

**Physics.** — “Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this.” By Prof. P. EHRENFEST and V. TRKAL.

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### Introduction.

NERNST's theorem, the theory of the specific heat of solids, of the vapour-pressure and of the dissociation-equilibrium must have their common root in the general foundations of statistical mechanics and in the quantum-hypothesis. O. STERN<sup>1)</sup> and H. TETRODE<sup>2)</sup> have shown how from NERNST's theorem by means of EINSTEIN's formula for the specific heat of solids and a vapour-pressure formula for high temperatures (derived kinetically) the chemical constants (hence also the dissociation-equilibrium) may be calculated. Notwithstanding the great advantages of this method a desire must be felt to calculate the chemical constants and the dissociation-equilibrium more directly by considering the hot gases themselves, without the use of a cycle consisting of a condensation, cooling of the crystals to the absolute zero, chemical transformation at  $T=0$ , heating of the new crystals and evaporation at the high temperature.

This desire explains the fact, that even after the publication of STERN's paper (1913) attempts have been made again and again to improve the earlier methods of calculating the chemical constants as given by O. SACKUR<sup>3)</sup> in 1911—1913 and H. TETRODE<sup>4)</sup> in 1912. These consist in considering a gas of  $N$  equal molecules in a volume  $V$  at the temperature  $T$ , calculating statistically by means of some formulation of the quantum-hypothesis the “thermodynamic probability  $W$ ” and by comparing  $r \log W$  with the thermodynamic entropy of the gas fixing the indeterminate constant in the entropy. It is not an accident that it is always the same point that remains obscure in these theories<sup>1)</sup>, viz, how an expression of the form  $N^{-N}$

<sup>1)</sup> O. STERN, Phys. Ztschr. **14** (1913), p. 629.

<sup>2)</sup> N. TETRODE. Verslag Kon. Ak. v. Wetensch., Amsterdam **23** (II), (1915), p. 1110. Proceedings Amsterdam **17** (1915), p. 1167. [henceforth to be quoted as “IInd paper”].

<sup>3)</sup> O. SACKUR. Ann. d. Phys. **36** (1911), p. 958; **40** (1913), p. 67; Nernst-Festschrift (1912), p. 405.

<sup>4)</sup> H. TETRODE. Ann. d. Phys. **38** (1912), p. 434. [to be quoted as “Ist paper”].

(SACKUR) or  $(N!)^{-1}$  (TETRODE I) can be forced into the “thermodynamic probability  $W$ ” in order to obtain an admissible value for the entropy. The law of dependence on  $N$  can only be satisfactorily settled by utilizing a process in which  $N$  changes reversibly and then comparing the ratios of the probability with the corresponding differences of entropy.

If condensation and evaporation (STERN and TETRODE II) are not to be used, and the whole process is to be carried out with gases, it will be necessary to work with a gas-mixture and change the numbers of molecules  $N_1, N_2, \dots, N_j$  of the various gases by dissociation.

Remembering the real object of the calculation of the chemical constants, viz the deduction of the dissociation-equilibrium, the following formulation of the problem is finally arrived at: Consider  $X, Y, Z, \dots$  atoms of different elements contained in a volume  $V$  and possessing an energy  $E$ . These atoms can unite to molecules of different kinds in a large number of different ways. Determine by means of the quantum theory directly, which of the various states of dissociation possesses relatively the greatest probability.

This problem is to be solved by methods belonging to statistical mechanics and the quantum-theory which will be set forth in § 2 and § 4. On comparing the dissociation-equations arrived at in this manner with the corresponding thermodynamical equations values are obtained for the expressions containing the chemical constants which occur in the latter (§ 6).

Our method removes, as we hope, any remaining obscurities as regards the occurrence of  $N_1! N_2! \dots$ . This could only be accomplished, as it appeared to us, by not stopping at the numbers of the molecules in the combinatory computations, but by going down to the atoms. This is the only way of obtaining a solid common basis for the computation of the relative probability of different states of dissociation (variations of the numbers of molecules  $N_1, N_2, \dots, N_j$ ), viz. the phase-space of  $6(X+Y+Z)$  dimensions (§ 4).

The introduction into the combinatory calculation of this refinement, viz. the consideration of the atoms, confirms a result already attained by TETRODE (II): the factor which depends on the permutation of the atoms of the same kind

$$\frac{X! Y! Z!}{N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j}} \quad (\text{comp. e.g. (18)})$$

<sup>1)</sup> Comp. § 9.

<sup>2)</sup> Comp. § 8.

contains not only the expression  $N_1! N_2! \dots N_j!$ , but also the "symmetry-numbers" of the molecules  $\sigma_1, \sigma_2, \dots, \sigma_j$  (comp. e.g. (6) § 3). These, therefore, influence the dissociation-equilibrium (comp. § 8).

Accordingly the numerical value of the chemical constant of a molecule should depend not only on its mass and moment of inertia, but also on the "symmetry-number" of the molecule.

The question whether any of the cases of dissociation-equilibrium or evaporation which have been investigated numerically, speak in favour of or against this modification, we shall leave to others who are more familiar with the experimental side of the question.

### § 1. Fully excited and non-excited degrees of freedom.

The thermodynamic theory of the dissociation-equilibrium considers the molecules as having constant specific heats in the range in question, i.e. possible changes of the specific heats are left out of account in the calculations. If they were taken into account, the expressions for the entropy and energy of the gasmixture would not have the special form, which is essential for the definition of the "chemical constant" <sup>1)</sup>.

In a kinetical theory of the dissociation-equilibrium analogous assumptions or approximations must therefore be admitted, if a kinetic interpretation of the chemical constant is aimed at.

We shall make the following assumption in our calculations:

I. The translational motions of the molecules as also their rotations <sup>2)</sup> (with the exception of those referred to under II) will be considered entirely free from any limitations depending upon quanta <sup>3)</sup> ("fully excited degrees of freedom").

II. On the other hand the following motions will be assumed to be absent <sup>4)</sup> ("non-excited degrees of freedom):

a. The rotation of di-atomic molecules about the axis of symmetry and all rotation of mon-atomic molecules.

<sup>1)</sup> Compare the expressions for the energy and entropy in § 5 and in M. PLANCK, Thermodynamik §§ 237 — 241.

<sup>2)</sup> We therefore exclude for the special object of our theory these cases, in which a rotation happens to be in the intermediate state of being "partially excited", as these would introduce a variable specific heat (Comp. NERNST. Theor. u. exp. Grundlagen d. neuen Wärmesatzes, p. 136 bottom p. 137 top).

<sup>3)</sup> i.e. we approximate for these degrees of freedom all summations over successive quanta-steps by the corresponding  $\iint dq dp$ ; comp. "addit notes I".

<sup>4)</sup> i.e. for these degrees of freedom we confine ourselves in our calculation of the sum to the lowest quantum-stage.

b. Internal motions of the atoms in the molecule <sup>1)</sup>.

Note. In accordance with PLANCK's first quantum-theory we have provisionally assumed the lowest quantum-grade to be that of no quanta. N. BOHR's investigations (On the Quantum Theory of line-spectra (Part II), D. Kgl. Danske Vidensk. Selsk. Skrifter, Naturvidensk. og mathem. Afd., 8. Raekke N. 1, København, 1918) show, that probably in many cases the stage with the quantum-number 1 must be taken as the lowest possible. The corresponding modifications might easily be introduced in the theory (and also specially the contribution of the kinetic side by side with the potential energy).

### § 2. The phase-space of a molecule ( $\mu$ -space).

#### The $\mu$ -weight $\{u\}$ .

If a molecule consists of  $\xi, \eta, \zeta$  atoms of say three different chemical elements, its "phase" may be determined by means of  $6(\xi + \eta + \zeta)$  cartesian co-ordinates and momenta, i.e. by a point in a  $6(\xi + \eta + \zeta)$ -dimensional " $\mu$ -space" (phase-space of the molecule). In consequence of the assumptions IIa and IIb of the previous section, however, as long as the molecule is not dissociated, its phase-point (" $\mu$ -point") is confined to a portion of the  $\mu$ -space, namely to a  $2 \times 6$ ,  $2 \times 5$  or  $2 \times 3$ -dimensional region according as the molecule is poly-atomic, di-atomic or monatomic.

Considering for a moment the case of a poly-atomic molecule ( $\xi + \eta + \zeta$  atoms), this sub-space may be described as follows: owing to the rigidity of the molecule the  $3(\xi + \eta + \zeta)$  cartesian co-ordinates of the atoms may be expressed by 6 co-ordinates  $q_1, q_2, \dots, q_6$ , which fix the position and orientation of the molecule. Similarly the cartesian momenta are determined by the six momenta  $p_1, p_2, \dots, p_6$  corresponding to the  $q_1 \dots q_6$ . If in accordance with assumption I of the previous section we imagine the quantities  $q_1 \dots p_6$  to vary continuously within any arbitrary limits, the " $\mu$ -point" describes inside the  $6(\xi + \eta + \zeta)$  dimensional  $\mu$ -space a

<sup>1)</sup> This assumption underlies so far all derivations of the chemical constants for di- or monatomic molecules; for the theories never go beyond "rigid" molecules. This assumption seems more extra-ordinary in the present theory, in which the dissociation of the molecules is directly considered. Indeed, the molecules must first be gradually loosened, before they can dissociate. Still our method of calculating agrees with the following assumption: either every internal degree of freedom of the molecule is on its lowest quantum-grade, or the molecule is completely dissociated. This is of course only meant as an approximation in the calculation, similar to what is done in the thermodynamic derivations, where the variable contribution to the specific heat is neglected which would be due to a loosening of the molecules.

portion of a "surface" of 12 dimensions and the quantities  $q_1 \dots p_6$  play the part of curvilinear parameters on this surface.

We define<sup>1)</sup> the following expression as the " $\mu$ -weight"  $\{\mu\}$  of this region:

$$\{\mu\} = h^3(\xi + \eta + \zeta) - 6 \cdot \int \dots \int dq_1 \dots dq_6 dp_1 \dots dp_6, \quad (1)$$

where the integration is to be extended over the region in question.

In future applications (§ 4) the molecule will have to pass through the total volume  $V$  of a vessel and similarly through all possible orientations. Accordingly, integrating with respect to the co-ordinates  $q$ , we have

$$\{\mu\} = h^3(\xi + \eta + \zeta) - 6 \cdot V \cdot 4\pi \cdot 2\pi \cdot \int \dots \int dp_1 \dots dp_6, \quad (2)$$

The corresponding expressions for di- and mon-atomic molecules are as follows

$$\{\mu\} = h^3(\xi + \eta + \zeta) - 5 \cdot V \cdot 4\pi \cdot \int \dots \int dp_1 \dots dp_5, \quad (3)$$

$$\{\mu\} = h^3(\xi + \eta + \zeta) - 3 \cdot V \cdot \int \dots \int dp_1 \dots dp_3, \quad (4)$$

In (3)  $\xi + \eta + \zeta = 2$  and in (4)  $= 1$ , but we have left the power of  $h$  in its above form in order to obtain the formulae in our calculations later on as symmetrical as possible (§ 4).

### § 3. The constitution of the gas-mixture.

In a vessel of volume  $V$   $X$ ,  $Y$ ,  $Z$  atoms of say 3 different chemical elements (atomic masses  $m_\xi$ ,  $m_\eta$ ,  $m_\zeta$ ) may be introduced. These molecules can associate to molecules in a number of different ways. At a special moment let there be present  $j$  different kinds of molecules; a molecule of the kind  $i$  may consist of  $\xi_i$ ,  $\eta_i$ ,  $\zeta_i$  atoms and may possess the following mass, moments of inertia and potential energy respectively:

$$M_i; P_i, Q_i, R_i; \chi_i \quad (5)$$

The arbitrary constant contained in  $\chi_i$ , we shall fix by the following rule: we shall ascribe to the atoms a potential energy 0, when they are completely separated from each other;  $\chi_i$  is therefore a *negative* quantity, viz. equal to the negative work which the atoms give off, in uniting to form the molecule.

It may happen that, owing to the special distribution of similar atoms in a molecule, the latter possesses more than one completely

<sup>1)</sup> Comp. the illustration of this definition by means of a special simple case in addit. notes I.

equivalent rotational orientation; its number may be called the

$$\text{Symmetry-number } \sigma_i \quad (6)$$

of the molecule. (For instance for  $J_2$   $\sigma$  would be  $= 2$ , for  $CH_4$  (methane)  $\sigma = 12$ ).

Finally we shall call  $f_i$  the number of fully-excited degrees of freedom of the molecule; therefore

$$f_i = 3, 5, 6 \quad (7)$$

according as the molecule in question contains one, two or more atoms.

The numbers of the molecules of different kinds  $N_1, N_2, \dots, N_j$ , have to satisfy the equations

$$\sum_1^j N_i \xi_i = X, \quad \sum_1^j N_i \eta_i = Y, \quad \sum_1^j N_i \zeta_i = Z, \quad (8)$$

i.e. with varying degree of dissociation the numbers  $N_1 \dots N_j$  change, as also the total number of molecules

$$N = \sum_1^j N_i \quad (9)$$

but not the numbers of the atoms.

The total energy of the gas-mixture is given by the equation

$$E = K + \sum N_i \chi_i \quad (10)$$

where  $K$  stands for the total kinetic energy of all the molecules.

In the thermodynamic calculation of the dissociation-equilibrium (§ 6) we shall use "molar" instead of molecular quantities. Calling AVOGRADO's number

$$\mathfrak{N} \quad (11)$$

we have the following relations for the number of gram-molecules  $n_i$ , for the potential and kinetic energies per gram-molecule ( $b_i, C_i, T$ ) and for the specific heat ( $C_i$ ) respectively

$$n = \frac{N_i}{\mathfrak{N}}, \quad b_i = \mathfrak{N} \chi_i, \quad C_i T = \mathfrak{N} \cdot f_i \frac{rT}{2}, \quad C_i = \mathfrak{N} \frac{f_i}{2} r \quad (12)$$

where

$$r = \frac{R}{\mathfrak{N}} \quad (13)$$

hence

$$n_i R = N_i r \quad (14)$$

### § 4. The phase-space of the gas ( $\gamma$ -space). The $\gamma$ -weight $\{\gamma\}$ .

The most general "phase" of our system may be represented by the 6 ( $X + Y + Z$ ) cartesian co-ordinates and momenta of the

$X+Y+Z$ ) atoms, and therefore by a " $\gamma$ -point" in a  $6(X+Y+Z)$ -dimensional " $\gamma$ -space". To a given condition of dissociation ( $N_1, N_2, \dots, N_j$ ) of the gas-mixture, owing to the assumptions II (§ 1), a sub-space corresponds of  $2F$  dimensions, where

$$F = \sum_1^j N_i f_i; \quad \dots \quad (15)$$

$f_i$  as before being equal to 3, 5, or 6 according as the index  $i$  refers to molecules of one, two or more atoms (comp. eq (7)).

We must now consider more in detail the structure of this sub-space.

Consider an individual "phase" of the system (any point  $\gamma_1$  of the  $\gamma$ -space); the  $X+Y+Z$  atoms, which we shall provisionally think of as being individualized by numbers attached to them, are associated to  $N$  molecules, which we shall also suppose to be individually numbered. The total energy of the system then also possesses a definite value  $E$ . We now apply to the phase of the system changes of two types ( $A$ ) and ( $B$ )<sup>1)</sup>, which both leave the dissociation ( $N_1, N_2, \dots, N_j$ ) and the total energy unchanged.

**Changes of type [A].** Starting from the initial phase  $\gamma_1$  we make the molecules independently of each other, pass through the total volume  $V$ <sup>2)</sup> and all possible rotational orientations, and also make them assume successively all possible velocities of translation and rotation, which are in accordance with the original total energy.

While in this manner the  $\gamma$ -point starting from  $\gamma_1$  describes a region ( $A_1$ ) of the  $\gamma$  space, the  $\mu$ -points of the various individual molecules — each in its own  $\mu$ -space — describe the regions which were discussed in § 2. In the classical theory the " $\gamma$ -volume" is obtained in cases of this kind by taking the product of the corresponding " $\mu$ -volumes". Analogously we shall here define the  $\gamma$ -weight  $\{\gamma\}_{(A_1)}$  of the region just mentioned by the relation

$$\{\gamma\}_{(A_1)} = \prod_1^j \{\mu_i\}^{N_i} \quad \dots \quad (16)$$

where for  $\{\mu_i\}$  we have to take the expressions (4), (3), or (2) of § 2 according to whether  $i$  corresponds to a molecule of one, two or more atoms. The limits of the integrations over the momenta occurring in (16) are determined by the fact, that on account of

<sup>1)</sup> Comp. the somewhat similar discussion in P. and T. EHRENFEST, Math. Enc. Bd. IV. Art. 32, § 12 b.

<sup>2)</sup> The volume-correction which is due to the finite dimensions of the molecules is left out of account.

the prescribed total energy  $E$  and dissociation  $N_1, N_2, \dots, N_j$  the total kinetic energy

$$K = E - \sum N_i \chi_i \quad \dots \quad (17)$$

is also fixed (comp. (10) in § 3 and the computations further on in § 6.

**Changes of type [B].** By the mutual permutations of similar-atoms starting from a given  $\gamma$ -point new  $\gamma$ -points arise<sup>1)</sup>. In connection with the  $X/Y/Z!$  possible permutations of the individual atoms of the same kind a set of  $X/Y/Z!$  different  $\gamma$ -points in the  $\gamma$ -space will be seen to belong together and all these points give the gas the same  $E$  and the same dissociation ( $N_1, N_2, \dots$ ).

In order to reach the total  $\gamma$ -region which agrees with  $\gamma$ , in the quantities  $N$  and  $N_1, N_2, \dots, N_j$  we must combine the changes of the two types [A] and [B], in such a manner, however, that no portion of the region is counted twice.

It may be proved, that including the region ( $A_1$ ) altogether  $\Psi$  identical regions ( $A_1$ ), ( $A_2$ ),  $\dots$ ,  $A_\Psi$ , are obtained, in this manner, where

$$\Psi = \frac{X! Y! Z!}{N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j}} \quad \dots \quad (18)^2)$$

We shall give a few short indications as regards the proof of this statement. For this purpose we introduce the notion of "internal" permutation.

A permutation of the atoms will be called internal, if the result may also be obtained by translations and rotations of the rigid molecules.

**Simple instances.** 1. Two molecules of the same kind are made to exchange their position and orientation by translation and rotation. 2. A molecule of symmetry-number  $\sigma_i$  (comp. eq. (6)) is made to pass from one orientation to another equivalent one<sup>3)</sup>. 3. The same operations are carried out at the same time with a number of molecules.

An internal permutation carries the phase-point of the system say from  $\gamma'$  to  $\gamma''$ ; but here the following circumstance must be remembered:  $\gamma'$  is still inside

<sup>1)</sup> Since each individual atom has six co-ordinate axes of the  $\gamma$  space referring to it. Thus when two atoms of the system are exchanged, nearly all co-ordinates of the  $\gamma$  point remain unchanged, only 12 co-ordinates exchanging their values two by two.

<sup>2)</sup> BOLTZMANN in his well-known paper: "Ueber das Arbeitsquantum, welches bei chemischen Verbindungen gewonnen werden kann," [Wied. Ann. 22 (1884), p. 39. Wissenschaft, Abh. III, p. 71] has determined a similar combinatory quantity. But in comparing the quantity  $Z$  in his equation (3) with our , the difference should be noted which is referred to in the next note 3.

<sup>3)</sup> In a molecule of the constitution  $ABA$ , therefore, the permutation of the two  $A$  atoms is an internal one, in a molecule of the form  $AAB$  it is not. With BOLTZMANN the latter permutation would also have to be regarded as internal. This difference is due to the fact that with him the changes of type [A] form a wider class than with us and contain all exchanges of similar atoms inside the same molecule.

the phase-region ( $A'$ ), which is formed from  $\gamma'$  by the changes of type  $[A] A^1$  (that is what the word "internal" is meant to express).

Taking any phase-point  $\gamma$  as starting point, there are always

$$\Omega = N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j} \dots \quad (19)$$

internal permutations<sup>2)</sup> and all  $\gamma$ -points reached in that way lie inside one and the same  $A$ -region.

It will therefore be clear, that, if from the original phase  $\gamma_1$  by an operation  $[A]$  we produce the phase-region  $A_1$ , and if we then apply the  $X! Y! Z!$  operations of type  $[B]$  to every point of the region ( $A_1$ ), we do not obtain  $X! Y! Z!$  regions similar to ( $A_1$ ), but altogether only  $\Psi$  (eq. (18)), since the  $X! Y! Z!$  permutations of the atoms divide into  $\Psi$  groups of  $\Omega$  internal permutations each.

Combining (16) and (18) we obtain for the total  $\gamma$ -weight of all the phases, which belong to given values of  $V, E$  and  $N_1, N_2, \dots, N_j$  the expression:

$$\{\gamma\} = \frac{X! Y! Z!}{N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j}} \{u_1\}^{N_1} \{u_2\}^{N_2} \dots \{u_j\}^{N_j} \quad (20)$$

The expressions  $\{u_i\}$  contain the integrals with respect to the momenta of all possible motions of translation and rotation of the molecules which have still to be computed.

The total kinetic energy of the molecules is fixed by equation (17); the integration is to be taken over all the values of the momenta which are compatible with it. Calling these momenta for a moment  $p_1, p_2, \dots, p_F$ ,  $F$  being given by equation (15), we have the following relation between these quantities:

$$\frac{p_1^2}{2A_1} + \frac{p_2^2}{2A_2} + \dots + \frac{p_F^2}{2A_F} = K, \quad (21)$$

where  $A_1, A_2, \dots, A_F$  represent the various molecular masses or moments of inertia

$$M_1, P_1, Q_1, R_1; \dots; M_j, P_j, Q_j, R_j, \dots \quad (22)$$

according to the index (comp. (5) in § 3).

The multiple integrals with respect to the momenta give together the surface of the "ellipsoid" (21). Neglecting numbers of the order 1 as compared with the large number  $F$ , we may use for it the following approximation<sup>3)</sup>.

<sup>1)</sup> For the operations  $[A]$  include all possible translations and rotations of the molecules, hence also those, which may replace our internal permutations

<sup>2)</sup> The centres of gravity of the  $N_i$  molecules of type  $i$  may mutually exchange their  $N_i$  positions and moreover each of these molecules can choose among the  $\sigma_i$  equivalent orientations.

<sup>3)</sup> The volume  $I$  of a sphere of radius  $R$  in a space of  $F$  dimensions and its

$$\frac{1}{\Gamma\left(\frac{F}{2}\right)} (\sqrt{2K\pi})^F \sqrt{A_1 A_2 \dots A_F} \quad (23)$$

If we now include the remaining factor in the expressions  $\{u_i\}$  (comp. eq. (2), (3), (4) in § 2), having regard to the meaning of the quantities  $A_1, A_2, \dots, A_F$ , the expression (20) for  $\{\gamma\}$  becomes as follows:

$$\{\gamma\} = \frac{X! Y! Z!}{N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j}} \cdot h^{3(X+Y+Z)} V^N \cdot \frac{1}{\Gamma\left(\frac{F}{2}\right)} \cdot \left. \begin{aligned} & (\sqrt{2K\pi})^F \cdot \prod_{i=1}^j (a_i'' h^{-f_i})^{N_i}, \end{aligned} \right\} \quad (24)$$

where

$$\left. \begin{aligned} a_i'' &= 4\pi \cdot 2\pi \sqrt{M_i^3 P_i Q_i R_i} && \text{for poly-atomic molecules} \\ a_i'' &= 4\pi \sqrt{M_i^3 P_i^2} && \text{,, di- ,, ,,} \\ a_i'' &= \sqrt{M_i^3} && \text{,, mon- ,, ,,} \end{aligned} \right\} \quad (25)$$

the quantities  $f_i, F$  and  $N$  being defined by equations (7) § 3, (15) § 4 and (9) § 3.

### § 5. log $\{\gamma\}$ and the entropy for an arbitrary degree of dissociation ( $N_1, N_2, \dots, N_j$ ).

Using STIRLING's formula log  $\{\gamma\}$  assumes the following approximate form

$$\log \{\gamma\} = I + N \log V + \frac{F}{2} \log K + F \log \sqrt{2\pi} + \sum N_i (\log a_i'' - f_i \log h - \log \sigma_i) - \sum N_i (\log N_i - 1) - \frac{F}{2} \left( \log \frac{F}{2} - 1 \right) \quad (26)$$

or

surface  $O$  (i.e. the differential coefficient of  $I$  with respect to  $R$ ) are respectively [comp. say P. H. SCHOUTE, Mehr-dimensionale Geometrie, Bd. II, (Sammlung Schubert, Leipzig 1905); J. H. JEANS, The Dynamical Theory of Gases, § 46]:

$$J = \frac{1}{\Gamma\left(\frac{F}{2} + 1\right)} \sqrt{\pi^F R^F}, \quad O = \frac{1}{\Gamma\left(\frac{F}{2}\right)} \sqrt{\pi^F R^{F-1}}.$$

It is in accordance with the usual approximations of the kinetic theory ( $F$  very large as compared with 1), if we put log  $J$  and log  $O$  equal to each other, since for instance, if we use STIRLING's approximation, expressions are obtained for these quantities, which coincide completely, if we do not make any difference between  $F$  and  $F-1$ . We have used a similar approximation with regard to the ellipsoid.

$$\log \{\gamma\} = I + \sum N_i \left[ \log V + \frac{f_i}{2} \log K + \log \alpha_i' \right] - \sum N_i [\log N_i - 1] - \frac{F}{2} \left[ \log \frac{F}{2} - 1 \right], \quad (27)$$

where

$$I = \log [X! Y! Z! h^{3(X+Y+Z)}], \quad (28)^1$$

$$\log \alpha_i' = \log \alpha_i'' - f_i \log h - \log \sigma_i + f_i \log \sqrt{2\pi} \quad (29)$$

therefore

$$\alpha_i' = \frac{\alpha_i''}{\sigma_i} \left[ \frac{\sqrt{2\pi}}{h} \right]^{f_i} \quad (30)$$

If there are  $n_1, n_2, \dots, n_j$  gram-molecules of ideal gases of different kinds in the volume  $V$  at the temperature  $T$ , the entropy and energy of the mixture are given by the expressions:

$$S = \Omega + \sum n_i \left( R \log \frac{V}{n_i} + C_i \log T + \kappa_i \right) = \quad (31)$$

$$= \Omega + \sum n_i (R \log V + C_i \log T + \kappa_i) - R \sum n_i \log n_i$$

$$E = \sum n_i (C_i T + b_i) \quad (32)$$

$\Omega$  is a quantity which is independent of  $V, T$  and the numbers  $n_i$ , but may depend on the numbers of gram-atoms of the different kinds of atoms in the system (say  $x, y, z$ )<sup>2</sup>,  $b_i$  is the potential energy of a molecule of the kind  $i$  as compared with the condition of complete dissociation, which is taken as the zero of potential energy, and  $C_i$  the specific heat at constant volume.

## § 6. Comparison of the kinetic and the thermodynamic calculations of the dissociation-equilibrium. The resulting values of the chemical constants.

We now introduce the following axiom: *With given numbers of atoms  $X, Y, Z$ , volume  $V$  and total energy  $E$  the dissociation-equilibrium is characterized by these values of the numbers of molecules  $N_1, N_2, \dots, N_j$ , for which  $\log \{\gamma\}$  is a maximum.*

<sup>1</sup>) It may be noted, that, when all the numbers of atoms and molecules, the volume  $V$  and the total kinetic energy are doubled, the numerical values of  $\log \frac{V}{N} \log \frac{K}{F}$  in the expression for  $\{\gamma\}$  remain the same and the value of the sums is therefore also doubled, whereas  $I$  increases to more than twice its value on account of  $X! Y! Z!$  Comp. § 9.

<sup>2</sup>) In the theory as usually given (comp. say M. PLANCK, Thermo-dynamik 4 Aufl. § 237)  $\Omega$  is left out. Incomparing the entropy with the "logarithm of the probability" this becomes the source of great obscurity (comp. § 9).

Let

$$\delta N_i = v_i \delta Q \quad \text{or} \quad \delta n_i = v_i \delta q \quad (33)$$

represent any possible<sup>1</sup>) chemical reaction in the system, i.e. a reaction which is compatible with the given numbers of atoms  $X, Y, Z$ ;  $v_1, v_2, \dots, v_j$  are certain positive or negative whole numbers, which give the numbers of the molecules which are formed or disappear in the elementary reaction<sup>2</sup>).

The kinetic and thermodynamic deductions of the dissociation-equilibrium may now be given side by side:

(kinetic)

$$\delta \log \{\gamma\} = 0 \quad (34)$$

$$\delta V = 0, \quad \delta N_i = v_i \delta Q \quad (35)$$

$$\delta E = \delta (K + \sum N_i \chi_i) = 0 \quad (36)$$

(thermodynamic)

$$\delta S = 0 \quad (34')$$

$$\delta V = 0, \quad \delta n_i = v_i \delta q \quad (35')$$

$$\delta E = \delta \sum n_i (C_i T + b_i) = 0 \quad (36')$$

Substitution of the expressions (26), (31) § 5 for  $\log \{\gamma\}$  and  $S$  and further development of the maximum-problems lead to

$$\sum v_i \log N_i = (\log V) \sum v_i + \sum v_i \log \alpha_i' \quad \sum v_i \log n_i = (\log V) \sum v_i + \frac{1}{R} \sum v_i (\kappa_i - C_i - R)$$

$$-\frac{F}{2K} \sum v_i \chi_i + \left( \log \frac{2K}{F} \right) \sum v_i \frac{f_i}{2} \quad (37) \quad -\frac{1}{RT} \sum v_i b_i + (\log T) \cdot \frac{1}{R} \sum v_i C_i \quad (37')$$

In (37') we shall express  $V$  in the pressure  $p$  of the gas-mixture by means of the equation

$$pV = RT \sum n_i \quad (38)$$

Further in (37) we shall put

$$K = F \cdot \frac{rT}{2}, \quad pV = rT \sum N_i \quad (39)^3$$

<sup>1</sup>) In general more than one reaction is possible between the molecules of the mixture each characterized by a special set of values of the numbers  $v_1, v_2, \dots, v_j$ .

In order to establish the dissociation-equilibrium completely, and to obtain the necessary number of equations between the equilibrium concentrations, all the different reactions [variations] have to be taken in succession [Comp. M. PLANCK, Thermodynamik § 247].

<sup>2</sup>) M. PLANCK, Thermodynamik § 244.

<sup>3</sup>) Properly speaking these two equations must be taken as giving definitions of the quantities  $p$  and  $T$ : the phase-region in the " $\gamma$ -space" which corresponds to the prescribed values of  $V, E$  and  $N_1, N_2, \dots, N_j$  contains beside MAXWELL-BOLTZMANN states, others which deviate strongly from those and for which therefore in themselves the conceptions of "pressure and temperature of the gas" have no meaning at all. However, the very great majority of the phase-points of this region are of the MAXWELL-BOLTZMANN-type of distribution or closely resembling ones, and for those the relations (39) hold with the ordinary meaning of the quantities  $p$  and  $T$ .

and instead of the numbers  $N_i$  ( $n_i$ ) we shall introduce the "concentrations"

$$c_i = \frac{N_i}{N_1 + N_2 + \dots + N_j} = \frac{n_i}{n_1 + n_2 + \dots + n_j} \quad (40)$$

This gives

$$\left. \begin{aligned} \sum v_i \log c_i &= -(\log p) \sum v_i \\ + \sum v_i \log a_i' - \frac{1}{rT} \sum v_i \chi_i \\ + (\log rT) \sum v_i \left( \frac{f_i}{2} + 1 \right) \end{aligned} \right\} (41) \quad \left\{ \begin{aligned} \sum v_i \log c_i &= -(\log p) \sum v_i \\ + \frac{1}{R} \sum v_i (\chi_i + R \log R - C_i - R) \\ - \frac{1}{RT} \sum v_i b_i + (\log T) \frac{1}{R} \sum v_i (C_i + R) \end{aligned} \right\} (41')$$

On comparing (41') with (41) and in view of (12) to (14) § 3, we obtain for the "chemical constants"

$$a_i = \chi_i + R \log R - C_i - R \quad (42)$$

following equation

$$\frac{1}{R} \sum v_i a_i = \sum v_i \left\{ \log a_i' + \left( \frac{f_i}{2} + 1 \right) \log r \right\} \quad (43)^1$$

or

$$\frac{1}{R} \sum v_i a_i = \sum v_i \alpha_i \quad (44)$$

where

$$\alpha_i = \log a_i' + \left( \frac{f_i}{2} + 1 \right) \log r \quad (45)$$

hence by (30) and (25)

$$\left. \begin{aligned} \alpha_i &= \log \left[ \frac{4\pi \cdot 2\pi}{\sigma_i} \sqrt{M_i^3 P_i Q_i R_i} \left( \frac{\sqrt{2\pi r}}{h} \right)^6 r \right] \\ \alpha_i &= \log \left[ \frac{4\pi}{\sigma_i} \sqrt{M_i^3 P_i^2} \left( \frac{\sqrt{2\pi r}}{h} \right)^6 r \right] \\ \alpha &= \log \left[ \sqrt{M_i^3} \left( \frac{\sqrt{2\pi r}}{h} \right)^3 r \right] \end{aligned} \right\} \quad (46)$$

for poly-atomic, di-atomic and mon-atomic molecules respectively.

### § 7. Remarks on additional contributions of the atoms to the chemical constant of the molecule which remain indeterminate.

Molecules of the kind as considered here may undergo a large number of different chemical reactions, each characterized by a

<sup>1)</sup> The term with  $\log r$  is derived from  $\log r T$  in equation (41).

different set of numbers  $v_1, v_2, \dots, v_j$ <sup>1)</sup>. Each time we obtain a corresponding equation for the chemical constants of these molecules

$$\frac{1}{R} \sum v_i a_i = \sum v_i \alpha_i \quad (47)$$

It will be seen, however, that the quantities  $a_i$  are not completely determined by these relations. For every chemical reaction which is possible the corresponding numbers  $v_1, v_2, \dots, v_j$  have to satisfy the relations:

$$\sum v_i \xi_i = 0, \quad \sum v_i \eta_i = 0, \quad \sum v_i \zeta_i = 0 \quad (48)$$

Therefore: for every chemical reaction the corresponding equation (47) will be satisfied by putting

$$\frac{a_i}{R} = \alpha_i + \xi_i u + \eta_i v + \zeta_i w \quad (49)$$

with completely arbitrary values of the numbers  $u, v, w$ , that is to say: the chemical constant of a molecule is completely determined but for certain additive constants, which the several atoms bring with them into the molecule and carry away, with them in chemical reactions<sup>2)</sup>. In the determination of the dissociation-equilibrium these arbitrary constants drop out, since in that case, as we have seen, we only deal with  $\sum v_i a_i$ .

### § 8. The influence on the dissociation-equilibrium of the "symmetry-numbers" $\sigma_i$ of the molecules.

The part played by the symmetry-numbers in the dissociation-equilibrium may be elucidated by a typical example.

Let the chemical elements  $A$  and  $B$  be able to form the following kinds of molecules

<sup>1)</sup> Comp. not 1 in § 6.

<sup>2)</sup> Obviously the entropy-constants  $K_i$  have exactly the same degree of determinateness and indeterminateness. The same indeterminateness remains, when the chemical constants are derived by means of the vapour-pressure equation (comp. "additional notes" III), and also, if following BOLTZMANN one would make use of the equation

$$S^* - S = r [\log \{\gamma^*\} - \log \{\gamma\}]$$

For also the numbers of molecules  $N_1^*, N_2^*, \dots, N_i^*$  and  $N_1, N_2, \dots, N_i$  occurring in this equation have again to satisfy relations of the form.

$$N_i^* - N_i = v_i \Delta Q \quad (\text{comp. (33) § 6}).$$

in order that the change may be compatible with the number of atoms  $X, Y, Z$ , present. We do not think that BOLTZMANN's equation can be replaced by an assumption of the form:

$$S = r \log \{\gamma\}$$

on grounds which will be set forth in § 9.

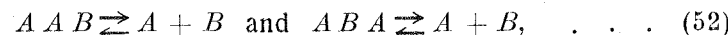


$$A, \quad B, \quad AAB, \quad ABA, \quad \dots \quad (50)$$

the concentrations, moments of inertia, potential-energies and symmetry-numbers being as follows

$$\begin{array}{cccc} c_1 & c_2 & c_3 & c_4 \\ 0 & 0 & P_3 & P_4 \\ 0 & 0 & \chi_3 & \chi_4 \\ 1 & 1 & 1 & 2 \end{array} \left. \vphantom{\begin{array}{cccc} c_1 & c_2 & c_3 & c_4 \\ 0 & 0 & P_3 & P_4 \\ 0 & 0 & \chi_3 & \chi_4 \\ 1 & 1 & 1 & 2 \end{array}} \right\} \dots \quad (51)$$

The two reactions



give dissociation-equations of the following form

$$\frac{c_3}{c_1^2 c_2} = G P_3 e^{-\frac{\chi_3}{rT}} \quad \frac{c_4}{c_1^2 c_2} = \frac{1}{2} G P_4 e^{-\frac{\chi_4}{rT}} \quad \dots \quad (53)$$

since all the quantities are the same in the two cases with the exception of  $P_3 \neq P_4$ ,  $\chi_3 \neq \chi_4$  and  $\sigma_3 \neq \sigma_4$ . ( $G$  is supposed to contain the quantities which are common to the two cases).

If therefore for instance approximately  $P_3 = P_4$  and  $\chi_3 = \chi_4$ , we should have

$$\frac{c_3}{c_4} = 2, \quad \dots \quad (54)$$

or the concentration of the unsymmetrical molecules is about twice that of the symmetrical molecules.

### § 9. Critical remarks on some allied deductions of the chemical constants.

Whereas BOLTZMANN in his theory uses the equation

$$S_2 - S_1 = r \log \frac{W_2}{W_1} \quad \dots \quad (59)$$

throughout, PLANCK and many others following him replace it by the relation

$$S = r \log W. \quad \dots \quad (60)$$

It was obviously NERNST's theorem that first started this preference of (60) over (59), as on the one hand it provided a natural zero-condition for the calculation of  $S$  and on the other a natural common unit for the estimation of  $W$ , viz. any condition of the system at  $T=0$ .

In the majority of calculations of the chemical constants a special obscurity remains as to the way in which the "thermodynamic probability" of a gas depends on the number of molecules.

We shall try to explain in a few words, how this obscurity is

connected with the use of equation (60)<sup>1)</sup>: it is generally assumed as self-evident, that the entropy of a gas is to be taken twice as large, if the number of molecules and the volume are both doubled. Now it is certainly true, that the *increase* of the entropy in a given process in a gas of twice the number of molecules is twice as large as the corresponding increase in the original gas. But what is the meaning of taking the *entropy itself* twice as large and *thereby settling the entropy-difference between the doubled and the original gas*? By what reversible process is the double quantity of gas to be generated from the original quantity? Without that the entropy-

difference  $\int \frac{dQ}{T}$  cannot be clearly defined. On account of equation (60) one is then confronted with the difficult problem of choosing the definitions in such a manner that the "thermodynamic probability, of the double quantity of a gas is equal to the square of the "thermodynamic probability of the single quantity."<sup>2)</sup>

In order to remove this obscurity it is necessary to return to BOLTZMANN's equation (59) and to apply it to a reversible process in which the numbers of the molecules change.

We shall now go a little more fully into the relation in which our theory stands to others which are closely allied to it.<sup>3)</sup> Special interest attaches to the manner, in which in the various theories the terms  $N_i \log N$  are produced. In our theory they originate in the combinatory factor:

$$\Psi = \frac{X! Y! Z!}{N_1! N_2! \dots N_j! \sigma_1^{N_1} \sigma_2^{N_2} \dots \sigma_j^{N_j}} \quad \dots \quad (61)$$

If instead of a *gas-mixture*, as in our case, a *single gas* of monatomic<sup>4)</sup> molecules is considered, this factor  $\Psi$  reduces to

$$\Psi = \frac{X!}{X!} = 1 \quad \dots \quad (62)$$

<sup>1)</sup> O. STERN, quite recently remarks: "The difficulty in this deduction lies in the introduction of the quantity  $N$ , which is done in a very arbitrary manner". (Z. f. Elektroch. 25 (1919), p. 79 at the top on the right).

<sup>2)</sup> Comp. our remarks in notes (1) and (2) § 5 with regard to the quantities  $\Omega$  and  $I$ , which in our theory occur in the entropy and in  $\log \{\gamma\}$ .

<sup>3)</sup> As regards the theories of LENZ (Vorträge der Wolfskehl-Stiftung 1913 in Göttingen, Teubner 1914, p. 125) and KEESOM (Phys. Ztschr. 14 (1913), p. 212), who apply DEBIJE's method for solids to gases, we may refer to papers by H. A. LORENTZ (Versl. Kon. Ak. v. Wet. Amst. 23 (1) (1914) p. 515, § 6 — Proceedings Amsterdam 19, (1917) p. 737) and O. STERN (Ztschr. für Elektrochemie, 25 (1919), 79 section C towards the end), where these theories are discussed.

The same holds for a gas with more atoms in the molecule, if  $\sigma = 1$ .



The question, therefore, is how those authors, who confined themselves to the consideration of a single gas, were able to obtain a "thermodynamic probability", the logarithm of which yields an admissible entropy-equation, in other words, how do they manage, that the entropy does not contain a term of the form

$$R \log V \quad \text{but} \quad R \log \frac{V}{n_i} \dots \dots \dots (63)$$

1. O. SACKUR<sup>1)</sup> reaches the desired result by a special method of "quanticising" the motion of the gas-molecules: we may express it by saying, that he quanticises, as if each molecule were separately contained in a cell of volume  $\frac{V}{N_i}$ .

2. M. PLANCK<sup>2)</sup> similarly only obtains the term (63) in the correct form by dividing the phase-space of the molecules ( $\mu$ -space) into an increasing number of "elementary" portions, as the number of molecules is larger ( $G = Ng$ ). The justification of this procedure and the fixing of  $g$  he considers to be open problems<sup>3)</sup>.

3. H. TETRODE [1<sup>st</sup> Paper]<sup>4)</sup> attaches a factor  $\frac{1}{N_i!}$  to the expression for the "thermodynamic probability", in order that its logarithm may show the law of dependence on  $N$  which is needed in the entropy. But he does not justify this procedure on combinatory grounds<sup>5)</sup>.

<sup>1)</sup> O. SACKUR, Annalen d. Physik, **40**, p. 76 (1913).

<sup>2)</sup> M. PLANCK, Wärmestrahlung, 2 Aufl. § 126, § 133.

<sup>3)</sup> M. PLANCK, Theorie der Wärmestrahlung, 2 Aufl. p. 131; also M. PLANCK Vorträge der Wolfskehl-Stiftung 1913 in Göttingen (Teubner 1914) p. 7; Phys. Zeitschr. **14** (1913), p. 258. In a later paper (Sitzber. d. Preuss. Akad., Berlin, 1916, p. 653—667) PLANCK once more returns to the problem; here he takes into account the permutability of the molecules, but he does not himself look upon this discussion as giving a combinatory justification of his assumption as to the "elementary regions".

<sup>4)</sup> H. TETRODE, Ann. d. Phys. **38**, p. 434 (1912).

<sup>5)</sup> H. A. LORENTZ, (Versl. Kon. Ak. v. Wetensch. Amsterdam **23** (1) (1914, p. 515, — Proceedings Amsterdam **19**. (1917), p. 737), at the end of section 5 draws attention to this. H. TETRODE in his 2nd paper, where he gives the new deduction by means of the process of evaporation, à propos of LORENTZ's remark in an appendix once more returns to his previous deduction. But again he explains — only more fully — that the division by the factor  $N_i!$  is required, in order that the entropy may show the desired law of dependence on  $N_i$ . P. SCHERRER, Gött. Nachr. 1916, p. 154 in following the same procedure simply refers to J. W. GIBBS, Statistical Mechanics without any further comment.

## ADDITIONAL NOTES.

### I. Elucidation of the choice of the $\mu$ - and $\gamma$ -weight: $\{\mu\}$ and $\{\gamma\}$ . (Note to sections 2, 4).

The definitions of  $\{\mu\}$  and  $\{\gamma\}$  may be elucidated by a simple example. Consider first a PLANCK-resonator. According to the theory of quanta its phase  $q, p$  must lie either at  $q = p = 0$  or on one of PLANCK's ellipses  $\varepsilon = h\nu, 2h\nu, \dots$ . Now two consecutive ellipses are known to enclose a ring whose area is

$$\iint dq dp = h \dots \dots \dots (64)$$

The classical theory would admit all the points of the plane and ascribe to any portion of it a "weight" equal to its area  $\iint dq dp$ .

It therefore seems natural in the statistical calculations of the quantum-theory to ascribe a weight  $h$  to each of the ellipses, in particular also to the point  $q = p = 0$ . Since in all statistical calculations it is ultimately only the relative weight that matters, the essential thing about this assumption is, that the same weight is ascribed to all the ellipses, which moreover is independent of the nature of the resonator (say its  $\nu$ ).<sup>1)</sup>

The choice of  $h$  itself as the weight in question has the following advantage in connection with (64): if in the  $q, p$  plane any portion is considered which contains a large number of ellipses, the total weight of all the ellipses inside this region coincides with its area owing to (64).<sup>2)</sup>

Let us next consider a material point elastically connected to a given position of equilibrium, say anisotropically. Its principal vibrations may be parallel to the co-ordinates  $q_1, q_2, q_3$ , its frequencies being supposed very different

$$\nu_1 \ll \nu_2 \ll \nu_3 \dots \dots \dots (65)$$

<sup>1)</sup> The choice of the weight must be subjected to certain limitations, in order that the statistical theory may not get into contradiction with the II<sup>nd</sup> law of thermodynamics. Comp. P. EHRENFEST, Phys. Zeitschr. **15** (1914), p. 657; Ann. de Phys. **51** (1916), p. 340, § 8 — Versl. Kon. Ak. v. Wetensch. Amsterdam **25** (1) (1916), p. 423, § 8 — Proceedings Amsterdam **19** (2 part.) (1917), p. 576, § 8. — The above choice is in accordance with the limiting conditions in question.

<sup>2)</sup> Hence for sufficiently high temperatures we shall have approximately

$$\sum_0^\infty h e^{-\frac{\varepsilon_n}{rT}} = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dq e^{-\frac{\varepsilon}{rT}}.$$

The  $\mu$ -point of the system in the six-dimensional  $\mu$ -space  $(q_1, \dots, p_3)$  is then limited by the quantum-hypothesis in the following manner: its projection on the plane  $q_1, p_1$  must fall on one of the PLANCK-ellipses; similarly the projections on the planes  $q_2, p_2$  and  $q_3, p_3$ . If the total energy  $E$  is contained between 0 and a moderate value, we see by (65) that  $q_1, p_1$  may still fall on a large number of different ellipses; (since for this degree of freedom the energy-stages  $\varepsilon_1 = 0, h\nu_1, 2h\nu_1, \dots$  follow each other closely),  $q_2, p_2$  on the other hand only on a few ellipses, whereas  $q_3, p_3$  is possibly completely confined to the position  $q_3 = p_3 = 0$ .

If the limitation which is due to the quantum-hypothesis did not exist, the "weight" to be given to a given region in the  $\mu$ -space would according to BOLZMANN simply be its volume

$$\int \dots \int dq_2 \dots dp_3 \dots \dots \dots (66)$$

To each region, whose three projections are three PLANCK-ellipses, we assign the weight

$$h^3 \dots \dots \dots (67)$$

The joint weight of all phases which the  $\mu$ -point can assume, when the energy is subjected to an upper limit, will then be

$$\{\gamma\} = \sum_{\tau_1} \sum_{\tau_2} \sum_{\tau_3} h^3, \dots \dots \dots (68)$$

where the summations are to be extended over all the quantum-numbers which the first, second and third degree of freedom can assume. With a moderate upper limit for the energy  $\tau_1$  as we saw would be able to rise to high values, and the corresponding sum may accordingly be replaced by  $\iint dq_1 dp_1$ ;  $\tau_3$  on the other hand would be confined to zero and the corresponding sum reduce to the first member  $h$ . Hence

$$\{\gamma\} = \iint dq_1 dp_1 \cdot (\sum_{\tau_2} h) \cdot h; \dots \dots \dots (69)$$

According as the upper limit for the energy is made to rise or fall (i.e. the second degree of freedom is made to pass from the state of being half-excited to that of full excitation or non-excitation) (69) changes into

$$\{\gamma\} = \int \dots \int dq_1 dp_1 dq_2 dp_2 \cdot h = h^{3-2} \int \dots \int dq_1 \dots dp_2 \dots \dots \dots (70)$$

or

$$\{\gamma\} = \int \int dq_1 dp_1 \cdot h \cdot h = h^{3-1} \int \int dq_1 dp_1 \dots \dots \dots (71)$$

Evidently of all the original degrees of freedom only those remain in the power of  $h$ , which are not excited. The other factors  $h$  are as it were absorbed by the integrals.

## II. Calculation relating to § 6.

We found [eq. (27) § 5].

$$\log \{\gamma\} = I + \sum N_i \left[ \log V + \frac{f_i}{2} \log K + \log \alpha_i' \right] - \sum N_i (\log N_i - 1) - \frac{F}{2} \left[ \log \frac{F}{2} - 1 \right] \dots \dots \dots (72)$$

If this expression is varied, having regard to

$$\delta V = 0, \quad \delta N_i = v_i \delta Q, \quad \delta E = \delta K + \sum \chi_i \delta N_i = 0, \dots \dots \dots (73)$$

the last equation provided with a multiplier  $(-\theta)$  being added to the variation of  $\log \{\gamma\}$ , we obtain:

$$0 = \delta \log \{\gamma\} - \theta \delta E = \frac{\delta K}{K} \sum N_i \frac{f_i}{2} + \sum \delta N_i \left[ \log V + \frac{f_i}{2} \log K + \log \alpha_i' \right] - \delta Q \sum v_i \log N_i - \left( \log \frac{F}{2} \right) \delta Q \cdot \sum v_i \cdot \frac{f_i}{2} - \delta K - \delta Q \cdot \sum v_i \chi_i \dots \dots \dots (74)$$

The condition that the co-efficient of  $\delta K$  disappears, gives:

$$\theta = \frac{F}{2K}; \dots \dots \dots (75)$$

that for  $\delta Q$

$$\sum v_i \log N_i = \sum v_i \left[ \log V + \frac{f_i}{2} \log K + \log \alpha_i' - \frac{f_i}{2} \log \frac{F}{2} - \theta \chi_i \right], \dots \dots \dots (76)$$

or by (75) after a small reduction

$$\sum v_i \log N_i = \sum v_i \left[ \log V + \frac{f_i}{2} \log \frac{2K}{F} + \log \alpha_i' - \frac{F}{2K} \chi_i \right], \dots \dots \dots (77)$$

q. e. d.

The thermodynamical calculation is entirely similar.

## III. Deduction of the vapour-pressure formula for very low temperatures.

The equilibrium of evaporation at very low temperatures may be deduced by the same means as that of dissociation. If again there are  $X, Y, Z$  atoms in a volume  $V$ , which, however, may now be associated in  $N$  poly-atomic molecules of one kind, of composition  $\xi, \eta, \zeta$ , mass and moment of inertia  $M, P, Q, R$  and symmetry-number  $\sigma$ ,  $N$  of these may be present in the form of vapour

(potential energy =  $N\chi$ ) and  $N'$  condensed to a crystal (potential energy =  $N'\chi'$ ).

For the vapour molecules we make again the assumptions I and II of section I. As regards the atoms in the crystal our assumption will be, that

III. In the calculations the motions of the atoms in the crystal are to be ignored <sup>1)</sup>.

The  $\{\gamma\}$  weight of the condition  $(N, N')$  is then found to be

$$\{\gamma\} = \frac{X!Y!Z!}{N!6} h^{3(X+Y+Z)-6NVN} \cdot \frac{1}{I(3N)} \cdot (V\sqrt{2K\pi})^{6N} \cdot (4\pi \cdot 2\pi \sqrt{M^3PQR}), \quad (78)$$

where

$$K = E - \Sigma (N\chi + N'\chi') \quad (79)$$

On the other hand the entropy and energy of the system are given by the equations

$$S = \bar{\Omega} + n \left\{ C \log T + R \log \frac{V}{n} + \kappa \right\} + n's'_0 \quad (80)^2$$

$$E = n \{ CT + b \} + n' b' \quad (81)$$

The condition of equilibrium is given by

$$\delta \log \{\gamma\} = 0 \quad (82)$$

with the conditions

$$\delta V = 0, \quad \delta E = 0, \quad \delta N + \delta N' = 0, \quad (83)$$

This yields an equation for  $N'$  as a function of  $V$  and  $K$ ; substituting

$$K = 3N \cdot rT \quad V = N \cdot \frac{rT}{p} \quad (84)$$

we find

$$\log p = -\frac{\chi - \chi'}{rT} + 4 \log T + \alpha \quad (85)$$

where  $\alpha$  has the same meaning as  $\alpha$ , in (46). The corresponding thermodynamic calculation gives

<sup>1)</sup> This assumption is again meant not as a physical hypothesis, but as an approximation in the calculations. (Comp. note 5, § 1). It comes to neglecting  $\int_0^T \frac{C'}{T} dT$  for the solid (comp. M. PLANCK, Thermodynamik, 4 Aufl., § 288, comp. (270) in the thermodynamic deduction of the vapour-pressure formula for low temperatures.

<sup>2)</sup> Properly speaking the last term should be  $n's'$ ; but with PLANCK we neglect  $\int_0^T \frac{C'}{T} dT$ .

$$\log p = -\frac{b-b'}{RT} + \frac{C_p}{R} \log T + \frac{a-s'_0}{R}, \quad (86)$$

where for shortness we have put

$$\kappa - C_p + R \log R = a \quad (87)$$

The comparison of (85) and (86) produces the equation

$$\frac{a}{R} = \alpha + \frac{s'_0}{R} \quad (88)$$

or for molecules of different kinds

$$\frac{a_i}{R} = \alpha_i + \frac{s'_{0i}}{R} \quad (89)$$

NERNST's theorem requires for every chemical reaction  $v_1, v_2 \dots v_j$ , which is possible the relation

$$\Sigma v_i s'_{0i} = 0, \quad (90)$$

which is satisfied by

$$s'_{0i} = \xi_i u' + \eta_i v' + \zeta_i w' \quad (91)$$

where  $u'v'w'$  remain perfectly arbitrary.

Evidently the chemical constant as calculated by means of the vapour-pressure formula and NERNST's theorem contains similar indeterminate contributions by the atoms as in our deduction from the dissociation-equilibrium.