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Physics. — “*Some remarks on the theory of monatomic gases*”.

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§ 1. Several physicists have recently applied the theory of quanta to gaseous bodies, especially to monatomic gases. The common object of their considerations, much though they differ from each other, may be said to have been the determination of the entropy S of a gas as a function of the volume v and the energy E .

If this function is known, the temperature T and the pressure p may likewise be expressed in terms of E and v by means of the thermodynamic relations

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial v} = \frac{p}{T}.$$

Further the relation between p , v , and T , i.e. the equation of state can be found and also that between v , T , and E , from which we can derive the specific heats.

In the case of an ideal monatomic gas classical thermodynamics lead to the formula

$$S = kN (\log v + \frac{3}{2} \log E) + a, \quad . \quad . \quad . \quad (1)$$

in which N denotes the number of molecules, k PLANCK's well known coefficient and a an undeterminate constant. In the way just mentioned we infer from this

$$pv = kNT, \quad E = \frac{3}{2} kNT \quad . \quad . \quad . \quad (2)$$

Now, the new theories differ from classical thermodynamics in so far as they assign to the entropy a completely definite value without an undeterminate constant. As to the way in which v and E occur in the formula, this may either remain as it is in (1) or the form of the connexion may be a more complicated one. In the first case the only change is, that a , which has been called by NERNST “the chemical constant” of the gas, takes a definite value, the equations (2) remaining unmodified. In the second case these latter equations have to be changed.

In the theories in question the entropy is always determined by means of BOLTZMANN's formula

$$S = k \log W,$$

where W is the “probability” of the state considered. Generally speaking there can be no doubt about the validity of this relation

and it certainly is one of the most important equations of modern physics. Nevertheless, difficulties may arise when we come to consider the rules according to which the value of W must be determined.

§ 2. The state of a gas may be defined by the coordinates of the N molecules and the components of their momenta. These parameters may be regarded as the coordinates of a point in a $6N$ -dimensional space R_{6N} , the "extension-in-phase". The part of this space corresponding to a given value of the volume and to values of the energy between E and $E + dE$, a part which we may call a thin "layer", will have a definite magnitude proportional to dE . Let this value expressed in some properly chosen unit be ΩdE . By putting W proportional to Ω one really finds formula (1) by means of BOLTZMANN'S equation.

Indeed, if we take as unit of space in R_{6N} a cube, the edges of which are parallel to the axes of coordinates and are of the length 1, we have

$$\Omega = \frac{(2\pi Em)^{3/2 N-1} \cdot 2\pi m v^N}{\Gamma\left(\frac{3}{2} N\right)}, \quad (3)$$

where the mass of a molecule is denoted by m .¹⁾

Let us now put $W = C\Omega$, understanding by C a factor that has the same value for all states of the gas. Omitting in the expression for $k \log \Omega$ all terms which do not contain the factor N , as we may do if N is very large²⁾, we find

$$S = kN \left\{ \frac{3}{2} \log (2\pi Em) + \log v - \frac{3}{2} \log \left(\frac{3}{2} N \right) + \frac{3}{2} \right\} + k \log C,$$

which is in agreement with (1), if we put

$$a = \frac{3}{2} kN \left\{ \log (2\pi m) - \log \left(\frac{3}{2} N \right) + 1 \right\} + k \log C.$$

¹⁾ The domain ΩdE in the extension-in-phase may be decomposed into a domain in the extension-in-configuration and one in the extension-in-velocity. The numerical values of these two must be multiplied by each other. The first domain is v^N and for the second we may write $\frac{dK}{dE} dE$, if K is the part of the extension-in-velocity, in which the energy has a value below E . K is a $3N$ dimensional sphere with radius $(2Em)^{1/2}$, so that we have

$$K = \frac{(2\pi Em)^{3/2 N}}{\Gamma\left(\frac{3}{2} N + 1\right)}.$$

²⁾ We may then write $\left(\frac{3N}{2e}\right)^{3/2 N}$ for $\Gamma\left(\frac{3}{2} N\right)$

§ 3. To get an idea of the probability of different states of the gas we can imagine that the state is determined by a lottery in which slips of paper with different numbers are drawn from an urn. This can be arranged in such a way that a slip is drawn for each molecule successively, the number on the slip indicating the place and the state of motion of the molecule. If for each molecule we take the coordinates of the centre and the components of the momentum as the coordinates in a six-dimensional space R_6 , the slip will indicate the point in this extension which represents the position and the state of motion of the molecule or, as we may say, the place of the molecule in R_6 .

Now PLANCK¹⁾ has introduced the fundamental conception of the theory of quanta by imagining that the space R_6 is divided into equal finite elements of a definite magnitude G and that only the question in which of these elements the molecule has to be placed is decided by the lottery. Whether the molecule will lie at one point of the element or at another is not determined in his theory by a consideration of probabilities. Instead of this PLANCK supposes that the molecules lying in the same element of space G are uniformly distributed over its extension. On these suppositions he finds an expression which he considers, not only as *proportional* to the probability but as *equal* to it and which leads to a formula for the entropy containing no indefinite additive constant.

We need not repeat here these calculations of PLANCK. It suffices to remark that the extension-in-phase R_{6N} , which we mentioned in § 2, may be regarded as composed of N extensions-in-phase R_6 each of which belongs to one molecule and that a division of each R_6 into elements of magnitude G involves a division of R_{6N} into elements of magnitude G^N . PLANCK's final result is found if the layer corresponding to dE (§ 2) is expressed in the domain G^N as unity, and if the value of Ω thus found is considered as the numerical value of W .

Instead of (3) we now get

$$\Omega = \frac{(2\pi Em)^{3/2 N-1} \cdot 2 \cdot mv^N}{\Gamma\left(\frac{3}{2}N\right) \cdot G^N} \quad \dots \dots \dots (4)$$

If we substitute this expression for W in BOLTZMANN's formula and again omit all terms not containing N as a factor we find

¹⁾ PLANCK, Vorlesungen über die Theorie der Wärmestrahlung, 2. Aufl. (1913), p. 125; Vorträge über die kinetische Theorie der Materie und der Elektrizität (Wolfskehl-Kongress, 1913), p. 1.

$$S = kN \left\{ \frac{3}{2} \log(2\pi Em) + \log v - \frac{3}{2} \log\left(\frac{3}{2} N\right) + \frac{3}{2} - \log G \right\}. \quad (5)$$

We must remark here that for a definite state of the gas the quantity in brackets is independent of the choice of the fundamental units of length, mass and time and that, therefore, the numerical value of S depends on this choice only in so far as this is the case with k . This becomes evident when we remember that the dimensions of G are $M^3 L^6 T^{-3}$.

PLANCK points out that in all probability G will be connected with the constant h which he has introduced into the theory of radiation and which, when multiplied by the frequency, determines the quantum of energy characteristic of a vibrator. As the dimensions of h are $ML^2 T^{-1}$ the elementary domain G must be proportional to h^3 .

We have finally to make a special supposition about the magnitude of the element G . If we combine n equal quantities of gas simply by putting them side by side, we certainly must assume that the entropy of the whole system will be equal to the sum of the entropies of each of the quantities taken separately. Thus S must be multiplied by n when N , v and E are made n times greater. Now it follows from (5) that this is possible only when G also becomes n times greater, so that the elementary domain must be supposed to be proportional to the number of molecules of the quantity of gas considered.

§.4. It may be objected to PLANCK's considerations that he has failed to attach a physical meaning to his elementary domain G . As it would have six dimensions its magnitude would have to be determined by certain intervals for the coordinates and the momenta. Now, in so far as we are concerned with the coordinates we can hardly see why we should have to introduce intervals of a fixed finite value into our considerations of probability. To this objection PLANCK replies that we must think of the relative coordinates of one molecule with respect to another and it must be owned indeed that a mutual action between the particles might give us a reason for introducing the finite intervals in question. In this line of thought PLANCK ¹⁾ even tries to account for the proportionality between G and the number of molecules. His reasoning may be reproduced as follows. Let all the molecules except one be already in their places and let $\Delta v_1, \Delta v_2, \dots, \Delta v_{N-1}$ be small elements of volume, each in

¹⁾ Vorträge Wolfskehl-Kongress, p. 7 and 8.

the neighbourhood of one of the molecules M_1, M_2, \dots, M_{N-1} , in such a way that Δv_1 has the same position with respect to M_1 as Δv_2 with respect to M_2 etc. Then it might be that the element G with which we are concerned in the case of the N th molecule consists of the volumes $\Delta v_1, \Delta v_2, \dots, \Delta v_{N-1}$ taken together and combined with certain intervals for the momenta; if it were so, G would really be proportional to $N-1$ or to N , as we may say as well.

It must be remarked however that, when we introduced the finite elements G , it was expressly stated that the distribution of the particles over one of them will *not* be determined by probability. Thus, if $\Delta v_1, \Delta v_2, \dots, \Delta v_{N-1}$ must be considered as constituting a single element of volume, the position of the N th molecule either in Δv_1 , or in $\Delta v_2, \Delta v_3$ etc. will not be determined by our lottery. This can hardly be admitted; whether the N th molecule will lie near the first or near any other of the molecules that are already present must certainly be considered as something accidental. Moreover the above reasoning applies only to places in the neighbourhood of one of the $N-1$ molecules, and in gases of small density these places form only a small minority of all those that may be occupied by the N th particle.

§ 5. Before PLANCK, TETRODE¹⁾ had already calculated the entropy of a gas in a similar way²⁾. He defines G in terms of the constant h by the relation

$$G = (\omega h)^3,$$

where ω ³⁾ is a numerical coefficient that has to be determined later on. So his elementary domain does not depend on N . But TETRODE divides the expression (4) by $N!$; by this he reaches the same result that PLANCK obtains by putting G proportional to N . Substituting the value found in this way for W in BOLTZMANN's formula TETRODE finds

$$S = kN \left\{ \frac{3}{2} \log(2\pi Em) + \log v - \frac{3}{2} \log \left(\frac{3}{2} N \right) - \log N + \frac{5}{2} - 3 \log(\omega h) \right\} \quad (6)$$

This expression really fulfills the condition that S shall become n times greater when N , v and E do so. I cannot see however a physical reason for the division of (4) by $N!$

¹⁾ Ann. d. Phys., **38** (1912), p. 434.

²⁾ Similar reasonings have been first published by SACKUR, Ann. d. Phys., **36** (1911), p. 958; **40** (1913), p. 67; Nernst-Festschrift (1912), p. 405.

³⁾ In the notation of TETRODE: z .

§ 6. The hypothesis of quanta has been used in a wholly different way in an other paper by TETRODE¹⁾ and also by LENZ and afterwards by KEESOM²⁾, the method followed in these cases being the same that has been used with much success in the theory of the specific heat of solid bodies. We shall confine ourselves to the considerations of LENZ, which have been communicated by SOMMERFELD³⁾. Let the gas be contained in a vessel having the form of a cube with the edge l . In this system stationary waves of sound of many different kinds can exist. If v is the volume of the cube the number of modes of motion for which the wave-length lies between λ and $\lambda + d\lambda$ is given by

$$\frac{4\pi v}{\lambda^4} d\lambda,$$

the largest value of λ being $2l$.

Now LENZ assumes that the ordinary theory of stationary waves of sound may be applied down to very small values of λ and that we may regard the state of motion of the gas as composed of a great number of such waves with wave-lengths between $2l$ and a certain minimum value, which he calls λ_0 . The latter is chosen in such a manner that the whole number of modes of motion is equal to the number of degrees of freedom of the system of molecules, i.e. to $3N$. This is expressed by the equation

$$\int_{\lambda_0}^{2l} \frac{4\pi v}{\lambda^4} d\lambda = 3N,$$

or

$$\frac{1}{\lambda_0^3} - \frac{1}{8l^3} = \frac{9}{4\pi} \frac{1}{\sigma^3},$$

if we put $\sigma^3 = \frac{v}{N}$, which means that σ is the distance at which, in the case of a cubical arrangement, the particles would lie from each other in the principal directions. If now the vessel contains a very large number of particles so that l is very much greater than σ , the term $\frac{1}{8l^3}$ may be neglected and we find

$$\lambda_0 = 1,12 \sigma.$$

It is further assumed that, for every mode of vibration, we have

¹⁾ Phys. Zeitschr., 14 (1913), p. 212.

²⁾ Proc. Acad. Amsterdam, 16 (1913), p. 227; 17 (1914), p. 20.

³⁾ Vorträge Wolfskehl-Kongress, p. 125.

the following relation between the frequency ν and the wave-length λ

$$\nu = \frac{c}{\lambda},$$

where c , the "velocity of sound", has the same value for all the modes of vibration. LENZ puts

$$c^2 = \frac{\alpha E}{Nm}, \quad \left(\alpha = \frac{10}{9} \right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This relation occurs in the ordinary kinetic theory of a monatomic gas and is maintained by LENZ, although the equations he wants to derive differ from those of the old theory of gases.

In cutting off the "sound spectrum" at the wave-length λ_0 , LENZ follows the example given by DEBYE in his beautiful theory of the specific heat of solid bodies. Just like DEBYE he assumes that the energy is distributed over the different modes of motion in the way required by the theory of quanta, the quantum proper to each mode having the value $h\nu = \frac{hc}{\lambda}$. By probability considerations upon which we need not dwell here the equations for the entropy etc. of the gas are then obtained.

§ 7. In my opinion all this is open to serious objection. In the case of a solid body we can imagine an "original" state in which all molecules are at rest. The different normal modes of vibration which can exist in the body are all deviations from this state and when they all exist at the same time with sufficiently small amplitudes, the total energy — if the energy in the original state is taken to be 0 — is equal to the sum of the energies belonging to the separate modes of motion. The heat motion too may be regarded as made up of all the possible normal vibrations.

The case of a gas is widely different. It is true that here also a wave motion may be regarded as an alternating deviation from an original state, but the latter is not now a state of rest. On the contrary, it is endowed already with the total energy of the molecular motion; in fact it is this latter motion that causes the "elasticity" which serves to maintain the vibrations of sound. It seems rather objectionable to ascribe the energy of the internal motions to a system of vibrations whose laws are deduced on the assumption of a molecular motion that existed already before the vibrations themselves.

It must further be remarked that the ordinary laws of sound motion are true only so long as the wave-length λ is large compared with the mean free path s between two collisions. Only in this case

a gas can be divided into elements of volume (the dimensions of which are small compared with λ and large compared with s) which have a certain individuality, each element dilating or contracting and exerting a pressure on the neighbouring ones, as is admitted in ordinary aerodynamics. Things begin to change already when λ is no longer *very* large compared with s . We must then take account of the phenomena that are caused by the intermixing of adjacent elements of volume. The viscosity and the conduction of heat, the effects of this intermixing, lead to a departure from the simple laws which hold for large wave-lengths. Stationary waves of a length even smaller than s , and yet following more or less the ordinary rules, are entirely out of the question. Indeed under these circumstances the greater part of the molecules that enter a layer of thickness $\frac{1}{2}\lambda$ or $\frac{1}{4}\lambda$ would traverse it without a collision. We cannot say any longer that one layer exerts a pressure on another; on the contrary, the molecular motion will cause a rapid mixing up of the layers.

Now, the smallest wave-length λ_0 introduced by LENZ is not much greater than the distance d of the molecules, while the mean free path s can be a considerable multiple of d . We therefore come to the conclusion that, of the modes of vibration which he considers in his theory, those with a wave-length near the lower limit λ_0 cannot really exist.

SOMMERFELD¹⁾ has tried to meet this objection by observing that neither at somewhat high temperatures, nor at very low ones we need fear considerable errors in LENZ's formulae. For high temperatures they agree with those which may be derived from the ordinary theory of gases and LENZ's equations show that at low temperatures the energy becomes more and more concentrated in the modes of vibration of large wave-length to which our objection does not apply. This is so indeed, but a simple calculation shows that it is not until the temperature is extremely low, that the greater part of the energy will have shifted to waves considerably longer than λ_0 .

According to LENZ's theory the energy belonging to the modes of vibration with wave-lengths between λ and $\lambda + d\lambda$ is given by

$$4\pi h\nu \cdot \frac{1}{\frac{2hc}{e^{k\lambda T} - 1}} \cdot \frac{d\lambda}{\lambda^5}.$$

We shall use this expression to seek a certain mean wave-length λ' which we define by the condition that the energy corresponding

¹⁾ L.c., p. 141, 142.

to the motions with wave-lengths beneath λ' has the same magnitude as that belonging to wave-lengths beyond λ' . This is expressed by the equation

$$\int_{\lambda'}^{\infty} \frac{1}{e^{\frac{2hc}{\lambda' T}} - 1} \cdot \frac{d\lambda}{\lambda^5} = \frac{1}{2} \int_{\lambda_0}^{\infty} \frac{1}{e^{\frac{2hc}{\lambda T}} - 1} \cdot \frac{d\lambda}{\lambda^5},$$

or if we put

$$\frac{2hc}{k\lambda T} = x, \quad \frac{2hc}{k\lambda_0 T} = x_0 \text{ and } \frac{2hc}{k\lambda' T} = x' \quad . \quad . \quad . \quad (8)$$

by

$$\int_0^{x'} \frac{x^3 dx}{e^x - 1} = \frac{1}{2} \int_0^{x_0} \frac{x^3 dx}{e^x - 1} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From this equation we can derive by suitable approximations for each x_0 the corresponding x' . If now we consider a gas of definite density, d and therefore λ_0 are given and we can determine the value of x_0 for each temperature T . It is true that the second of the equations (8) does not suffice for this, as c depends, in the way indicated by (7), on E , which is a complicated function of T . But LENZ gives the formula

$$x_0^5 = \frac{\Theta}{T} \int_0^{x_0} \frac{x^3 dx}{e^x - 1} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which can be used to determine x_0 . The quantity

$$\Theta = \frac{18\alpha h^2}{mk\lambda_0^3} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

is a certain temperature which can be indicated for each gas as soon as its density is given. After having chosen T , we find x_0 from (10), x' from (9) and finally λ' from the relation

$$\lambda' = \frac{x_0}{x'} \lambda_0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

following from (8).

Let us consider as an example helium of the density corresponding to 0° C. and 1 atm. Then $\Theta = 7^\circ$ and according to (10) $x_0 = 1$, if $\frac{T}{\Theta} = 0,22$; for we have

$$\int_0^1 \frac{x^3 dx}{e^x - 1} = 0,22.$$

From (9) we find approximately $x' = 0,75$, so that (12) gives

$$\lambda' = \frac{4}{3} \lambda_0.$$

So we see that at the temperature $T = 0,22 \Theta = 1^\circ,5$, which is very low indeed, still half of the energy belongs to modes of motion with wave-lengths below $\frac{4}{3} \lambda_0$, i.e. below $1,5\theta$ and therefore far below the mean free path s .

§ 8. According to the theory of LENZ the entropy of a gas does not depend on E and v in the way expressed by (1); the equation of state and the formulae for the specific heats become different from those in the ordinary theory of gases. For temperatures high compared with Θ however we are led back to the form (1). For then we find from LENZ's formulae

$$E = \frac{3}{2} kNT \left(1 - \frac{1}{8} \sqrt{\frac{3\Theta}{T}} \right),$$

$$S = 3kN \left(\frac{4}{3} - \frac{1}{2} \log \frac{\Theta}{3T} \right), \quad (13)$$

and after some reductions

$$S = kN \left\{ \frac{3}{2} \log (2 \pi Em) + \log v - \frac{3}{2} \log \left(\frac{3}{2} N \right) - \log N \right. \\ \left. - \frac{1}{2} \log (12000 \pi) + 4 - 3 \log h \right\},$$

This agrees with the formula of TETRODE [(6) above] if we put $\omega = 3,5$.

It must, however, be remarked that, even if one leaves aside the first of the objections mentioned in § 7, one cannot expect a somewhat exact determination of the chemical constant. Equation (13) shows that this constant is connected with $\log \Theta$ and therefore on account of (11) with $\log \lambda_0$, λ_0 being the minimum wave-length, and we have seen already that the part of the theory relating to the smaller wave-lengths is the most contestable one.

§ 9. TETRODE has determined the chemical constant for the monatomic vapour of mercury, a substance whose properties are well known, or rather he has derived the coefficient ω of equation (6) from the results of observation. He found ¹⁾

$$\omega = 1,05.$$

Following the same course of thought and using the same data

¹⁾ Ann. d. Phys., **39** (1912), p. 255.

I have repeated this determination in the following somewhat different way. I shall consider a gram molecule, so that N becomes AVOGADRO's constant and kN the gas constant R .

Let, at the temperature T , p be the vapour pressure of fluid mercury, S the entropy of the vapour, S' that of the fluid, v the volume of the vapour and v' that of the fluid. Then we have according to a well known thermodynamic relation

$$S - S' = (v - v') \frac{dp}{dT},$$

for which we may write

$$S - S' = v \frac{dp}{dT},$$

as v is much greater than v' .

If the vapour pressure is very low we may treat the vapour as an ideal gas, so that

$$v = \frac{RT}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$S - S' = RT \frac{d \log p}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If now in (6) we substitute R for kN , (14) for v , $\frac{M}{N}$ for m , M being the molecular weight, and $\frac{3}{2} RT$ for E , we get

$$S = R \left\{ \frac{5}{2} \log(RT) - \log p - 4 \log N + \frac{3}{2} \log(2\pi M) + \frac{5}{2} - 3 \log(\omega h) \right\}.$$

By substituting this in (15) we find

$$3 \log \omega = -\frac{S'}{R} - \frac{d}{dT} (T \log p) + A, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where for shortness' sake I have put

$$A = \frac{5}{2} \log(RT) - 4 \log N + \frac{3}{2} \log(2\pi M) + \frac{5}{2} - 3 \log h \quad . \quad (17)$$

This quantity is completely known. Thus we can calculate the coefficient ω as soon as we know p as a function of T and besides the entropy S' of the fluid.

§ 10. For the pressure we may use HERTZ's formula¹⁾

$$\log p = a - \beta \log T - \frac{\gamma}{T}.$$

¹⁾ H. HERTZ, Ann. d. Phys., 17 (1882), p. 193.

with ¹⁾ $\alpha = 31,583$; $\beta = 0,847$; $\gamma = 7697$, from which we draw

$$\frac{d}{dT} (T \log p) = (\alpha - \beta) - \beta \log T. \quad (18)$$

To be able to determine S' too, we shall take for T the melting point of mercury (234°). If r is the heat of fusion and S'' the entropy of solid mercury we have

$$S' = S'' + \frac{r}{T}. \quad (19)$$

We must remark here that strictly speaking this formula gives the value of S' for a pressure of 1 atm. (if we consider the equilibrium between solid and fluid mercury under that pressure), while in the preceding equations S' denotes the entropy of the fluid under the pressure of its vapour. It is easily seen that we may neglect this difference.

It remains to determine the entropy S'' of solid mercury. This can be found by supposing, as is often done in connection with NERNST's heat theorem, that this entropy is 0 at the absolute zero. Then it can be calculated for any other temperature by means of the specific heat c_p of solid mercury. We have

$$S'' = \int_0^T \frac{c_p}{T} dT, \quad (20)$$

if we assume the pressure to be 1 atm. during the heating from 0° to T° .

NERNST ²⁾ has given a formula for the specific heat of a gram molecule, based on POLLITZER's measurements and by means of which we find ³⁾

¹⁾ According to HERTZ we have, using Briggian logarithms and expressing the vapour pressure in millimetres of mercury

$$\log p = 10,59271 - 0,847 \log T - \frac{3342}{T}.$$

If we want to know the pressure in dynes per cm^2 , we must add $\log 1330$, as a pressure of 1 mm. of mercury corresponds to 1330 dynes per cm^2 . To pass finally to Neperian logarithms we must divide the first and the third term by $\log_{10} e$.

²⁾ Ann. d. Phys., **36** (1911), p. 431.

³⁾ According to NERNST we have in C.G.S. units

$$c_v = \frac{3}{2} R [\varphi(\sigma) + \varphi(\frac{1}{2}\sigma)],$$

where the function φ is determined by

$$S'' = 6,95 R.$$

Now the heat of fusion per gram molecule is 554,5 cal. so that $r = 279 R$,

$$\frac{r}{T} = 1,19 R$$

and, according to (19),

$$S' = 8,14 R.$$

From (18) follows

$$\frac{d}{dT} (T \log p) = 26,12$$

and from (17) ¹⁾

$$A = 33,92.$$

Substituting these different values in (16) we find

$$\omega = 0,7.$$

§ 11. As to the degree of precision of this result it must be remarked in the first place that, according to (16) and (17), ω is proportional to low powers of RT , n and h . Therefore, an uncertainty in the values of these quantities will not cause an error of many percentages in ω .

$$\varphi(x) = \frac{\left(\frac{x}{T}\right)^2 \frac{x}{e^T}}{\left(\frac{x}{e^T} - 1\right)^2}.$$

For mercury σ must be put equal to 97. Further

$$c_p = c_v + fT^{3/2}.$$

For the coefficient f NERNST gives $21 \cdot 10^{-5}$, but here a calory is taken as unit of heat. Choosing the erg instead and substituting gR for f , so that

$$c_p = c_v + RgT^{3/2}$$

we have

$$g = 10,6 \cdot 10^{-5}$$

From (20) we now find

$$S'' = \frac{3}{2} R [\chi(\sigma) + \chi(\frac{1}{2}\sigma)] + \frac{2}{3} RgT^{3/2}.$$

if we put

$$\chi(x) = \frac{\frac{x}{T} \cdot e^{\frac{x}{T}}}{e^{\frac{x}{T}} - 1} - \log \left(\frac{x}{e^{\frac{x}{T}}} - 1 \right).$$

¹⁾ Calculated with: $R = 83,2 \cdot 10^6$; $N = 67 \cdot 10^{23}$; $M = 200$; $h = 6,42 \cdot 10^{-27}$.

On the contrary the value substituted for $\frac{S'}{R}$ may be in error to a considerable extent. A change of a full unit however in this value (one eighth of the amount) produces a change in ω of about 14% only. So we may perhaps conclude that the value of ω will not differ much from 1 and that the values found for the vapour pressure of mercury agree in a rather satisfactory way with the theory of TETRODE, if we give the elementary domain G the value h^3 ¹⁾.

Nevertheless, in my opinion, we may not attach much value to this result. Besides the difficulties which we pointed out already there is still another serious objection.

Formula (15) connects the vapour pressure with the entropy-difference between gaseous and fluid mercury or, when we take into account the relation (19), with the difference between gaseous and solid mercury. Now we must doubt seriously whether this *difference* can be rightly evaluated if the undeterminate constants in S and S'' are fixed in the above mentioned rather arbitrary way. On the ground of BOLTZMANN'S formula we may account for the entropy S'' , viz. for the *change* which the entropy of solid mercury undergoes when heated from 0° to T° ; to this effect we have to compare the probabilities of different states of the solid mercury. This is done e.g. by DEBYE in his theory of specific heats. In this comparison we are concerned only with quantities referring to the solid state, e.g. the modulus of elasticity. In the deduction of (6), on the other hand, only the gaseous state has been considered. The question arises whether it will be possible, by a combination of these results, to determine the difference $S-S''$, which according

¹⁾ The objection might be raised that in the above calculation HERTZ'S formula for the vapour pressure has been applied for a temperature at which this pressure has never been measured. In reality however the value of ω given by (16), (17) and (18) is independent of the choice of the temperature.

Indeed, the differential coefficient of the right hand side of (16) with respect to T is

$$-\frac{1}{R} \frac{dS'}{dT} - \frac{d^2}{dT^2} (T \log p) + \frac{5}{2T}$$

$\left(T \frac{dS'}{dT} \right.$ is the specific heat of the fluid under its vapour pressure). According to a well known thermodynamic theorem this quantity must be zero. In virtue of (18) it becomes

$$-\frac{1}{R} \frac{dS'}{dT} + \frac{\beta}{T} + \frac{5}{2T}$$

and this expression really is zero because HERTZ has chosen the coefficient β in accordance with the theorem in question.

to BOLTZMANN's theorem is connected with the probability that, in a system consisting of a solid and a gaseous phase, a greater or a smaller part belongs to the latter. The circumstance that, in considering this latter probability, we must attend to the difference in potential energy of the two phases cannot but increase our doubt, for neither in the determination of S'' nor in the determination of S in the above mentioned way we have had to speak of this difference. If, as we should expect, the difference $S-S''$ depended to a considerable extent on the relative values of the potential energy, we might still put the entropy $S''=0$ for $T=0$, but it would no longer be possible to determine the constant a which occurs in formula (1) for the gaseous state by considering only the phenomena in the gas, as is done in the theories discussed here. We ought rather to derive it from an examination of the equilibrium between the two phases.

I think we may conclude from what precedes that, though the value found for ω , if it be not quite accidental, pleads in favour of the application of the theory of quanta to the problem of vaporisation, yet the way in which this application has been made requires further explanation and justification.

Physics. — “On HAMILTON's principle in EINSTEIN's theory of gravitation”. By H. A. LORENTZ.

(Communicated in the meeting of January 30, 1915).

The discussion of some parts of EINSTEIN's theory of gravitation¹⁾ may perhaps gain in simplicity and clearness, if we base it on a principle similar to that of HAMILTON, so much so indeed that HAMILTON's name may properly be connected with it. Now that we are in possession of EINSTEIN's theory we can easily find how this variation principle must be formulated for systems of different nature and also for the gravitation field itself.

Motion of a material point.

§ 1. Let a material point move under the influence of a force with the components K_1, K_2, K_3 . Let us vary every position x, y, z

¹⁾ EINSTEIN u. GROSSMANN, Entwurf einer verallgemeinerten Relativitätstheorie und einer Theorie der Gravitation. Zeitschr. f. Math. u. Phys. 62, (1914), p. 225.

EINSTEIN, Die formale Grundlage der allgemeinen Relativitätstheorie, Sitz. Ber. Akad. Berlin, 1914, p. 1030.