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high. We are uncertain as to the cause of this difference: most probably it is due to an uncertainty in the temperature with the absolute manometer.

It is of special interest to compare these observations with NERNST's formula. The fourth column of Table II contains the pressures according to this formula, calculated with the constants which FALCK¹⁾ has determined with the data at his disposal. FALCK found the following expression

$$\log p = -\frac{6000}{4,571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0,009983}{4,571} T + 3,1700$$

where p is the pressure in atmospheres.

The correspondence will be seen to be satisfactory considering the degree of accuracy of the observations. It does not look as if the constants could be materially improved.

Physics. — “*On the equation of state of an ideal monatomic gas according to the quantum-theory.*” By Dr. W. H. KEESOM. Supplement N^o. 30a to the Communications from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of May 31, 1913).

§ 1. *Introduction.* Summary. DEBIJE²⁾ has shown that agreement with the observations concerning the specific heat of solid substances can be obtained by modifying the theory of EINSTEIN³⁾ in this sense, that the formula⁴⁾ which PLANCK has given for the mean energy at the temperature T of a linear electrical oscillator is applied to the different principal modes of vibration of a solid.

It seems natural to apply the same principle to other material systems which can behave as an oscillator and hence to investigate the correctness of the consequences which follow from the hypothesis

¹⁾ FALCK: Physik. Zeits. 1908, p. 433.

²⁾ P. DEBIJE. Ann. d. Phys. (4) 39 (1912), p. 789.

³⁾ For the literature see: H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N^o. 23, § 74c.

⁴⁾ DEBIJE makes use of the original formula of PLANCK, Wärmestrahlung, 1^{ste} Aufl., p. 157. The more recent formula, Wärmestrahlung, 2^{te} Aufl., p. 140, which differs from the first by the introduction of a zero point energy, leads to the same results as regards the specific heat as long as the frequencies do not depend upon the temperature. For processes in which the frequencies change, cf. P. DEBIJE, Programme for the WOLFSKEHL lecture, Physik. ZS. 14 (1913), p. 259, it can give diverging results for solids too.

that PLANCK's principle of finite elements of energy holds for each principal mode of vibration of an oscillator whose motions can be described by linear differential equations, whatever its constitution may otherwise be.

In this paper those consequences will be deduced for an ideal monatomic gas. Similar applications of the quantum-theory to an ideal monatomic gas were already made by TETRODE¹⁾ and by LENZ²⁾. SACKUR³⁾ also makes use of the quantum-theory for the deduction of the equation of state, but in a different way.

The deductions of TETRODE and of LENZ are based on the supposition that each principal mode of vibration of a gas enclosed in a given vessel exchanges its energy by whole energy elements at once. If this supposition is accepted it can be made probable by contemplating the exchange of energy between the gas and the radiation which is in equilibrium with it, that these energy elements have a magnitude $\frac{1}{2} h\nu$, ν being the frequency of the (longitudinal) waves in the gas, h the well known PLANCK's constant. The mean "temperature energy" per mode of vibration is then found to be

$$\frac{1}{2} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

k being the well known constant of BOLTZMANN's entropy

principle.

As Prof. KAMERLINGH ONNES and I communicated to the WOLFSKEHL congress last month, this treatment gives results which do not conflict with observations on the equation of state of helium only⁴⁾ on the condition that, in writing down the mean energy per mode of vibration for an ideal gas, a *zero point energy* to an amount of $\frac{1}{4} h\nu$ is added to the above-mentioned expression for the temperature energy⁵⁾. The same zero point energy was recently assumed for

¹⁾ H. TETRODE. Physik. ZS. 14 (1913), p. 212.

²⁾ Cf. A. SOMMERFELD, Programme for the WOLFSKEHL lecture, Physik. ZS. 14 (1913), p. 262.

³⁾ O. SACKUR. Jahresber. der Schles. Gesellschaft für vaterl. Cultur, Febr. 1913.

⁴⁾ Viz. on the supposition that the determination of the frequencies of a gas in a way corresponding to that which DEBIJE follows for a solid may be considered as approximately correct.

⁵⁾ Hence the fundamental assumptions of this paper diverge from those of TETRODE and of LENZ by the introduction of the zero point energy, from those of LENZ moreover by the fact (§ 2), that for the magnitude of the energy elements $\frac{1}{2} h\nu$ is accepted.

the molecular rotations by EINSTEIN and STERN¹⁾ for the explanation of the behaviour of the specific heat of hydrogen.

The supposition of a zero point energy corresponds to the newest ideas of PLANCK, according to which an electrical oscillator absorbs energy from radiation continuously, but emits energy by whole quanta at once. According to the fundamental hypothesis underlying this paper, a similar behaviour should therefore be made also for the ideal gas.

In order to be able to write down an expression for the total energy of the whole system we need the knowledge of the "spectrum" of the gas. We will suppose, that this spectrum can be determined in a way corresponding to that in which the spectrum of a solid is determined by DEBYE.

With these data the equation of state of an ideal monatomic gas can be deduced, and then all thermodynamic quantities for such a gas can be derived. The pressure is found²⁾ to be greater than the "equipartition value" $p = RT/v$; at high temperatures it deviates little from this value, the ratio of this deviation to the value itself approaching ultimately indefinitely to 0; at low temperatures, if the gas may then still be treated as an ideal one, the pressure approaches to a value which depends upon the molecular weight and upon the density, but does not depend upon the temperature. That value we call the *zero point pressure*.

For a gas like helium at normal density and say 0° C. the deviation from the equipartition value appears to be still small. It has, however, already such a value that for instance in determining the VAN DER WAALS quantities a_w and b_w , or in the discussion of the virial coefficients, as was done for the second one in Suppl. N^o. 25 (Sept. '12) and N^o. 26 (Oct. '12), that deviation has to be taken into account. The zero point pressure for helium at normal density is found to be $1/4$ mm. At greater densities deviations from the equipartition laws become more important.

For the specific heat at constant volume of a gas like helium (supposed to be ideal) at normal density an appreciable deviation from the constant equipartition value is found only at extremely low temperatures³⁾. Ultimately the specific heat also decreases and

¹⁾ A. EINSTEIN and O. STERN. Ann. d. Phys. (4) 40 (1913), p. 551. SACKUR, l.c., assumes the zero point energy also, as is done in this paper, for the molecular translations.

²⁾ Cf. O. SACKUR, l.c.

³⁾ That the specific heat of monatomic gases deviates from the equipartition value in an appreciable measure only at extremely low temperatures was already predicted by NERNST and LINDEMANN, ZS. f. Electrochem. 17 (1911), p. 826, note 1; NERNST, Physik. ZS. 13 (1912), p. 1066. [Note added in the translation.]

approaches to 0. The suppositions underlying the deductions of this paper imply that also for ideal gases NERNST's heat theorem is valid.

The results derived in this paper for an ideal gas may also be of value for the theory of free electrons in metals. For this we refer to the next paper.

§ 2. *The energy elements.* We may imagine the equilibrium between radiation and molecular translatory motion in an ideal¹⁾ monatomic gas enclosed in a given vessel to be brought about in the following way: let the vessel which contains the gas be surrounded totally or partially by a vessel which contains radiation. The walls of the latter vessel are thought to be perfectly reflecting on the inner side. In the wall which is common to the two vessels a cylindrical hole is made, in which moves a piston (reflecting on the side of the radiation). This piston is held, e.g. by a suitable constructed spring, in such a way that under the action of the pressure of those rays which have a frequency ν' it is forced to vibrate. We may interpret the newest theory of PLANCK so that exchange of energy (absorption as well as emission) takes place only by whole quanta at once, if we take care to add the zero point energy to the value of the energy at equilibrium of an oscillator derived on that supposition. So we may suppose that those rays can give their energy to the piston only by quanta of magnitude $h\nu'$. The pressure of radiation, being proportional to the product of electric and magnetic force, has the frequency $\nu = 2\nu'$. The piston is forced to vibrate with the same frequency under the action of the pressure.

We suppose ν' to be chosen in such a way that ν is a principal frequency of the gas. The motion of the piston will then excite vibrations in the gas of the same frequency ν . We will suppose that the piston can transfer the quanta $h\nu'$ immediately to the gas in the form of energy of rays with its frequency ν (whether the piston transfers all the quanta, which it receives, in this form, or only part of them, and perhaps remits another part to the radiation, is immaterial). A mode of vibration ν of the gas then receives energy by quanta $h\nu' = \frac{1}{2} h\nu$.

The reverse, *viz.* transfer of energy of a mode of vibration ν in the gas by the aid of the above-mentioned piston to the mode of vibration ν' in the radiation must also be assumed, in fact in the case of equilibrium to the same amount per unit of time. We could

¹⁾ By this I understand in this paper a gas such, that the volume of the molecules themselves and their mutual attraction need not be considered.

imagine that the energy transferred to the gas in the first process is remitted to the radiation by another way, *e.g.* with another frequency. In this case energy would, however, move continuously in a cycle. This one will not feel inclined to accept.

In the way indicated above, say by the application of a sufficient number of similar pistons, the equilibrium with the radiation can be brought about for all principal frequencies of the gas. If there are still other ways in which energy can be transferred from radiation to the gas molecules or vice versa, the nature of the equilibrium will presumably not be changed thereby.

The result of these considerations is that we shall admit — in so far as the above argument is not considered sufficiently cogent we will put as a hypothesis which may be justified or not in its consequences — that in the equilibrium between the molecular translatory motion in a gas and radiation energy elements of a magnitude $\frac{1}{2} h\nu$ play a part, if ν is a principal frequency of the gas.

§ 3. *The energy and the entropy of an ideal monatomic gas.* In calculating the mean¹⁾ energy and entropy to be ascribed to a definite mode of vibration with frequency ν of the gas, we follow the reasoning which PLANCK, *Wärmestrahlung* 2^{te} Aufl. § 135—143 follows for ideal linear electrical oscillators. Considering that for the gas according to § 2 we have to do with energy elements $\frac{1}{2} h\nu$ we obtain (cf. PLANCK *l.c.* equation (22)):

$$s_\nu = k \left\{ \left(\frac{2u_\nu}{h\nu} + \frac{1}{2} \right) \ln \left(\frac{2u_\nu}{h\nu} + \frac{1}{2} \right) - \left(\frac{2u_\nu}{h\nu} - \frac{1}{2} \right) \ln \left(\frac{2u_\nu}{h\nu} - \frac{1}{2} \right) \right\}. \quad (1)$$

where s_ν and u_ν represent the mean entropy and energy for the mode of vibration considered.

The temperature T is determined by $\left(\frac{\partial s_\nu}{\partial u_\nu} \right) = \frac{1}{T}$. In this differentiation at constant volume the wave-length λ remains constant; ν is connected with λ by the relation $\nu = c/\lambda$, c representing the velocity of propagation. In § 4 it will appear that in the gas, when in thermodynamic equilibrium, on the suppositions for which the simple laws of propagation of sound hold, c is proportional to $U^{1/2}$, also when equipartition does not hold, where U is the total energy of molecular translatory motion of the gas. We will now assume that for each mode of vibration we may put $c = u^{1/2}$. This hypothesis is inconsistent with observations for vibrations which we can observe as sound, *e.g.* for vibrations with small amplitude, if they are

¹⁾ Numerical mean if we think the gas to be repeated many times.

considered isolated. For vibrations with very small wave-lengths, which are here the most important, it may, however, be assumed to hold, in connection with their relation to heat motion, at least as an approximate hypothesis for states which differ only little from the state of equilibrium. It then follows¹⁾ that

$$u_\nu = \frac{1}{2} \left\{ \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} h\nu \right\} \dots \dots \dots (2)$$

As the different modes of vibration, which are possible in a gas enclosed in a given vessel, must be supposed to have the same T in the state of equilibrium, equation (2) at the same time represents the part which each mode of vibration in the gas in the state of equilibrium at the temperature T contributes to the whole energy.

We now assume that we obtain an approximately correct value for the whole energy if, in a way corresponding to that which DEBJÆ follows for a solid, we suppose the number of different principal modes of vibration which are contained in the region determined by the frequencies ν and $\nu + d\nu$ to be equal to²⁾

$$\frac{4\pi V}{c^3} \nu^2 d\nu \dots \dots \dots (3)$$

and cut off the so determined "spectrum" at ν_m , given by putting the total number of modes of vibration equal to the number of degrees of freedom $3N$. V represents the volume of the gramme-molecule of the gas, N is the number of AVOGADRO. We then obtain:

$$U = \frac{9N}{2\nu_m^3} \int_0^{\nu_m} \left\{ \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} h\nu \right\} \nu^2 d\nu, \dots \dots \dots (4)$$

where ν_m is determined by

$$\nu_m^3 = \frac{9}{4\pi} \frac{N}{V} c^3 \dots \dots \dots (5)$$

For the total entropy an expression can now also be easily given.

¹⁾ As SOMMERFELD *loc. cit.* observes, the hypothesis mentioned above causes as it were automatically that at high temperatures the mean energy per degree of freedom becomes $= \frac{1}{2} kT$, as it must be for the molecular translatory motion. For the difference of equation (2) from the corresponding one of LENZ cf. p. 228 note 5.

²⁾ In accordance with a remark by TETRODE, *l.c.* this expression can be easily deduced for a cubical vessel from the formula for the wave-lengths occurring in it: RAYLEIGH, *Theory of Sound II*, 2nd ed. London 1896 p. 71.

§ 4. *The pressure. a.* We will assume that the relation

$$p = \frac{2}{3} \frac{U}{V}, \dots \dots \dots (6)$$

as depending on the isotropy of molecular motion and on the elementary fundamental law of dynamics regarding the connection between force and momentum, remains generally valid. As TETRODE l. c. shows, we have then also in general

$$c^2 = \frac{10}{9} \frac{U}{M}, \dots \dots \dots (7)$$

M being the molecular weight. By (4), (5), (6) and (7) the equation of state of the ideal monatomic gas is given.

It is easily demonstrated, that the expression for the entropy deduced from (1) is consistent with this equation¹⁾.

If we introduce

$$\frac{h\nu}{kT} = \xi, \frac{h\nu_m}{kT} = x, \dots \dots \dots (8)$$

we obtain

$$U = \frac{9}{2} Nk T \left\{ \frac{1}{8} x + \frac{1}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \right\} \dots \dots \dots (9)$$

By introducing the "characteristic temperature" θ , determined by

$$\theta = \frac{h\nu_m}{k} = \frac{h}{k} \cdot \left(\frac{9}{4\pi} \frac{N}{V} \right)^{1/3} \cdot \left(\frac{10}{9} \frac{U}{M} \right)^{1/2}, \dots \dots \dots (10)$$

we can write

$$x = \frac{\theta}{T} \dots \dots \dots (11)$$

b. High temperatures. Developing for high temperatures²⁾, we obtain

$$U = \frac{3}{2} Nk T \left\{ 1 + \frac{3}{5} \frac{B_1}{2!} x^2 - \frac{3}{7} \frac{B_2}{4!} x^4 + \frac{3}{9} \frac{B_3}{6!} x^6 \dots \right\} \dots \dots \dots (12)$$

where $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$, $B_3 = \frac{1}{42}$ are the BERNOULLIAN coefficients, or

$$U = \frac{3}{2} Nk T \left\{ 1 + \frac{1}{20} x^2 - \frac{1}{1680} x^4 + \frac{1}{90720} x^6 \dots \right\} \dots \dots \dots (13)$$

Limiting ourselves to the two first terms the pressure becomes

$$p = \frac{Nk T}{V} \left\{ 1 + \frac{1}{20} \frac{\theta^2}{T^2} \right\} \dots \dots \dots (14)$$

and according to (10), substituting for U only the first term of (13):

¹⁾ Cf. H. TETRODE, l. c.

²⁾ According to DEBIJE l. c. this development is suitable from $x=0$ to $x=2$.

$$\theta_{(T \gg \theta)} = \frac{h}{k} \cdot \left(\frac{9 N}{4\pi V} \right)^{1/3} \cdot \left(\frac{5 N k T}{3 M} \right)^{1/2} \dots \dots (15a)$$

Taking $N = 6,85 \cdot 10^{23}$, $\frac{h}{k} = 4,86 \cdot 10^{-11}$, $k = 1,21 \cdot 10^{-16}$, we obtain

$$\theta_{(T \gg \theta)} = 45,1 \cdot M^{-1/2} V^{-1/3} T^{1/2} \dots \dots (15b)$$

$\theta_{(T \gg \theta)}$ is connected with θ_0 to be introduced in c by the relation

$$\theta_{(T \gg \theta)} = \left(\frac{8}{3} \theta_0 T \right)^{1/2} \dots \dots (15c)$$

For helium at 0° C. and 1 atm. we find $\theta = 13.2$. From (14) follows a deviation from BOYLE'S law to an amount of 0.12% . This deviation is in the direction found by experiment and has such an amount that with reasonable suppositions about the VAN DER WAALS constants it is not in conflict with the value experimentally observed¹⁾: 0.512% . On the other hand there would have been contradiction if in the expression (2) for the energy the zero point energy had not been taken up. This, and a similar result concerning the pressure coefficient of helium between 0° and 100° C. were the reasons which led Prof. KAMERLINGH ONNES and me in our communication to the WOLFSKEHL-congress to the hypothesis of the zero point energy for an ideal gas.

Although the deviation from BOYLE'S law, which follows from the application of the quantum-theory in the way explained in this paper, is still small in the special case discussed above, it nevertheless appears (and for greater densities this is even more the case), that in discussing the equation of state this deviation has to be taken into account. Further discussion in this direction has to be postponed, however, to a later communication.

c. Low temperatures. For low temperatures the following development²⁾ is more appropriate:

$$U = \frac{9}{2} NkT \left\{ \frac{1}{8} x + \frac{\pi^4}{15 x^3} - x \sum_{n=1}^{\infty} e^{-nx} \left(\frac{1}{nx} + \frac{3}{n^2 x^2} + \frac{6}{n^3 x^3} + \frac{6}{n^4 x^4} \right) \right\}, (16)$$

with x according to (11) and (10). The first two terms give ($T \ll \theta$):

$$U = \frac{9}{16} Nk\theta_0 \left\{ 1 + \frac{16\pi^4 T^4}{15 \theta_0^4} \right\}, \dots \dots (17)$$

where

$$\theta_0 = \frac{h^2}{k^2} \cdot \left(\frac{9 N}{4\pi V} \right)^{2/3} \frac{5 N k}{8 M} \dots \dots (18a)$$

or (cf. *b*)

$$\theta_0 = 761 \cdot M^{-1} V^{-2/3} \dots \dots (18b)$$

¹⁾ H. KAMERLINGH ONNES, Comm. N^o. 102a, Dec. 1907.

²⁾ According to DEBYE, l.c., suitable from $x = \infty$ to $x = 2$.

For the pressure p is found:

$$p = \frac{3}{8} \frac{Nk\theta_0}{V} \left\{ 1 + \frac{16\pi^4 T^4}{15 \theta_0^4} \right\} \dots \dots \dots (19)$$

For helium at normal density $\theta_0 = 0.239$. Hence formula (17) could be valid for helium at normal density at extremely low temperatures only. At these low temperatures helium at that density can no longer exist as an ideal gas. If we call *zero point pressure*, the value which p according to (19) assumes for $T=0$, p_0 is a quantity which immediately enables us to get an estimate of the deviations from the CHARLES'S law which are to be expected at low temperatures. For helium at normal density the zero point pressure is found to be ¹⁾ 332 baryes = 0.25 mm. If from this we deduced the temperature according to $p = RT/v$, a temperature $\frac{3}{8} \theta_0 = 0^\circ.09$ would correspond to it. The error in the reading of such a thermometer, which would occur according to the above application of the quantum-theory, will remain below this amount.

For the purpose of the theory of free electrons in metals we write (19) in the form ²⁾

$$p = a V^{-1/3} + b T^4 V, \dots \dots \dots (20)$$

where a and b are constants whose values can be easily derived. It is easily verified that the first term of (20) does not cause any decrease of temperature at adiabatic expansion: external work done at $T=0$ at the expense of the zero point energy.

§ 5. *The specific heat. a.* From (4) the specific heat at constant volume can be derived: for this purpose it is to be taken into consideration that v_m depends according to (5) and (7) on the temperature ³⁾. We will write down only a few terms of the two corresponding developments.

¹⁾ The result obtained here differs from that obtained by SACKUR l.c., although the above deductions in many respects run parallel to his.

²⁾ The occurrence of the positive power of V gives a warning that the range of validity of this formula at larger V extends to correspondingly lower T only.

³⁾ An expression is found, which can be brought to the following form:

$$\frac{C_v}{C_{v\infty}} = \frac{2}{5} \left(\frac{C}{C_\infty} \right)_{sol} \cdot \frac{\left(\frac{C}{C_\infty} \right)_{sol} + \frac{3}{2} x \frac{e^x + 1}{e^x - 1}}{\left(\frac{C}{C_\infty} \right)_{sol} + \frac{3}{10} x \frac{e^x + 1}{e^x - 1}}$$

For the values of $\left(\frac{C}{C_\infty} \right)_{sol}$, i.e. the ratio of the specific heat for a solid belonging to its limiting value at high temperatures see DEBJE l.c. p. 803, or NERNST, in Sitz.-Ber. 5 Dec. 1912.

b. High temperatures. For high temperatures ($T \gg \theta$) we find:

$$C_v = \frac{3Nk}{2} \left(1 - \frac{1}{525} \frac{\theta^4}{T^4} \right) \dots \dots \dots (21)$$

Hence the deviation in the specific heat is of a smaller order of magnitude than that in the pressure. The temperature at which C_v deviates 1% from the constant equipartition value, is determined by $x = 0,85$. For helium at normal density this temperature is found to be $T = 0,9$; hence except at a considerably larger density a deviation of the specific heat from the equipartition value could not be observed experimentally.

c. Low temperatures. For the theory of free electrons in metals it is of interest to develop the formula for the specific heat at low temperatures. From (17) we find immediately ($T \ll \theta_0$):

$$C_v = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_0} \right)^3 = \frac{8\pi^4}{5} C_{v\infty} \left(\frac{T}{\theta_0} \right)^3 \dots \dots \dots (22)$$

$C_{v\infty}$, the value to which C_v approaches at high T , being one half of the corresponding value for a solid the multiplicand of $\left(\frac{T}{\theta_0} \right)^3$ is equal to that for a solid: cf. DEBJE, *l.c.* p. 800.

From (20) in connection with (22) it follows on account of the well known thermodynamic relation between C_p and C_v that their ratio α approaches to the value 1 as T approaches to 0.

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§ 1. *Introduction. Summary.* It seems natural to transfer to the theory of free electrons¹⁾ in metals the considerations of the former paper regarding the application of the quantum-theory to the equation of state of an ideal monatomic gas. The frequencies in an electron

¹⁾ PLANCK, Berlin Sitz.-Ber. April 3, 1913, has recently treated the equilibrium between oscillators, free electrons and radiation on very special suppositions, which for the free electrons lead to the equipartition laws. The mode of treatment followed in this paper may in some measure be considered as the reverse of that by LORENTZ, These Proceedings April 1903, where from the motions of the free electrons (in the case of equipartition) he deduced the law of radiation (which holds in that case).