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

I am occupied with the application of the above described degra-
dation method to other sugars such as pentoses.

The more fully detailed communication will be given elsewhere.

I have. to tender my thanks to Prof. BLANKSMA for kindly giving
me the opportunity to work in the organic-chemical laboratory of
the University.

Leiden, February 1915. Organic-Chemical
Laboratory of the University.

Physics. — "Theoretical determination of the entropy constant of
gases and liquids." By H. TETRODE. (Communicated by Prof.
H. A. LORENTZ).

(Communicated in the meeting of Febr. 27, 1915).

§ 1. Introduction and survey.

If the entropy of an ideal gas per gramme molecule for the
temperature T and the pressure p is given by:

$$S = C_p \log T - R \log p + a + C_p, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which R is the gas constant and C_p denotes the heat capacity
under constant pressure assumed as invariable for the range of
temperature considered, then a is a constant remaining undetermined
in classical thermodynamics. This value has, however, a definite
value according to NERNST's heat theorem, when namely the entropy
is defined so that it becomes zero for $T = 0$ for the condensed gas,
i. e. for a chemically homogeneous solid or liquid substance, which
we shall always tacitly supposed to be done in what follows. Then
we can determine a from measurements of the vapour tension, when
we also know the course of the specific heat of the solid (or liquid)
substance also at the lowest temperatures[1].

On the ground of a general definition of the thermodynamic
probability in connection with the hypothesis of quanta I have
derived the value of a for different cases in a previous paper[2], in
which, however, at first undetermined universal values z, z_1, and z_2
still occurred, which I supposed to be $= 1$, while others thought
they had to assign a different value at least to z[3].

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[1] The quantity $C = \dfrac{a}{R} \log_{10} e$ is generally called the chemical constant of the gas.

[2] H. TETRODE, Ann. d. Phys. 38, 434 and 39, 255 (1912). .

[3] O. SACKUR, Ann. d. Phys. 40, 67 (1913).

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In what follows we shall now determine the entropy constant a through the direct calculation of the vapour tension according to classical statistical mechanics, hence for higher temperatures, while we shall of course have to know again the thermodynamic behaviour of the condensed phase for very low temperatures; the latter is, however, the case at present for solid substances on certain simplifying suppositions. In this way we shall not only get a direct confirmation of the formulae given before (with $z = z_1 = z_2 = 1$), but shall also be able to establish the general [1]) definition of probability (of course for higher temperatures) for gases and liquids, which must be applied for the entropy determination.

As a further elucidation of the results found for multi-atomic molecules we shall also insert a few hypothetical considerations on the forces acting in the chemical binding between the atoms.

The main point in our considerations is the discussion of the exchangeability of similar atoms and molecules and of the influence of this on the thermodynamic probability and the entropy.

§ 2. Suppositions on the properties of the solid substance.

As we shall have to know the entropy of the solid substance, and as we can only give this at present theoretically when the motions of the molecules and atoms consist of sine vibrations, hence when the potential energy is a quadratic function of their coordinates, we shall have to suppose this of our solid substance. We may do this when the amplitude of the molecular motion is slight on the whole, when the molecules therefore depart little from their position of equilibrium. This, however, does not exclude that some rare molecules possessing an exceptionally great energy pass over larger distances, for which the general assumption does not hold, that they even now and then slip through between the surrounding molecules, or can detach themselves from the molecule complex, and pass into the vapour state, provided their number be so small at the considered temperature that it may be neglected for the calculation of averages.

Our assumption implies that the volume of the solid substance is independent of pressure [2]) and temperature. The specific heat at constant pressure then becomes equal to that at constant volume, whereas in reality it is as much as from 4 to 12 % greater at the temperatures that are to be considered. Though our theoretical

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[1]) Cf. however, the conclusion of § 3.

[2]) Large pressures do not occur in our problem.

substance in this respect differs more or less from a real substance, yet this will not cause a very great error in the final result, seeing that the difference is comparatively small. It seems even probable to me that when we consider a system approaching reality still more closely whose vibrations are not purely sine shaped, an accurate knowledge of the thermodynamic behaviour of it at low temperatures would lead us to no other final result for the entropy constant of the gas, that therefore the expressions to be found possess universal validity.

The thermal energy of a solid substance as assumed by us according to a formula which has been accepted and confirmed of late years, is given by :

$$U = \Sigma \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1} + const.,$$

in which h and k are the constants of PLANCK, while the summation is to be extended over all the degrees of freedom of the system, each of a frequency ν_i. The entropy is then given by :

$$S = \int \frac{1}{T} \frac{dU}{dT} dT = \Sigma \frac{h\nu_i}{T} \cdot \frac{1}{e^{\frac{h\nu_i}{kT}} - 1} - k \Sigma \log\left(1 - e^{-\frac{h\nu_i}{kT}}\right), \quad . \quad (2)$$

which for the higher temperatures, with which we shall be exclusively occupied in what follows, passes into :

$$S = k\Sigma \left(1 - \log \frac{h\nu_i}{kT}\right) = k\lambda \left(1 - \overline{\log \frac{h\nu}{kT}}\right), \quad . \quad . \quad . \quad (3)$$

in which λ is the number of degrees of freedom, and the line expresses the mean value.

§ 3. *Calculation of the vapour pressure of a monatomic solid substance and of the entropy constant of the gas* [1]).

Let us now consider a gramme molecule of a monatomic substance consisting of N molecules. inclosed within the invariable volume V and in temperature equilibrium with its surroundings. This system may then be considered as part of a much larger one of the same temperature. If $q_1, \ldots, q_{3N}$ are the coordinates of the molecules,

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[1]) A similar calculation with the correct final result has already been published by O. STERN (Phys. Zeitschr. 14, 629 (1913)), however with an imaginary solid substance, which perhaps departs somewhat too much from reality. Nor is in this way the occurrence of $N!$ in the general formula (see below), caused by the exchangeability of the molecules, made clear.

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$p_1, \ldots, p_{3N}$ the corresponding quantities of motion, then the proba-bility that at an arbitrarily chosen moment the system will be in a state for which the coordinates will successively have values lying between q_1 and $q_1 + dq_1$, q_2 and $q_2 + dq_2$ etc., and the quantities of motion between p_1 and $p_1 + dp_1$, etc., will be given by :

$$w\, dG = w\,(p_1, \ldots, q_{3N})\, dp_1 \ldots dq_{3N} = I e^{-\frac{E}{kT}}\, dp_1 \ldots dq_{3N}, \quad . \quad . \quad (4)$$

in which E is the energy of the system, and

$$\frac{1}{I} = \int \ldots \int e^{-\frac{E}{kT}}\, dp_1 \ldots dq_{3N}$$

the integration being extended over all the values of the q's within the volume V and all the p's from $-\infty$ tot $+\infty$.[1])

If we now assume that T and V have been chosen so that part of the system is gaseous, the other solid, we may write for the probability that the molecules 1 up to n (n inclusive) are in the gaseous state, $n+1$ up to N (N inclusive) on the other hand in the solid state, as follows :

$$\left(\int w\, dG\right)_n = I \int e^{-\frac{\varepsilon}{kT}}\, dp_1 \ldots dq_{3n} \int e^{-\frac{\varepsilon'}{kT}}\, dp_{n+1} \ldots dq_{3N}, \quad . \quad (5)$$

in which the $6n$-fold integral must be taken with respect to the gaseous part of the system, the $6\,(N-n)$-fold one with respect to the solid part. The volumes of both are determined by V and the volume of the solid part that is only dependent on $N-n$.[2]) Further :

$$\varepsilon = \frac{1}{2m}(p_1^2 + \ldots p_{3n}^2)$$

is the energy of the gas,

$$\varepsilon' = \varepsilon'_p + \varepsilon'_q + n'c = \frac{1}{2m}(p_{3n+1}^2 + \ldots p_{3N}^2) +$$

$$+ \sum_{3n+1}^{3N} \sum_{3n+1}^{3N} a_{ij}\, q_i q_j + \sum_{3n+1}^{3N} b_i q_i + b_0 + n'c,$$

in which $N - n = n'$ is put, the energy of the solid body, so $\varepsilon + \varepsilon' = E$. c and the a's and b's are constants; $-c$ is the work which is to be applied to detach a molecule resting in its position

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[1]) We may also say that the system, as it is at a definite moment, forms part of a canonical ensemble, with modulus kT.

[2]) In principle also other arrangements of the molecules than those of solid substance or gas are of course conceivable, at least for a short time; they will, however, be so improbable, that they may be disregarded. Nor is it necessary to consider a solid phase of variable density.

of equilibrium from its connection with the solid body, and to bring it in the gas space, hence c is negative.

We can immediately integrate with respect to the gas, through which we get:

$$\left(\int w \, dG\right)_n = I \, (2\pi \, m \, kT)^{3/2 \, n} \, v^n \int e^{-\frac{\varepsilon'}{kT}} \, dp_{3n+1} \ldots dq_{3N}, \quad \ldots \quad (6)$$

in which v is the volume of the gas.

Now we can replace the values q_{3n+1} to q_{3N} (inclusive) by variables $q'_1, \ldots, q'_{3n'}$ which are in linear connection with them, so that $\varepsilon'_q = \frac{1}{2} \sum_1^{3n'} f_i q'^2_i$ with all positive f's, while $\varepsilon'_p = \frac{1}{2m} \sum_1^{3n'} p'^2_i$,

when p'_i is the value corresponding to q'_i, hence $\frac{\partial \varepsilon'}{\partial q'_i}$. The quantities q'_i are evidently a criterion for the deviations of the molecules from their positions of equilibrium.

As according to a known thesis $dp_1' \ldots dq'_{3n'} = dp_{3n+1} \ldots dq_{3N}$, we get:

$$-e^{-\frac{\varepsilon'}{kT}} dp_{3n+1} \ldots dq_{3N} = e^{-\frac{n'c}{kT}}, \, e^{-\frac{\sum \frac{1}{2} f_i \, q'^2_i + \sum \frac{1}{2m} p'^2_i}{kT}}, \quad dp_1' \ldots dq_{3n'} \, . \quad (7)$$

When we however should simply integrate on the right with respect to all the values of $-\infty$ to $+\infty$, and substitute the result in (6), as being equal to the integral with respect to the leftside member of (7), we should commit a serious error and arrive at an absurd final result.

We had namely originally to integrate with respect to all the values of the q's inside the volume occupied by the solid body. In this those values are naturally left out of account for which the energy is very great, for which a molecule is therefore pretty far from its position of equilibrium, as this according to the formula for the probability very rarely occurs. The proportionality of the energy with q'^2, however, only holds for slight departures out of the position of equilibrium, and no longer when a molecule has got so far that it can pass between the neighbouring ones. This must actually occasionally occur, though very seldom, and in this way two molecules can interchange their original positions, and each molecule can successively be found at all possible points of the solid body, and have a position of equilibrium which was before

peculiar to another.[1]) This new position is a priori as probable as the preceding one.

As it is now tacitly assumed by simply integrating the righthand side of (7) over the range from $-\infty$ to $+\infty$ that a molecule cannot leave its place, the thus obtained integral must still be multiplied by $n'!$, this being the number of the interchanges possible between the molecules of the solid body.

When this is taken into account, we find:

$$\left(\int w \, dG\right)_n = I e^{-\frac{n'\varepsilon}{kT}} (2 \pi m kT)^{3/2 n} v^n \, n'! \, (kT)^{3n'} \, \Pi , \quad . \quad . \quad (8)$$

in which Π denotes the product of the $3n'$ values $\left(\frac{4\pi^2 m}{f_i}\right)^{1/2}$.

This is therefore the probability that the molecules from 1 to n inclusive form a gas with the volume v, the n' remaining ones a solid body with the volume $v' = V - v$.[2])

It is, however, of no importance whatever for thermodynamics whether it is just the molecules numbered 1 up to n that are in the gas state. What we want to know is rather the probability that n arbitrary molecules are in the gas state, the remaining ones in the solid state. This probability, which we shall call $W(n)$, is obtained by multiplying the expression (8) by $\frac{N!}{n!n'!}$, being the number of different ways in which the N molecules can be divided between gas and solid body on the condition that always n remain in the gas. We get:

$$W(n) = I \frac{N!}{n!} e^{-\frac{n'\varepsilon}{kT}} (2\pi m kT)^{3/2 n} v^n (kT)^{3n'} \, \Pi \quad . \quad . \quad . \quad (9)$$

Bearing in mind that $\frac{1}{2\pi} \sqrt{\frac{f_i}{m}}$ is the frequency v_i for the variable q_i', we may also write:

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\begin{aligned}
log \, W(n) = log \, I + N \, log \, N - N - n \, log \, n + n - \frac{n'\varepsilon}{kT} + \tfrac{3}{2} n \, log \, (2\pi m) + \\
+ \tfrac{3}{2} n \, log \, (kT) + n \, log \, v - 3n' \, \overline{log \, v} + 3n' \, log \, (kT),
\end{aligned}
\right\} \quad (10)
$$

in which $\overline{log \, v}$ is the mean value of $log \, v_i$.

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[1]) In this it is assumed that the energy required for a molecule to slip through the surrounding ones, is not infinite; at any rate it is, however, possible to imagine the interchange of the molecules to be brought about by evaporation and renewed condensation, which must really continually take place at the surface.

[2]) As we have assumed the density of the solid substance to be invariable, $v = V - v'$ is determined by n', and therefore by n.

In order to find the most probable distribution of the molecules between gas and solid substance for given values of T and V, which is the only one that need be considered for the thermodynamical equilibrium, we must see for what value of n the function $W(n)$ is a maximum, so that $dW = 0$, or what comes to the same thing $d \log W = 0$.

As $dn' = - dn, \dfrac{dv}{v} = - \dfrac{v'}{v} \cdot \dfrac{dv'}{v'} =^1) - \dfrac{v'}{v} \cdot \dfrac{dn'}{n'} = + \dfrac{v'}{v} \cdot \dfrac{dn}{n'}$, and l is

independent of n, we get the equation :

$$0 = - \log n + \frac{c}{kT} + \tfrac{3}{2} \log (2\pi m) + \log v + \frac{nv'}{n'v} + 3 \overline{\log v} - \tfrac{3}{2} \log (kT) \quad (11)$$

We know from the ordinary kinetic gas theory that the pressure p of the gas is $\dfrac{nkT}{v}$, on account of which we may write for (11):

$$0 = \frac{c}{kT} + \tfrac{3}{2} \log (2\pi m) - \log p + \frac{pv'}{n'kT} + 3 \overline{\log v} - \tfrac{3}{2} \log (kT) \quad . \quad (12)$$

The entropy S' of a gramme molecule of solid substance is now

(see § 2) $= 3kN \left(1 - \overline{\log \dfrac{hv}{kT}} \right)$.

Equation (12) then becomes:

$$0 = \frac{c}{kT} + \tfrac{3}{2} \log (2\pi m) - \log p + \frac{pv'}{n'kT} - \frac{S'}{kN} + \tfrac{5}{2} \log (kT) - 3 \log h + 3 \quad (13)$$

It is further clear that the increase of the internal energy at the evaporation amounts to [2]:

$$U = - Nc + \tfrac{3}{2} kNT - 3 kNT = - Nc - \tfrac{3}{2} kNT. \quad . \quad (14)$$

If S is now the entropy of a gramme molecule of gas, the increase of entropy at the evaporation is:

$$S - S' = \frac{U + \left(\dfrac{N}{n} v - \dfrac{N}{n'} v' \right)}{T} = - \frac{Nc}{T} - \tfrac{1}{2} kN - \frac{N}{n'} \frac{pv'}{T} \quad . \quad (15)$$

We finally find for S from (13) and (15):

$$S = kN \{ \tfrac{5}{2} \log (kT) - \log p + \tfrac{3}{2} \log (2\pi m) - 3 \log h + \tfrac{5}{2} \} \quad . \quad (16)$$

KOHNER and WINTERNITZ [3] have calculated the chemical constant of hydrogen for low temperatures, in which this behaves as a mona-

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[1]) On account of the constant density $\dfrac{v'}{n'}$.

[2]) A possible zero point energy had to be simply taken into account in c here and in the following §§.

[3]) v. KOHNER und P. WINTERNITZ, Phys. Z.S. 15, 393 and 645 (1914).

tomic gas [1]), from thermochemical data; they have found with the atmosphere as pressure unity:

$$C = - 1,303$$

with an uncertainty which they estimate at most at $\pm$ 0,15. They calculate from (16):

$$C = - 1,17,$$

which may be considered as a very satisfactory agreement.

On the other hand O. STERN[2]) has also derived the entropy of monatomic gaseous iodine from thermochemical data, and found a value which very greatly deviates from that following from (16). He infers from this that either the heat theorem is not valid for the reaction $2I_{solid} \rightleftarrows I_{2solid}$, that therefore the difference of entropy remains finite for $T = 0$, or that the vapour tension of monatomic iodine cannot be accurately calculated with the aid of (16). He seems to think the former rather probable. It seems to me that they come to the same thing. It may namely be very well the case that the heat theorem only holds for substances that really exist, and this cannot be said of monatomic solid iodine. Then the calculation of the vapour tension as we have carried it out in this §, has no longer any meaning: monatomic gaseous iodine cannot exist at low temperatures either. The formulae of this and the following §§ for the entropy constant can lay claim to validity only for such substances as also occur in the same molecular form at low temperatures, as the gases of the He group, the metal vapours, further also gases as H_2, O_2, CO, I_2 etc.; but not gases as I, Br or such like ones. Of course the possibility continues to exist that an unexpectedly great error occurs in the data used by STERN.

§ 4. *On the vapour pressure of a diatomic solid substance and the entropy constant of the gas.*

In a corresponding way the vapour pressure of a diatomic substance and the entropy of the vapour can be calculated, when it is assumed ,that here too the atom motions consist of sine vibrations, while moreover the two atoms of one molecule are always at a definite distance from each other[3]) as they also are in the gas for

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[1]) A. EUCKEN, Sitz. Ber. Berl. Akad., 1 Febr. 1912.

[2]) O. STERN, Ann. d. Phys. 44, 497 (1914).

[3]) When the possibility of existence of the solid substance falls below the region within which classical mechanics may still be applied to the rotation of the molecules, the calculation has of course no direct meaning, and it will be preferred to follow another method; see § 5.

A possible mutual vibration of the atoms with a zero point energy $\frac{1}{2}h\nu$ would

· an extensive temperature region, so that the molecule has five degrees of freedom. It is then still necessary to assume that at a definite point of the solid body which is to be thought as a crystal, the molecule axis passing through the centres of gravity of the atoms can only have one definite direction, from which it will of course deviate periodically by small angles on account of the heat motion. If the two atoms are then still supposed to be different, so that the opposite direction does not mean the same thing, and is therefore not possible, we find for the entropy of the gas[1]:

$$S = kN\{\tfrac{5}{2} log(kT) - log p + \tfrac{3}{2} log(2\pi m) + log(2\pi J) - 5 log h + log(4\pi) + \tfrac{7}{2}\}, \quad (17)$$

and for the constant a

$$\frac{a}{R} = \tfrac{5}{2} log k + \tfrac{3}{2} log \frac{2\pi m}{h^2} + log \frac{2\pi J}{h^2} + log(4\pi), \quad . \quad . \quad . \quad (18)$$

in which J is the principal moment of inertia of a molecule, of course for an axis which is normal to that passing through the centres of gravity of the atoms.

If on the other hand we assume the two atoms in the molecule as perfectly equal and indistinguishable, so that at any point in the crystal the axis of the molecule might as well be rotated by 180°, we find for S, resp. a a $kN log 2$ smaller value. In the formula analogous with (8) we get then namely $2^{n'} n'!$ instead of $n'!$.

In reality we shall have to assume at least in most cases, that also 2 similar atoms in a molecule perform a different function, e.g. that one is positive, the other electrically negative, or else that the molecule possesses a magnetic moment, that they are therefore indeed to be distinguished and the molecule can only have one direction at any place in the crystal. Then the formulae (17) and (18) will be universally valid.

§ 5. On the dissociation of di-atomic gas molecules.

We can come to the same conclusion when we investigate the dissociation of a di-atomic gas statistically-mechanically, and assume the formula (16) for the entropy of the mon-atomic components to be correct.

We must then assume that the atoms in the molecule vibrate against each other with a frequency v, so that the energy of the

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render the distance variable by only a practically insignificant amount for molecules consisting of heavier atoms; for hydrogen this would, however, be considerable (The value of v may be calculated from the specific heat at high temperatures, the moment of inertia from Eucken's experiments and formulae (16) and (17)).

[1] For the calculation cf. §§ 6 and 7.

vibration becomes $= \dfrac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + const.$ according to the formula of

PLANCK-EINSTEIN. It could be neglected for the temperatures that are to be taken into account for the evaporation[1]. For very high values of the energy of vibration, which, however, will be so rare at not too high temperatures that they may be left out of account in the calculation of the mean value, the mutual motion of the atoms is no longer a simple sine vibration; and at still greater value of the energy the attractive force between the atoms becomes very small, they get detached from each other, and the molecule is dissociated.[2]

We may imagine that each of the (spherical) atoms has a pole, and that in the molecule the two poles coincide or are removed from each other a small distance through the heat motion, however in such a way that the axes of the two atoms passing through pole and centre are always in the production of each other.

When the atoms are of different kinds, say A and B, we find for the constant of equilibrium of the reaction $AB \rightleftarrows A + B$[3]:

$$\frac{n^2_2}{n_1} = e^{-\frac{c}{kT}} \left(\frac{m_A m_B}{m_A + m_B} \right)^{3/2} \cdot \frac{1}{J} \cdot \frac{1 - e^{-\frac{h\nu}{kT}}}{h} \cdot \frac{1}{2} \sqrt{\frac{kT}{2\pi}}, \quad \cdot \quad \cdot \quad (19)$$

in which n_2 resp. n_1 is the number of split resp. unsplit molecules per volume unity, m_A and m_B the masses of the atoms, and J the moment of inertia of the molecule. c is the heat of dissociation, as it would be for the absolute zero.

For lower temperatures this reduces to:

$$\frac{n^2_2}{n_1} = e^{-\frac{c}{kT}} \left(\frac{m_A m_B}{m_A + m_B} \right)^{3/2} \frac{1}{2Jh} \left(\frac{kT}{2\pi} \right)^{\frac{5}{2}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (20)$$

On the other hand according to thermodynamics:

$$\frac{n^2_2}{n_1} = A e^{-\frac{c}{kT}} T^c \left(\frac{1}{kT} \right)^{2-1}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (21)$$

in which $log\, A = \dfrac{a_A + a_B + a_{AB}}{R}$, c has the same meaning as in (20)

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[1] If namely a possible zero point energy is not so great that the moment of inertia becomes variable in consequence.

[2] In reality it may of course occur that the vibrations are already no longer sine-shaped for small values of the energy; it is, however, not possible for the present to take this into account theoretically.

[3] J. D. VAN DER WAALS Jr., these Proceedings XVI, p. 1082.

and c is the algebraic sum of the heat capacities of the reacting gases at constant pressure, divided by R, i. e. $= \frac{5}{2} + \frac{5}{2} - \frac{7}{2} = \frac{3}{2}$. a_A, a_B and a_{AB} are the entropy constants of the gases defined in (1).

By equating (20) and (21) we find :

$$\tfrac{3}{2} \log m_A + \tfrac{3}{2} \log m_B - \tfrac{3}{2} \log m_{AB} - \log (2J) - \log h + \tfrac{1}{2} \log (kT) - \tfrac{1}{2} \log (2\pi) =$$

$$= \frac{a_A}{R} + \frac{a_B}{R} - \frac{a_{AB}}{R} + \tfrac{1}{2} \log T - \log k,$$

in which $m_{AB} = m_A + m_B$ is the mass of a molecule AB.

When in this we substitute for a_A and a_B the values following from (16) and (1), we find :

$$\frac{a_{AB}}{R} = \log J + \tfrac{7}{2} \log k - 5 \log h + \tfrac{3}{2} \log m_{AB} + \tfrac{19}{12} \log 2 + \tfrac{7}{2} \log \pi,$$

corresponding to (18).

When, however, we assume the two atoms to be of the same kind, we shall find a value of half the amount for the dissociation constant $\dfrac{n_2^2}{n_1}$ in the kinetic calculation : the probability that two atoms meet that can unite is now namely twice as great as before, all the rest remaining the same.

Thermodynamically we find, however, a four times smaller value : in (21) $\dfrac{(2n_2)^2}{n_1}$ must then be substituted for $\dfrac{n_2 \times n_2}{n_1}$, the righthand side remaining unchanged. In this case, just as in the preceding §, we should, therefore, find an $R \, \log 2$ smaller value for a_{AB}.

As, however, as was said above, it must be generally assumed that two similar atoms do not perform the same function in chemical combination, we shall have to give a somewhat more general form to the suppositions made by VAN DER WAALS Jr. about the chemical forces. We suppose every atom to possess two poles, a positive and a negative one, and that in a certain combination of two dissimilar atoms A and B always e.g. the positive pole of A gets in contact with the negative pole of B. In a combination of two similar atoms the positive pole of the one will always be connected with the negative pole of the other; in this case it is of no consequence, however, which atom is connected through its positive, which through its negative pole. This makes the number of possibilities of binding still 2 $\times$ greater than for dissimilar atoms, and the change of coming together becoming already 2 $\times$ greater through the mere fact of the atoms being equal (see above). it now becomes 4 $\times$ greater, which is in harmony with the thermodynamic formula, so that also in this case we have to assign the value (18) to a_{AB}.

It should, however, be kept in view that the suppositions on the chemical forces used in this §, possibly do not sufficiently agree with reality; nor do they any longer appertain to pure classical mechanics: we have, namely, assumed that in case of a chemical binding the atoms must have a definite relative orientation, though we have not spoken at all of a rotation of the atoms. We might imagine other representations of the acting forces, but the one used seems to me the simplest and the most obvious. After what has been said at the conclusion of § 3, it will be clear that the application of (16) is probably not permissible for the entropy of the monatomic components, viz. in the case of one kind of atoms.

The contents of this § is then only interesting from a theoretical point of view, viz. to show how the same result as in § 4 can be found in another way too. A third derivation of the entropy constant of the rotation for di-atomic molecules has been given by O. Stern[1]) by the aid of Langevin's theory of paramagnetism. From this we see that this derivation only holds for the case that the two atoms do not perform the same function. The result agrees with ours.

§ 6. *General formula for the vapour pressure of a multi-atomic solid substance and the entropy of the vapour.*

We will now calculate the vapour pressure of arbitrary multi-atomic solid substances in an analogous way as we did in § 3 for monatomic ones. We then only assume (for simplicity's sake)[2]) that the vapour is an ideal gas, i.e. a gas with independent molecules, whose energy, therefore, does not depend on the volume; the specific heat, however, may indeed vary with the temperature, if only classical mechanics remain of application. Hence the internal molecule movements need not exclusively consist of rotations and sine vibrations. For the solid substance we continue, of course, to consider the suppositions of § 2 as valid, to which we may add, as in § 4 that at every place in the crystal the molecule present there can only have one definite orientation.[3])

Thus we find for the probability that n of the N-molecules belong to the vapour, the formula which is analogous with (10):

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[1]) O. Stern, Ann. d. Phys. **44**, 497 (1914).

[2]) It is shown in § 8 that the formula to be found for the entropy holds just as well for non-ideal gases and for liquids.

[3]) The impossibility of another orientation must of course be understood so that a very great energy would be required for this.

$$\log \, W(n) = \log \, J + \log \, \Phi - \frac{n'c}{kT} + N \log \, N - N$$
$$- n \log n + n + jn' \log \, (kT) - jn' \, \overline{\log \, v},$$

$$\left. \begin{array}{c} \\ \\ \\ \\ \end{array} \right\} \quad . \quad . \quad (22)$$

in which j is the number of degrees of freedom per molecule,

$$\Phi = \int \, .. \, \int e^{-\frac{z}{kT}} \, dp_1 \ldots dq_{jn}$$

and the other quantities have a meaning corresponding to that which they had before. ε is now of course the whole energy of the n gas molecules, $\dfrac{1}{J}$ the jN-fold integral

$$\int \ldots \int e^{-\frac{E}{kT}} dp_1 \ldots dq_{jN}.$$

As $3n$ of the jn coordinates of the gas molecules denote the positions of the molecular centres of gravity, they do not occur in ε; in consequence of this and on account of what was said above Φ is of the form:

$$\Phi = v^n \, [f(T)]^n \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

in which the function f is a $(2j-3)$-fold integral referring only to one molecule, which therefore besides on T, depends only on the mechanical constants of the molecules. It follows from this that:

$$\frac{\partial \Phi}{\partial v} = \frac{n}{v} \, \Phi, \quad \text{or} \quad \frac{\partial \log \Phi}{\partial \log v} = n \quad . \quad . \quad . \quad . \quad (24)$$

The equation for the most probable value of n, hence for the thermodynamic equilibrium becomes:

$$0 = \frac{d \log \Phi}{dn} + \frac{c}{kT} - \log n - j \log \, (kT) + j \, \overline{\log \, r}. \quad . \quad . \quad (25)$$

Now:

$$\frac{d \log \Phi}{dn} = \left(\frac{\partial \log \Phi}{\partial n} \right)_v + \left(\frac{\partial \log \Phi}{\partial v} \right)_n \frac{dv}{dn} = \frac{1}{n} \log \Phi + \frac{n}{v} \cdot \frac{v'}{n'} \cdot \left(\frac{dv}{dn} = \frac{r'}{n'} \right)$$

just as in § 3).

Hence we get:

$$0 = \frac{1}{n} \log \Phi + \frac{n}{v} \cdot \frac{v'}{n'} + \frac{c}{kT} - \log n + j \log \overline{\frac{v}{kT}}. \quad . \quad . \quad (26)$$

The entropy of the solid substance is:

$$S' = kj \, N \left(1 - \overline{\log \frac{hv}{kT}} \right) \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Further:

$$S - S' = -\frac{Nc}{T} + \frac{E}{T} - kjN + \frac{p\left(\frac{N}{n}n - \frac{N}{n'}v'\right)}{T}, \quad . \quad (28)$$

when E is the energy of N molecules of gas

$$\frac{N}{n} \cdot \frac{1}{\Phi} \int \ldots \int \varepsilon\, e^{-\frac{\varepsilon}{kT}}\, dp_1 \ldots dq_{jn} \quad . \quad . \quad . \quad , \quad . \quad (29)$$

When it is borne in mind that $pv = knT$, it follows from (26), (27), (28), that:

$$S = -kN\log n + \frac{kN}{n}\log \Phi - kj\,N\log h + \frac{E}{T} + kN, \quad \cdot \; _\llcorner$$

or when for the sake of simplicity we put $n = N$:

$$S = k\log \Phi - kN\log N + kN + \frac{E}{T} - kj\,N\log h. \quad . \quad . \quad (30)$$

Hence the free energy is:

$$F = E - TS = -kT\log \frac{\Phi}{h^{jN}N\,!} \quad . \quad . \quad . \quad . \quad (31)$$

We find for the free energy, either by substituting the value (29) for E in (30), or by differentiating (31) with respect to T:

$$S = -k'\int f\log f\, dG - k\log(h^{jN}) - k\log(N\,!), \quad . \quad . \quad (32)$$

in which:

$$\frac{1}{\Phi}\,e^{-\frac{\varepsilon}{kT}} = f \quad \text{en} \quad dp_1 \ldots dq_{jN} = dG$$

§ 7. Calculation of the entropy of gases with arbitrary rigid molecules.

We will now apply the formulae (31), resp. (32) found in the preceding § to two simple cases of general occurrence.

We can of course first find back the formula (16) of § 3. We further find for a gas, the molecules of which possess two rotation degrees of freedom with the moment of inertia J, and will be rigid for the rest:

$$S = k\left\{\tfrac{3}{2}N\log\frac{2\pi mkT}{h^2} + \log\frac{v}{N\,!} + N\log\frac{2\pi JkT}{h^2} + N\log(4\pi) + \tfrac{5}{2}N\right\} \quad (33)$$

which formula we already meet in §§ 4 and 5.

For rigid molecules with three rotation degrees of freedom and the chief moments of inertia J_1, J_2, and J_3, we find:

$$S = k \left\{ \tfrac{3}{2} N \log \frac{2\pi m k T}{h^2} + \log \frac{v}{N!} + \tfrac{1}{2} N \log \frac{2\pi J_1 k T}{h^2} + \right.$$
$$\left. + \tfrac{1}{2} N \log \frac{2\pi J_2 k T}{h^2} + \tfrac{1}{2} N \log \frac{2\pi J_3 k T}{h^2} + N \log (8\pi^2) + 3 N \right\} \quad . \quad (34)$$

Without entering further into the calculation it is yet easy to see the analogy of the formulae (33), (34), and (16). If we write the last in the form:

$$S = k \left\{ \tfrac{1}{2} N \log \frac{2\pi m k T}{h^2} + \log \frac{v}{N!} + \tfrac{1}{2} N \right\} ,$$

we see that in each of the three expressions per degree of freedom first of all a term $\tfrac{1}{2} N \log \frac{2\pi m k T}{h^2}$ resp. $\tfrac{1}{2} N \log \frac{2\pi J k T}{h^2}$ occurs, according as it is one of rectilinear or of rotatory motion. For the three degrees of freedom of rectilinear motion moreover a term $\log \frac{v}{N!}$ is everywhere found. In this v is the three-dimensional extension of the coordinates denoting the place of the centre of gravity of a molecule, while the division by $N!$ is caused by the interchangeability of the molecules, as has been fully set forth in § 3.

We find in (33) 4π instead of v and in (34) $8\pi^2$ for the rotatory motion. In (33) 4π is the two-dimensional extension of the angular coordinates, which indicate the direction of that axis of the molecule round which it does not revolve, while in (34) another factor 2π is added, being the extension of the third angular coordinate, which denotes the revolution round the said axis, which now, indeed, does take place. Finally there is everywhere still a term $\tfrac{1}{2} N$ per degree of freedom.

§ 8. *On the general definition of the thermodynamic probability for gases and liquids.*

We know from ordinary statistical mechanics that the changes of the expressions (32) and (31) denote generally the change of the entropy, resp. free energy for changed values of v and T. As they, as we have seen, indicate for a system in one definite condition (ideal-gas), the absolute values of S and F, (i.e. those with the accurate additive constant), they will have to do this for all conditions. In this it should of course be taken into account that ε for smaller values of v can also depend on the mutual distances (and possibly orientations) of the molecules.

The formulae (31) and (32) are therefore of general validity on the suppositions made, also for non-ideal gases and for liquids,

which latter can namely be formed from gases in a continuous way. They would also have to hold for solid substances, when these were considered in the same way; as it is however customary to consider the molecules in this case as not interchangeable. $N!$ resp. the term with $log(N!)$ must be omitted. This is namely the case when the solid substance is imagined as a system of fixed "oscillators".

Though properly speaking we have only generally proved the formulae on the assumption that the system can pass into an ideal solid body without loss of degrees of freedom, it yet seems plausible that a general validity may be ascribed to it.

We have, namely, seen in § 5 that it may also be derived in another way for a definite case, and the conclusion suggests itself that this will also be possible in other cases. We have, however, at the same time learnt to know the probable limits of the validity.

If we want to drop the supposition that no indistinguishable atoms occur in a molecule, we shall have to add still a term $-kN \log p$ to (32), when p is the number of different ways, in which a molecule can be made to cover itself.

We can finally give still another form to (32). When the integration is replaced by a summation, and when in this $dG = h^N$ is always put, we get:

$$S = -k \Sigma f_i \, d \, G_i \, log \, (f_i \, d \, G_i) - k \, log \, (N!) - k \, log \, (p^N). \quad (35)$$

When a canonical ensemble consists of so great a number M of systems that the number $M_i = M f_i \, dG_i$ lying in an elementary region dG_i is a large number, we can write:

$$MS = -k\Sigma M f_i \, dG_i \, log \, (M f_i \, dG_i) + kM \, log \, M - kM \, log \, (N!) - kM \, log \, (p^N) =$$

$$k \, log \, \frac{M!}{p^{MN} \, (N!)^M \cdot M_1! M_2! M_3! \dots} \quad . \quad . \quad . \quad (36)$$

This being the entropy of a system of MN molecules, the expression must only depend on the product MN, independent of the way in which this has been separated into factors. This may be seen still better as follows.

When in (35) N is replaced by MN, we get according to (23):

$$\Phi_{MN} = v_{MN}^{-MN} [f(T)]^{MN} = (M v_N)^{MN} [f(T)]^{MN} = M^{MN} \, \Phi^{MN}.$$

Hence

$$f_{iMN} = \left(\frac{e^{-\frac{\varepsilon_i}{kT}}}{\Phi} \right)_{MN} = \frac{f_{iN}^M}{M^{MN}},$$

because when corresponding elementary regions are compared, $\varepsilon_{MN} = N$. Further $dG_{iMN} = h^{jMN} = (dG_{iN})^M$.

Then $\Sigma f_i dG_i$ taken over an arbitrary group of elementary regions, is the probability that the system lies in one of them; when this group is now chosen so that the interval ε_{MN} corresponding to it becomes equal to the M-fold of that of the group of a system of N molecules compared with the group, evidently:

$$(\Sigma f_i dG_i)_{MN} = (\Sigma f_i dG_i)_N$$

As the interval $\Delta\varepsilon$ of ε may be chosen so small that $\dfrac{\Delta\varepsilon}{kT} = 0$ may be put, the argument of the logarithm in (35) may be put constant in the summation extended over a group.

In this way we get:

$$S_{MN} = - k \Sigma f_{i,MN} dG_{i,MN} log (f_{i,MN} dG_{i,MN}) - k log (MN)! - k log (p^{MN}) =$$

$$- k \Sigma f_i dG_i log \left(\frac{f_{iN}^{M}}{M^{MN}} [dG_{iN}]^M \right)$$

$$- kMN log M - kMN log N + kMN - kMN log p = - kM \Sigma f_i dG_i log (f_i dG_i)$$

$$+ k(MN log M) . (\Sigma f_i dG_i) + \text{etc.} =$$

(as $\Sigma f_i dG_i = 1$)

$$- kM \Sigma f_i dG_i log (f_i dG_i) - kMN log N + kMN - kMN log p = MS_N,$$

which we have now derived from an expression depending only on the product MN, which expression we had, of course, to treat differently, as far as M and N are concerned.

Prof. LORENTZ, whose communication "*Opmerkingen over de theorie der eenatomige gassen*"[1]) induced me to take up the treated problems, points out to me, among different valuable remarks, for which I am greatly indebted to him, that I have now indeed demonstrated that my formulae may be considered as convenient precepts for the calculations for the thermodynamic probability of the gas, but that I have not yet explained how through the consideration of the gas alone they could be derived, in particular why after all it is in this case necessary to divide by $N!$. This is a difficult question. In some connection with it is what follows:

We have seen that a di-atomic gas, the molecules of which consist of perfectly equal atoms, at higher temperatures must have a $k log (2^N)$ smaller entropy than when the atoms are different. Must not the specific heat of the gas then have a different course in the two cases at low temperatures, and how could this be accounted for[2]

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[1]) II. A. LORENTZ, Zittingsversl. Akad. Amsterdam, 23, 515 (1914). Not yet translated.

Or will the entropy of the gas, which is monatomic from a thermo-dynamic point of view at very low temperatures, perhaps not be represented by (16), but have a value $kN \log 2$ smaller? This seems improbable, at least at first sight. A perfectly satisfactory answer to this question is probably to be expected only from a general theory of quanta.

However, something can be said about the division by $N!$ also without having recourse to the solid phase. Suppose we have the general theory of quanta We come to the conclusion that for the determination of the thermodynamic probability we have not to reckon with infinitely small regions, but with such of a definite finite extent. This, however, holds only without reservation for systems the molecules of which are all different. Of a gas for which this is the case, we could not say that the entropy was proportional to the mass; it would much sooner contain a term $k \log N!$. Now, however, the entropy of a mixture of different gases is $k \log \dfrac{N!}{n_1'\, n_2!\ldots}$, greater than when the gases are equal, which can be thermody-namically derived for large values n_1 etc., while it seems natural to consider it also as valid for small n's, (n_1 etc. are of course the numbers of molecules for the different kinds, N is $= \Sigma n_i$). If now all n's are $= 1$, in other words, if the gas consists of nothing but different molecules, the entropy will be $k \log (N!)$ greater than for a gas consisting of nothing but equal molecules. For the latter we shall then have to subtract $k \log (N!)$ from the original entropy expression. Such considerations have originally led me to the division by $N!$ and to the formula (16).

Physics. — "*On interference phenomena to be expected when Röntgen rays pass through a di-atomic gas.*" By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORFNTZ.)

(Communicated in the meeting of February 27, 1915).

As is known W. FRIEDRICH[1]) has ascertained that a beam of Röntgen rays passing through yellow wax and other amorphous *solid* substances gives interference rings on a photographic plate placed behind it. *Liquid* paraffin also gives a ring, which, however, does not represent a maximum of darkness, but an inflection point of

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1) W. FRIEDRICH, Eine neue Interferenzerscheinung bei Röntgenstralen: Phys. Zschr. 14, (1913), p. 317.