* Since the two great advances made by VAN DER WAALS in deducing his equation and in developing the theory of corresponding states therefrom, the theoretical investigation of the equation of state for a single component substance has been developed in various directions, particularly by VAN DER WAALS himself; these developments have cleared up and enriched our knowledge of various circumstances which influence the equation of state, and which had

been left out of account in the first deduction of the equation. For example, we may refer in particular to the recent researches of VAN DER WAALS on the influence of apparent association. On the other hand, there has been collected much valuable experimental material, which has already, on various occasions, been compared with the results obtained from theoretical assumptions. In the meantime, while these researches are being continued, it seems desirable and opportune to undertake a systematic investigation of the equation of state over a region in which not only reliable experimental data can be obtained, and are in fact already accessible in part, but which also permits of a rigorous theoretical investigation.

KAMERLINGH ONNES [1]) has started to systematically collect, arrange and incorporate into his empirical equation the experimental results already accessible over the whole region which has been already investigated for the equation of state. Amongst other effects of this empirical equation is that it makes it easy to compare different substances from the point of view of the principle of similarity, and in this respect it has already led to a number of valuable conclusions. For a general review of these conclusions we may refer to an article on the equation of state which is to appear in the Encyklopädie der Mathematischen Wissenschaften and is now passing through the press; we shall refer to this paper as Suppl. N°. 23.

In investigating the most suitable expression for the equation of state preference was finally given (cf. Comm. N°, 71 § 3) to a series of increasing powers of v^{-1} (omitting the odd powers above 2 and closing the series with v^{-8}). With a small deviation from the notations of Comms. N°. 71 and 74 we may write the equation in the form

$$pv = A \left\{ 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \right\} \quad . \quad . \quad . \quad . \quad (1)$$

(cf. Suppl. N°. 23).

The form of this equation shows that, from an experimental point of view, the method most immediately indicated for proceeding to obtain correspondence between theory and experiment is to successively determining, both theoretically and experimentally, the various virial-coefficients A, B, C etc., over a temperature region as extensive as possible for substances for which one would expect it necessary to make the least complicated assumptions regarding molecular structure

---

[1]) H. KAMERLINGH ONNES, Comm. No. 71 (June 1901), No. 74, Arch. Néerl. (2) 6 (1901), p. 874.

and molecular action. This is especially the case with the first coefficients A, B and C, as their values can be experimentally obtained with pretty high accuracy quite independently of any special assumptions which may be made regarding subsequent terms; while, from the theoretical point of view, the means are at hand for deducing these virial-coefficients from various special assumptions regarding the structure and action of the molecules[1]).

With regard to the first virial-coefficient A we may remark that one may write

$$A = RT \quad \ldots \ldots \ldots \ldots \quad (2)$$

(R is the gas constant, T the temperature on the KELVIN scale) for non-associative substances over the whole temperature region hitherto investigated. With regard to the question as to whether such substances would exhibit another law of dependence upon temperature in another region (e.g. at the lowest possible temperatures) we may refer the reader to Suppl. N°. 23.

Both the present and the following paper aim at making a beginning with the deduction of the second virial-coefficient, B, from certain special assumptions, having in view its completion in subsequent papers by a comparison with results obtained from experiment.

In his *Elementary Principles in Statistical Mechanics* GIBBS developed methods which in principle enable us to deal with any molecular-kinetic problem concerning the equation of state, as long as we limit ourselves by the assumption that the mutual actions of the molecules conform to the HAMILTONian equations. ORNSTEIN [2]) adapted this method to the deduction of the equation of state and applied it. In Suppl. N°. 23 the method indicated by BOLTZMANN in his Gastheorie II § 61 and based immediately upon the BOLTZMANN entropy principle is developed in general terms. This method, too, seems suitable for the solution of all problems concerning the equation of state of systems in which the mutual actions of the molecules conform to the HAMILTONian equations. It has been shown by LORENTZ [3])

---

[1]) In this connection it must be remembered that, as noticed in § 1 of Comm. No. 74, the virial-coefficients in the polynomial (1) differ from those of the corresponding infinite series in which all the positive powers of v^{-1} are present. The more attention must be paid to this point, the higher the coefficients concerned; it will be quite appreciable with C on account of the absence of the v^{-3} term in (1), while D in (1) can no longer be regarded as approximating to the coefficient of v^{-4} in the infinite series (cf. Comm. N°. 74 § 1).

[2]) L. S. ORNSTEIN. Diss. Leiden 1908.

[3]) H. A. LORENTZ. Physik. Z. S. 11 (1910), p. 1257.

that it leads to the same results as the GIBBS method of the canonical ensemble. Although the two methods can therefore be regarded in principle as equivalent, the BOLTZMANN method seems to possess certain advantages over the other, e.g. its terminology can be more directly applied to the physical conception.[1])

As Suppl. N°. 23 is not yet published we may here give a short general account of this method, which forms the basis of the subsequent developments.

§ 2. *General formulation of the method of obtaining the equation of state of a single component substance from the* BOLTZMANN *entropy principle.* In the general formulation of the method we shall follow BOLTZMANN, *Gastheorie* II. § 36, and determine the momentary state (PLANCK's micro-state[2])) of a system of molecules whose motions, under the influence of their mutual forces, can be regarded as determined by HAMILTON's equations[3]) in terms of a finite number of generalised coordinates and the corresponding momenta for each molecule. We shall define a *micro-complexion*[4]) as a state in which, for instance, the coordinates $q_1 \ldots q_s$ and the momenta $p_1 \ldots p_s$ of the first molecule lie between the limits q_{1i} and $q_{1i} + dq_{1i}$, q_{2i} and $q_{2i} + dq_{2i} \ldots q_{si}$ and $q_{si} + dq_{si}$, p_{1i} and $p_{1i} + dp_{1i}$, p_{2i} and $p_{2i} + dp_{2i}, \ldots p_{si}$ and $p_{si} + dp_{si}$, those of the second molecule between q_{1j} and $q_{1j} + dq_{1j}$ etc.

In this, the micro-differentials[5]) dq_{1i} etc. must so be chosen that the specified distribution of molecules according to generalised coordinates and momenta is sufficient to fix the energy of each molecule in the micro-complexion as lying between definite limits which, in the problem under consideration, may be regarded as coincident, and also to enable one to ascertain if possible special conditions (e.g. mutual impenetrability, in the case of molecules supposed rigid) have been fulfilled. We assume that $dq_{11} = \ldots = dq_{1i} = dq_{1j} = \ldots dq_{1s}$, $dq_{21} = \ldots$, $dp_{11} = \ldots dp_{1i} = dp_{1j} = dp_{1s}$ etc. or, at least, that the

---

[1]) And also in this that by this method the most probable distribution of molecules according to definite coordinates or momenta is at the same time determined, and also an expression is found for the BOLTZMANN H-function for the particular case under consideration.

[2]) M. PLANCK. Acht Vorlesungen p. 47 sqq

[3]) In the application to collisions between molecules which are regarded as rigid bodies we shall, if necessary, regard the collision as a continuous motion subject to very great accelerations.

[4]) Derived from BOLTZMANN's "Komplexion". Comp. L. BOLTZMANN. Wien Sitz.-Ber. 76 (1877), p. 373; Wiss. Abh. 2, p. 164.

[5]) M. PLANCK. Acht Vorlesungen, p. 59.

different elements of the $2s$-dimensional space involving the coordinates p and the momenta q (the micro-elements) are of the same size.

We consider now, in general, states of the system of molecules which are defined by certain conditions — formulated in detail for each special problem — in such a way that the number of molecules or of groups of molecules is determinate for which e.g. certain coordinates, mutual distances or orientations of the molecules, their momenta or their relative velocities lie between limits previously assigned. The formulation of these special conditions and the choice of limits must so be made that the supposed numbers of molecules etc., are sufficient to determine, in so far as the particular problem under discussion is concerned, the state of the system as seen by a macro-observer at the particular moment for which those numbers are given. In this we are in no case concerned with the individuality of the molecules (we assume throughout that we are dealing with a single component substance). The limits to which we referred must, moreover, be so chosen that the macro-state thus determined can be realised from a very large number of different micro-complexions. The assemblage of these micro-complexions we shall call a *group macro-complexion*[1]).

As a foundation for further development we shall now assume that all micro-complexions represent cases of equal probability[2]). From this it follows immediately that the *probability*, W, of the occurrence of any group macro-complexion is proportional to, or, if we care to neglect an arbitrary factor, is equal to the number of micro-complexions contained in the group macro-complexion[3]).

In many cases it will facilitate the calculation of this number to first obtain the number of micro-complexions contained in an *individual*

1) For constructing a clear molecular kinetic interpretation of a definite macro-state, in particular regarding the number of the different micro-states by which it can be realised, we regard here as in the GIBBS method at any particular moment an assemblage (ensemble) of systems, independent of each other identical as regards number, structure and actions of their component particles and as regards their exterior coordinates, each of these systems forming a definite micro-complexion realising that macro-state. Cf. BOLTZMANN, Wiss. Abh. 1, p. 259; 3, p. 122; MAXWELL, Scient. pap. 2, p. 713. [Note added in the translation.]

2) In the present paper we shall not justify this assumption, which, in so far as it affects the choice of micro-elements, is founded upon LIOUVILLE's theorem, but for it we may refer to the writings of BOLTZMANN, PLANCK (e.g. Acht Vorlesungen, p. 56), and others. (Compare also Art. IV 32 by P. and T. EHRENFEST in the Math. Encykl., particularly note 170).

3) In order to conform to the common definition of probability as a fraction between 0 and 1 in value we should have to divide by the assumed value of the constant total number of micro-complexions possible, which would have to include all possible values of energy and volume which occur in our considerations. This constant is of no importance in any of our considerations, so we shall omit it.

macro-complexion. The definition of the latter complexion follows from that of the group macro-complexion by taking account of the individuality of the molecules. The number of micro-complexions in the individual macro-complexion has to be separately determined for each special problem, and this, multiplied by the number of individual macro-complexions contained in the group macro-complexion gives the number of micro-complexions contained in the group macro-complexion. The number of individual macro-complexions contained in the group macro-complexion, which is readily obtained from the theory of permutations, we shall call the *permutability index* of the macro-complexion [1]).

From the value thus obtained for the probability of a group macro-complexion one can ascertain which group macro-complexion is the most probable in a self-contained system of molecules of given energy and volume. According to BOLTZMANN the distribution of molecules according to the coordinates etc. determining it, obtained for this macro-complexion, corresponds macroscopically to a state of equilibrium of the system of molecules.

BOLTZMANN's entropy principle can now be formulated in such a way that the entropies of different macroscopically determined states are, if we omit an arbitrary additive constant, proportional to the logarithms of the probabilities of the different group macro-complexions corresponding to those macro-states. In this it is understood that these macro-complexions are determined with the same limits (equal elements of corresponding spaces) for the coordinates etc.

In the simple case, in which the same number of micro-complexions is present in each of the individual macro-complexions, as in the deduction of the equation of state for molecules whose dimensions and mutual attractions are neglected [2]), the entropy is then simply proportional to the permutability index of the macro-complexion.

In general we may write

$$S = k_P \, log_e \, W. \qquad \qquad (3)$$

in which S represents the entropy, and $k_P = R_M/N$ where R_M is the molecular gas constant and N is the AVOGADRO number (i. e. the number of molecules in the gram molecule). We then obtain for the entropy in the state of equilibrium of a gas whose molecules are regarded as having no dimensions and as exerting no mutually attractive forces, a function of volume and temperature which agrees with the thermodynamic expression for the entropy.

---

[1]) Differing slightly from L. BOLTZMANN, loc. cit. p. 243 note 4.

[2]) Comp. M. PLANCK, Wärmestrahlung, p. 140 sqq.; Acht Vorlesungen, Vierte Vorlesung.

If, by introducing special assumptions regarding the molecules and their mutual forces, one calculates, in the manner here indicated, the entropy S in the equilibrium condition for given energy U and volume V, one obtains directly a fundamental equation of state from which both the specific heats and the thermal equation of state can be deduced.

§ 3. *Deduction of the virial-coefficient B for rigid, smooth spheres of central symmetry and subject to* VAN DER WAALS' *forces of attraction.*

Although this problem has already been repeatedly treated, first by VAN DER WAALS himself in the deduction of his equation of state, and since then, in particular, by PLANCK [1]) by a method which is essentially the same as that here developed, we may yet utilise this simple case as an introduction to our treatment of the succeeding more complex cases. The description of these can then be shortened by referring to corresponding definitions and operations in the present problem.

Determination of the macro-complexion:

Two states which a macro-observer can distinguish as different may be regarded as having their differences arise from the presence in definite elements of volume of different numbers of molecules in the two cases, and also from different distributions of speed in those volume-elements. To determine a macro-complexion we therefore take the three-dimensional spaces which are available for each molecule with respect to its coordinates x, y, z and the velocities ξ, η, ζ of its centre, and divide them up into equal elements $(dx_1 dy_1 dz_1 =)$ $dv_1, dv_2 \ldots dv_k$, and $(d\xi_1 d\eta_1 d\zeta_1 =) dw_1, dw_2 \ldots dw_l$.

In this we make $dv_1 \ldots$ so great that each contains on the whole a great number of molecules, and yet sufficiently small for the density variations within those elements of volume to escape the notice of the macro-observer; the elements $dw_1 \ldots$ are also chosen so great that to each corresponds a large number of molecules in $dv_1 \ldots$ and yet so small that $d\xi_1, d\eta_1, d\zeta_1 \ldots$ are small in comparison with the mean speed.

The group macro-complexion is now determined by the conditions that

$$n_{11} \text{ unspecified molecules "are present" in } dv_1 dw_1$$
$$\vdots \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4)$$
$$n_{kl} \quad\text{''}\qquad\quad\text{''}\qquad\text{''}\qquad\text{''}\qquad\text{''}\quad dv_k dw_l .$$

Determination of the micro-complexion:

As far as velocities [2]) are concerned, the micro-complexion can be

[1]) M. PLANCK, Berlin Sitz.-Ber. 32 (1908), p. 633.
[2]) As the velocities differ from the momenta only by a constant factor, we may

determined from the same elements of the proper space as the macro-complexion. With regard to the distribution of the molecules throughout the space we must distinguish between various elements of volume, which are supposed small in comparison with the dimensions of a molecule, for, in ascertaining if a certain micro-complexion occurs in the macro-complexion determined by (4), it is of importance to know if the centre of any particular molecule lies within or without the distance sphere of any other molecule. Hence we divide the volume-elements of the macro-complexion into smaller volume-elements, thus

$$dv_1 \text{ into } \varkappa \text{ equal volume-elements } d\omega_{11} \ldots d\omega_{1\varkappa}$$
$$dv_2 \text{ „ „ „ „ } d\omega_{21} \ldots d\omega_{2\varkappa}$$
etc.

A micro-complexion is now determined by specifying for each molecule in which of the elements $d\omega$ and dw it is present at the particular moment under consideration (understanding that a molecule is present in the micro-volume-element $d\omega$, when its centre of mass is there).

W is now the number of micro-complexions thus determined present in the macro-complexion given by (4); in this we must remember that all micro-complexions are excluded in which the distance separating the centres of any two molecules is smaller than the diameter of a molecule.

For the permutability index of the macro-complexion we obtain

$$\frac{n!}{n_{11}! \, n_{12}! \, \ldots \ldots \, n_{kl}!}.$$

As we shall have to deal only with such macro-complexions as correspond to states of equilibrium or to states differing but little therefrom, it follows from the conditions laid down regarding the magnitude of dv and dw, that for each element $dv_i dw_j$ of the 6-dimensional space in which, for any specified state, molecules may be present, the number n_{ij} will be large. We shall, in the meantime, be obliged to compare macro-complexions whose total volumes v are not the same [1]), for instance in the development of the thermal equation of state. This can be done if, in the determination of the macro-complexion, we also take account of volume-elements lying

in this case use equal elements in the velocity diagram for determining micro-complexions of equal probability.

[1]) When, as in the present instance, we consider states in which the substance is not split up into different phases, we shall indicate the volume etc. by small letters v, u, s, which, when referred to 1 gram of the substance, can then be regarded as specific quantities.

outside the volume v. A similar remark holds regarding the energy u. The conditions represented by (4) must then be so understood that the number of molecules in each of these outlying elements of the 6-dimensional space is zero, and for each of these elements the figure 1 must be put in the denominator of the permutability index.

We have still to calculate the number of micro-complexions contained in the individual macro-complexion; this is determined by specifying that

$$n_{11} \text{ specified molecules are present in } dv_1 dw_1$$
$$\vdots \tag{5}$$
$$n_{kl} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad dv_k dw_l.$$

These micro-complexions differ only in the different dispositions of the $n_1 = n_{11} + \dots n_{1l}$ molecules in the volume-element dv_1 etc. The diffe-. rent volume-elements are here to be regarded as independent of each other. We then obtain the total number of micro-complexions by calculating the number of different ways in which the n_1 molecules can be placed in the volume dv_1, the same then for dv_2 etc., and by then multiplying these numbers together.

Let us first put the first of the n_1 molecules in dv_1. For this there are x places available. For the second molecule there are then left

$$x \left\{ 1 - \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\} \text{places available. Of these there is a comparatively small}$$

number for which the distance between the centres of molecules is such that the distance spheres of the two molecules partially overlap. In placing the third and succeeding molecules we shall omit these cases, for bringing them into the calculation would introduce terms of the second order of small quantities compared with the principal terms of W, and would have no effect upon the value of the virial-coefficient B. The influence of these terms would have to be more closely investigated only in the determination of C and succeeding coefficients. The number of places available for the third.

molecule can then be written $x \left\{ 1 - 2 . \dfrac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\}$. Proceeding in this fashion we obtain

$$x^{n_1} \prod_{\iota=1}^{\iota=n_1-1} \left\{ 1 - \iota\, \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \right\}$$

different dispositions of the n_1 molecules in dv_1. Doing the same for dv_2 etc., we obtain the number of micro-complexions in the individual macro-complexion.

After multiplying by the permutability index, a little reduction in which use is made of STIRLING's formula, gives with sufficient approximation

$$log_e W = - \sum_{dv} \sum_{dw} n_{11} \, log_e \, n_{11} - \frac{\frac{4}{3}\pi\sigma^3}{dv_1} \sum_{dv} \frac{n_1^2}{2}. \quad \ldots \quad (6)$$

In this, terms have been omitted which remain constant when n is constant and the division into elements remains the same. $\sum_{dv}$ and $\sum_{dw}$ indicate summations taken over all the elements dv and dw. Use has also been made of the fact that the elements dv are all of the same size.

The expression which one obtains for BOLTZMANN's H-function by reversing the sign of (6), agrees to the degree of approximation here given, with the expression given by ORNSTEIN[1]) for this case.

State of equilibrium:

This is determined by the condition that for constant v and u, W is a maximum. The condition $v =$ const. is fulfilled by varying only the values of n_{11}, etc. which occur in (6), and keeping $n_{11} + \ldots n_{kl} = n$ constant. With regard to the condition $u =$ const. the assumption that the molecules behave as if they were rigid *smooth* spheres, of central symmetry (so that their density is constant or only a function of the distance from the centre, and therefore their mass centres and their geometrical centres coincide) enables us to disregard angular speeds about axes through their mass centres. To enable us to find an expression for the potential energy we shall assume that the macro-volume-elements are great in comparison with the sphere of action of a molecule. With reference to the potential energy we shall, in conformity with the assumptions underlying the VAN DER WAALS attractive forces, further assume that, in states of equilibrium and in states closely approximating thereto, each sphere of action can be regarded as being uniformly filled with the number of molecules which that sphere would contain if the molecules were uniformly spread over the whole macro-volume element. In making this assumption cover even the molecules which lie near the boundaries of the volume-element we neglect the influence of capillary forces. Calling the potential energy of n molecules uniformly spread over the volume v, $-\dfrac{a_w}{v}$, with a_w constant, we may write the whole potential energy contained in the element dv_1 as $-\dfrac{a_w n_1^2}{n^2 dv_1}$. The condition for the energy then becomes

[1]) L. S. ORNSTEIN. Diss. 1908, p. 60.

$$u = \sum_{dv} \sum_{dw} n_{11}\, u_{w_1} - \sum_{dv} \frac{a_w\, n_1^2}{n^2\, dv_1} = \text{const.}, \quad \ldots \quad (7)$$

in which $u_{w_1} = \frac{1}{2} m\, (\xi_1^2 + \eta_1^2 + \zeta_1^2)$ represents the kinetic energy of translation of a molecule whose velocity lies in dw_1.

The condition for a maximum, in conjunction with (7) and $n = \text{const.}$[1]) gives

$$- \log_e n_{11} - n_1 \frac{\frac{4}{3}\pi\sigma^3}{dv_1} - h\left(u_{w_1} - \frac{2a_w\, n_1}{n^2 dv_1}\right) + \log_e c = 0, \quad (8)$$

in which h and c are constants. A few reductions lead to

$$n_1 = \frac{n}{v}\, dv_1$$

and

$$(9,$$

$$n_{11} = \frac{n}{v}\left(\frac{h\, m}{2\,\pi}\right)^{3/2} e^{-h\, u_{w_1}}\, dv_1\, dw_1,$$

the well known conditions for equilibrium: macroscopically uniform distribution throughout the space, and MAXWELL's distribution of velocities with the same constant h for each macro-volume-element. This constant h can be found by obtaining an expression for the energy u

$$u = \frac{3}{2}\frac{n}{h} - \frac{a_w}{v}. \quad \ldots \quad \ldots \quad (10)$$

From (6) and (9) we obtain for the state of equilibrium

$$\log_e W = n \log_e v - \frac{3}{2} n \log_e h + h\, u_w - \frac{1}{2}\frac{n}{v}\, n\,\frac{4}{3}\pi\sigma^3,$$

in which u_w represents the total kinetic energy, and certain constants are omitted. In conjunction with (3) this gives

$$s = k_p\, n \log_e v - \frac{3}{2} k_p\, n \log_e h + k_p\, h\, u_w - \frac{1}{2}\frac{k_p\, n}{v}\, n\,\frac{4}{3}\pi\sigma^3. \quad (11)$$

On eliminating h between this equation and (10) one obtains a fundamental equation of state expressing u as a function of s and v, or s as a function of u and v, which PLANCK calls the canonical equation of state. On keeping v constant and differentiating (10) and (11) with respect to h, since $T = \left(\dfrac{\partial u}{\partial s}\right)_v$ one easily obtains

$$T = \frac{1}{k_p\, h}, \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

---

[1]) It will be seen that in the case of the most probable distribution the total momentum and the total moment of momentum vanish for each macro-volume-element. If one wished to evaluate the entropy for states in which these magnitudes were not zero one should have to introduce here suitable conditions to allow for them.

from which with (11) it follows that

$$\psi = u - \frac{s}{k_p h} = -\frac{n}{h} \log_e v + \frac{3}{2} \frac{n}{h} \log_e h - \frac{a_w}{v} + \frac{1}{2} \frac{n}{hv} n \frac{4}{3} \pi \sigma^3.$$

Using (12) and the relation $k_p = R/n$, in which R is the gas constant for the quantity under consideration, this equation is transformed into

$$\psi = -RT \log_e v - \frac{3}{2} RT \log_e T - \frac{a_w}{v} + \frac{RT}{v} b_w, \quad . \quad . \quad (13)$$

in which b_w has been written for $\frac{1}{2} n. \frac{4}{3} \pi \sigma^3$ and a linear function of T has been omitted.

From this equation one obtains the value $\frac{3}{2} R$ for the specific heat at constant volume, while the thermal equation of state becomes

$$p = \frac{RT}{v} \left(1 + \frac{b_w}{v} \right) - \frac{a_w}{v^2}.$$

Hence (cf. § 1)

$$B = b_w - \frac{a_w}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

§ 4. *The virial-coefficient B for rigid ellipsoids of revolution subject to* VAN DER WAALS *attractive forces.*

Determination of the macro-complexion.

We shall first assume that in collision between two ellipsoids the speed of rotation around the axis of revolution can also vary. To make sure that HAMILTON's equations are sufficient to determine the mutual action of two such ellipsoids (cf. also p. 243 note 3) we shall make it essential that the surfaces of the colliding bodies which we are considering can never-exert other than normal forces upon each other at their point of contact. We shall, however, assume that it is found on closer investigation that the surfaces of the ellipsoids are not perfect surfaces of revolution but show, it may be, a universal wave-formation ; but in the meantime we shall assume that deviations from the true shape of an ellipsoid of revolution are so small that they may be altogether neglected except in so far as they give rise to a moment around the "axis of revolution" during collision. Hence in formulating the condition that the energy has a given value, we shall also have to allow for the speed of rotation around the axis of revolution. To express that condition, then, it is desirable to determine the macro-complexion as was done in § 3 and also with respect to the speeds of rotation around the three axes of

17

inertia, p_r, q_r, r_r, in which p_r represents the speed of rotation around the axis of revolution.

The group macro-complexion is now determined by specifying that n_{111} unspecified molecules are present in $dv_1 \, dw_1 \, dw_{r1}$

n_{211} ,, ,, ,, ,, ,, dv_2 ,, ,, etc. . . (15)

in which dw_{r1} represents an element of the space involving the coordinates $p_., q_.,$ and r_1; these elements are also assumed to be equal.
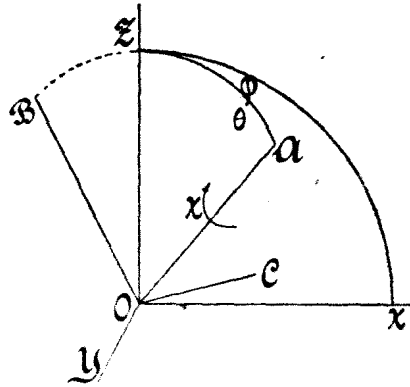
Determination of the micro-complexion :

For this it is necessary to specify the position of the ellipsoid. To do this choose a fixed system of axes XYZ, and through the origin draw a line OA parallel to the axis of revolution; we shall determine the position of the ellipsoid by the angles $AZX = \varphi$, $AOZ = \theta$ and the angle χ between the plane AOZ and a fixed meridian plane of the ellipsoid (Fig. 1).

Fig. 1.

Angular momenta: We may represent the kinetic energy of rotation, L_1, by the formula

$$L_r = \tfrac{1}{2} A_r p_r{}^2 + \tfrac{1}{2} B_r (q_r{}^2 + r_r{}^2), \quad \ldots \ldots \quad (16)$$

in which $A_r =$ the moment of inertia about the axis of revolution, and

$B_r =$,, ,, ,, ,, ,, an equatorial axis.

We shall choose the equatorial axis to which q_r refers, OB, in the plane AOZ, OC perpendicular to OA and OB in such a direction that a rotation from A towards B seen from C is in the same direction as a rotation from X towards Y seen from Z.

It is seen that

$$p_r = \dot{\varphi} \cos \theta + \dot{\chi}$$
$$q_r = \dot{\varphi} \sin \theta \qquad \ldots \ldots \ldots \ldots \quad (17)$$
$$r_r = -\dot{\theta}$$

in which the dots represent differentiation with respect to the time.

If we call the angular momenta with reference to $\varphi, \theta, \chi, \; \overline{\varphi}, \overline{\theta}, \overline{\chi}$ respectively, we then obtain

$$\overline{\varphi} = A_r \cos \theta \cdot p_r + B_r \sin \theta \cdot q_r,$$
$$\overline{\theta} = - B_r \, r_., \qquad \qquad \ldots \ldots \quad (18)$$
$$\overline{\chi} = A_r \, p_r,$$

in which $p_r, q_r,$ and r_r have the values given in (17).

Instead of determining the micro-complexion by $d\varphi \, d\theta \, d\chi \, \overline{d\varphi} \, \overline{d\theta} \, \overline{d\chi}$ we shall introduce a slight modification. From (18) we find

$$d\overline{\varphi}\, d\overline{\theta}\, d\overline{\chi} = A_r\, B_r^2\, sin\ \theta\ dp_r\, dq_r\, dr_r,$$

if we stipulate that the sign of equality in this and similar expressions means that in the integral the expression on the left may be replaced by that on the right with the proper modification of the limits of integration.

Let us further write do for an element of the surface of the sphere of unit radius, by points on which we can indicate the direction of the axis of revolution of the ellipsoid; we then obtain

$$d\varphi\, d\theta = \frac{do}{sin\ \theta}.$$

Hence

$$d\varphi\, d\theta\, d\chi\, d\overline{\varphi}\, d\overline{\theta}\, d\overline{\chi} = A_r\, B_r^2\, do\, d\chi\, dp_r\, dq_r\, dr_r.$$

We shall therefore obtain micro-elements of equal probability (cf. p. 246 note 2) if we measure equal $d\omega$'s, equal $d\overline{\omega}$'s, equal do's, equal $d\chi$'s and equal dw_r's, and combine them.

If each molecule is assigned to a particular micro-element, then the micro-complexion is completely determined.

The number of individual macro-complexions in the group macro-complexion is

$$\frac{n\ !}{n_{111}\ !\ n_{112}\ !\ \ldots}$$

(compare what was said concerning the corresponding expression in § 3).

The number of micro-complexions in the individual macro-complexion is determined as follows:

The various volume-elements dv are again independent of each other (cf. § 3). Let us consider the n_1 molecules in dv_1. To each molecule we ascribe its proper speed of translation ξ, η, ζ and speed of rotation p_r, q_r, r_r determined by (15). We then "place" the first molecule in one of the v elements $d\chi$, then in one of the $\varkappa$ elements $d\omega$ and lastly in one of the μ elements do. This can be done in $\varkappa\mu v$ different ways.
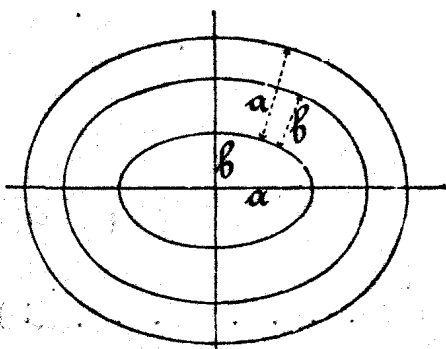

Fig. 2.

We now dispose of the second molecule. For this we have still v elements $d\chi$ at our disposal, but for the other coordinates there are fewer places available than was the case with the first molecule. Outwards along the normal to each point of the first ellipsoid mark off a distance a (equal to half the major axis) (Fig. 2), then each $d\omega$ outside the surface thus

17*

obtained is a possible position for the centre of the second ellipsoid, and in any of those positions all orientations of the axis of revolution of this ellipsoid are possible. Calling v_e the volume enclosed by the *outer distance surface* thus obtained, then the above volume-elements give rise to $\varkappa\mu\nu \left| 1 - \dfrac{v_e}{dv_1} \right|$ possibilities.

Along the normal to each point of the ellipsoid mark off a distance b (equal to half the minor axis), we thus obtain a surface within which no centre of another molecule can lie. We shall call this the *inner distance surface*, and designate by v_1 the volume which it encloses. In the shell enclosed between these two distance surfaces the centre of the second ellipsoid can be placed, but then all μ orientations do are not possible, but only a portion of them, which can be determined in the following fashion (Fig. 3). Let A be the first ellipsoid which we shall regard as immovable. Let P be a point of the shell determined by the coordinates relative to A : x in the direction of the
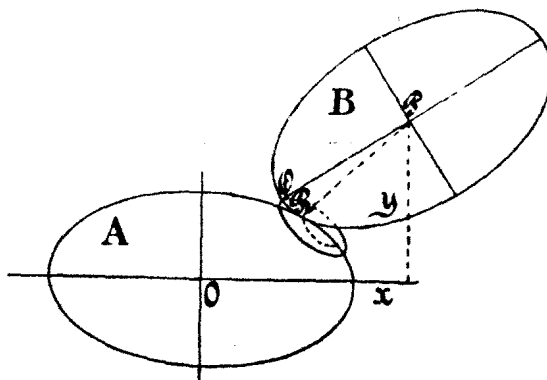
Fig. 3.

axis of revolution, y in the direction perpendicular to it. Now place the second ellipsoid with its centre at P, and, keeping its centre fixed, allow it to roll on the surface of A; during this rolling the point of contact R describes a trace on the surface of A. We can write for the solid angle of the cone which is described during the rolling by the semi-axis of revolution, PQ, $2\pi\varphi$ if the ellipsoid is prolate, $2\pi(1-\varphi)$ if oblate, in which φ is a function of x and y; there are then $\mu(1-\varphi)$ orientations do possible for the ellipsoid B with its centre fixed at P. Altogether we shall have $\varkappa\mu\nu \left| 1-\dfrac{\beta}{dv_1} \right|$ cases, where

$$\beta = v_1 + \int \varphi d\omega . \qquad\qquad\text{(19)}$$

the integration being taken throughout the shell.

β may be regarded as the mass obtained taking the volume contained within the inner distance surface as having unit density, and adding to it the sum of the volume-elements contained within the shell between the two surfaces, each multiplied by its own density ϱ.

The placing of the third molecule can be done in $\varkappa\mu\nu \left\{1-2\dfrac{\beta}{dv_1}\right\}$ ways if one takes no account of the complication introduced by the approach of three molecules (cf. § 3). Finally we get

$$W = (\varkappa\mu\nu)^n \frac{n!}{n_{111}!\ldots} \prod_{dv} \prod_{\iota=1}^{\iota=n_1-1} \left\{1 - \iota\frac{\beta}{dv_1}\right\}.$$

Omitting constants this gives

$$log_e\, W = -\sum_{d}\sum_{dw}\sum_{dw_{\rm r}} n_{111}\, log_e\, n_{111} - \sum_{dv} \frac{n_1^2}{2}\frac{\beta}{dn_1}.$$

Subsequent treatment of this problem differs from that given in § 3 only in so far as the energy condition, under the same assumption as was there made regarding the potential energy, must now be written

$$\sum_{dv}\sum_{dw}\sum_{dw_{\rm r}} n_{111}\left\{\tfrac{1}{2}\,m\,(\xi_1^2+\eta_1^2+\zeta_1^2) + \tfrac{1}{2}\,A_\iota p_\iota^2 + \tfrac{1}{2}\,B_{\rm r}\,(q_r^2+r_\iota^2)\right\} -$$

$$- \sum_{dv} \frac{a_{\rm w} n_1^2}{n^2 dv_1} = const. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The result then follows that the specific heat at constant volume for these rigid (but not smooth) ellipsoids is $3R$, while as regards the thermal equation of state equation (14) gives the value of B if we substitute

$$b_{\rm w} = \frac{n\beta}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

As far then as concerns the term with the virial-coefficient B, we find the same equation of state as for rigid spheres [1]), only with the ellipsoids, $b_{\rm w}$ is not such a simple function of the volume of the molecules as with rigid spheres.

We shall now introduce the assumption that the ellipsoids are perfectly *smooth*, so that the velocities of rotation around the axis of revolution undergo no change on collision. We shall also assume that the attractive forces cause no modification in these angular speeds. In that case it is not necessary to allow for the value of

---

[1]) This may be regarded as a particular case of the general proposition indicated by BOLTZMANN (Gastheorie II § 61), for molecules which behave as solid bodies of shape other than spherical.

p_r in the equation for the constant energy; hence we shall also take no account of p_r in the determination of the macro-complexion.

The group macro-complexion is then specified thus:

n_{111} unspecified molecules are present in dv_1 dw_1 $(dq_r dr_r)_1$

n_{112} ,,   ,,   ,,   .,   ,, ,, ,, etc. . . (22)

in which $(dq_r dr_r)_1$ represents one of the different elements (supposed equal) of the space involving the coordinates q_r and r_r. The equation for given energy then becomes

$$\Sigma\, n_{111}\, \{\tfrac{1}{2}\, m\, (\xi_1{}^2 + \eta_1{}^2 + \zeta_1{}^2) + \tfrac{1}{2}\, B_r\, (q_{r_1}{}^2 + r_{r_1}{}^2)\} - \underset{d_0}{\Sigma}\, \frac{a_w\, n_1{}^2}{n^2 dv_1} = \text{const.}$$

As far as the thermal equation of state is concerned the result is the same as that obtained for rough ellipsoids, but the specific heat at constant volume is different, viz. $\dfrac{5}{2} R$, for smooth ellipsoids.

Physics. — *On the deduction from* BOLTZMANN's *entropy principle of the second virial-coefficient for material particles (in the limit rigid spheres of central symmetry) which exert central forces upon each other and for rigid spheres of central symmetry containing an electric doublet at their centre.* By Dr. **W. H. KEESOM**. Supplement N°. 24[b] to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 26, 1912).

§ 5 [1]) *The deduction of the second virial-coefficient, B, for material points (in the limit rigid spheres of central symmetry) which exert central forces upon each other.*

In this section we shall deduce the equation of state, as far as the second virial-coefficient, B, is concerned (cf. § 1), for a system of molecules which act upon each other as if they were material particles (in the position of the centres, which are also the centres of gravity of those molecules) and with forces which are given invariable functions of the distance. All mutual actions other than that just described will be excluded. The case in which the spheres can be regarded as rigid spheres of central symmetry (§ 3) exerting central attractive or repulsive forces upon each other which are a function of the distances between their centres, will be treated as a limiting case.

---

[1]) To facilitate reference to Suppl. N'. 24a sections, equations and diagrams in the present paper are numbered as continuations of those in Suppl. N°. 24a.