1 On an Improvement of Wien's Equation for the Spectrum†

M. PLANCK

THE interesting results of long wave length spectral energy measurements which were communicated by Mr. Kurlbaum at today's meeting, and which were obtained by him and Mr. Rubens, confirm the statement by Mr. Lummer and Mr. Pringsheim, which was based on their observations that Wien's energy distribution law is not as generally valid, as many have supposed up to now, but that this law at most has the character of a limiting case, the simple form of which was due only to a restriction to short wave lengths and low temperatures.‡ Since I myself even in this Society have expressed the opinion that Wien's law must be necessarily true, I may perhaps be permitted to explain briefly the relationship between the electromagnetic radiation theory developed by me and the experimental data.

The energy distribution law is according to this theory determined as soon as the entropy S of a linear resonator which interacts with the radiation is known as function of the vibrational energy U. I have, however, already in my last paper on this subject[1] stated that the law of increase of entropy is by itself not yet sufficient to determine this function completely; my view that Wien's law would be of general validity, was brought about rather by special considerations, namely by the evaluation of an infinitesimal increase of the entropy of a system of n identical

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† *Verh. Dtsch. Phys. Ges. Berlin* **2,** 202 (1900).

‡ Mr. Paschen has written to me that he has also recently found appreciable deviations from Wien's law.

resonators in a stationary radiation field by two different methods which led to the equation

$$dU_n \,.\, \Delta U_n \,.\, f(U_n) = n\,dU \,.\, \Delta U \,.\, f(U),$$

where $$U_n = nU \quad \text{and} \quad f(U) = -\frac{3}{5}\frac{d^2S}{dU^2}.$$

From this equation Wien's law follows in the form

$$\frac{d^2S}{dU^2} = \frac{\text{const}}{U}.$$

The expression on the right-hand side of this functional equation is certainly the above-mentioned change in entropy since n identical processes occur independently, the entropy changes of which must simply add up. However, I could consider the possibility, even if it would not be easily understandable and in any case would be difficult to prove, that the expression on the left-hand side would not have the general meaning which I attributed to it earlier, in other words: that the values of U_n, dU_n and ΔU_n are not by themselves sufficient to determine the change of entropy under consideration, but that U itself must also be known for this. Following this suggestion I have finally started to construct completely arbitrary expressions for the entropy which although they are more complicated than Wien's expression still seem to satisfy just as completely all requirements of the thermodynamic and electromagnetic theory.

I was especially attracted by one of the expressions thus constructed which is nearly as simple as Wien's expression and which deserves to be investigated since Wien's expression is not sufficient to cover all observations. We get this expression by putting†

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta + U)}.$$

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† I use the second derivative of S with respect to U since this quantity has a simple physical meaning.

It is by far the simplest of all expressions which lead to S as a logarithmic function of U—which is suggested from probability considerations—and which moreover reduces to Wien's expression for small values of U. Using the relation

$$\frac{dS}{dU}=\frac{1}{T}$$

and Wien's "displacement" law† one gets a radiation formula with two constants:

$$E=\frac{C\lambda^{-5}}{e^{c/\lambda T}-1},$$

which, as far as I can see at the moment, fits the observational data, published up to now, as satisfactorily as the best equations put forward for the spectrum, namely those of Thiesen,[2]‡ Lummer–Jahnke,[4] and Lummer–Pringsheim.[5] (This was demonstrated by some numerical examples.) I should therefore be permitted to draw your attention to this new formula which I consider to be the simplest possible, apart from Wien's expression, from the point of view of the electromagnetic theory of radiation.

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† The expression of Wien's displacement law is simply

$$S=f(U/\nu),$$

where ν is the frequency of the resonator, as I shall show elsewhere.

‡ One can see there that Mr. Thiesen had put forward his formula before Mr. Lummer and Mr. Pringsheim had extended their measurements to longer wave lengths. I emphasise this point as I have made a statement to the contrary[3] before this paper was published.

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2 On the Theory of the Energy Distribution Law of the Normal Spectrum†

M. PLANCK

GENTLEMEN: when some weeks ago I had the honour to draw your attention to a new formula which seemed to me to be suited to express the law of the distribution of radiation energy over the whole range of the normal spectrum,[1] I mentioned already then that in my opinion the usefulness of this equation was not based only on the apparently close agreement of the few numbers, which I could then communicate, with the available experimental data,‡ but mainly on the simple structure of the formula and especially on the fact that it gave a very simple logarithmic expression for the dependence of the entropy of an irradiated monochromatic vibrating resonator on its vibrational energy. This formula seemed to promise in any case the possibility of a general interpretation much rather than other equations which have been proposed, apart from Wien's formula which, however, was not confirmed by experiment.

Entropy means disorder, and I thought that one should find this disorder in the irregularity with which even in a completely stationary radiation field the vibrations of the resonator change their amplitude and phase, as long as one considers time intervals long compared to the period of one vibration, but short compared to the duration of a measurement. The constant energy of the

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† *Verh. Dtsch. Phys. Ges. Berlin* **2**, 237 (1900).

‡ In the meantime Mr. H. Rubens and Mr. F. Kurlbaum[2] have given a direct confirmation for very long wave lengths.

stationary vibrating resonator can thus only be considered to be a time average, or, put differently, to be an instantaneous average of the energies of a large number of identical resonators which are in the same stationary radiation field, but far enough from one another not to influence each other. Since the entropy of a resonator is thus determined by the way in which the energy is distributed at one time over many resonators, I suspected that one should evaluate this quantity in the electromagnetic radiation theory by introducing probability considerations, the importance of which for the second law of thermodynamics was first of all discovered by Mr. L. Boltzmann.[3] This suspicion has been confirmed; I have been able to derive deductively an expression for the entropy of a monochromatically vibrating resonator and thus for the energy distribution in a stationary radiation state, that is, in the normal spectrum. To do this it was only necessary to extend somewhat the interpretation of the hypothesis of "natural radiation" which is introduced in electromagnetic theory. Apart from this I have obtained other relations which seem to me to be of considerable importance for other branches of physics and also of chemistry.

I do not wish to give today this deduction—which is based on the laws of electromagnetic radiation, thermodynamics and probability calculus—systematically in all details, but rather to explain as clearly as possible the real core of the theory. This can be done most easily by describing to you a new, completely elementary treatment through which one can evaluate—without knowing anything about a spectral formula or about any theory—the distribution of a given amount of energy over the different colours of the normal spectrum using one constant of nature only and after that also the value of the temperature of this energy radiation using a second constant of nature. You will find many points in the treatment to be presented arbitrary and complicated, but as I said a moment ago I do not want to pay attention to a proof of the necessity and the simple, practical details, but to the clarity and uniqueness of the given prescriptions for the solution of the problem.

Let us consider a large number of monochromatically vibrating resonators—N of frequency ν (per second), N' of frequency ν', N'' of frequency ν'', ..., with all N large numbers—which are at large distances apart and are enclosed in a diathermic medium with light velocity c and bounded by reflecting walls. Let the system contain a certain amount of energy, the total energy E_t (erg) which is present partly in the medium as travelling radiation and partly in the resonators as vibrational energy. The question is how in a stationary state this energy is distributed over the vibrations of the resonators and over the various colours of the radiation present in the medium, and what will be the temperature of the total system.

To answer this question we first of all consider the vibrations of the resonators and assign to them arbitrarily definite energies, for instance, an energy E to the N resonators ν, E' to the N' resonators ν', ... The sum

$$E+E'+E''+\ldots = E_0$$

must, of course, be less than E_t. The remainder E_t-E_0 pertains then to the radiation present in the medium. We must now give the distribution of the energy over the separate resonators of each group, first of all the distribution of the energy E over the N resonators of frequency ν. If E is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways. We consider, however—this is the most essential point of the whole calculation—E to be composed of a very definite number of equal parts and use thereto the constant of nature $h = 6{\cdot}55 \times 10^{-27}$ erg sec. This constant multiplied by the common frequency ν of the resonators gives us the energy element ε in erg, and dividing E by ε we get the number P of energy elements which must be divided over the N resonators. If the ratio is not an integer, we take for P an integer in the neighbourhood.

It is clear that the distribution of P energy elements over N resonators can only take place in a finite, well-defined number of ways. Each of these ways of distribution we call a "complexion", using an expression introduced by Mr. Boltzmann for a similar quantity. If we denote the resonators by the numbers $1, 2, 3, \ldots, N$, and write these in a row, and if we under each resonator put the number of its energy elements, we get for each complexion a symbol of the following form

1	2	3	4	5	6	7	8	9	10
7	38	11	0	9	2	20	4	4	5

We have taken here $N = 10, P = 100$. The number of all possible complexions is clearly equal to the number of all possible sets of numbers which one can obtain for the lower sequence for given N and P. To exclude all misunderstandings, we remark that two complexions must be considered to be different if the corresponding sequences contain the same numbers, but in different order. From the theory of permutations we get for the number of all possible complexions

$$\frac{N(N+1).(N+2)\ldots(N+P-1)}{1.2.3\ldots P} = \frac{(N+P-1)!}{(N-1)!P!}$$

or to a sufficient approximation,

$$= \frac{(N+P)^{N+P}}{N^N P^P}.$$

We perform the same calculation for the resonators of the other groups, by determining for each group of resonators the number of possible complexions for the energy given to the group. The multiplication of all numbers obtained in this way gives us then the total number R of all possible complexions for the arbitrarily assigned energy distribution over all resonators.

In the same way any other arbitrarily chosen energy distribution $E, E', E'', \ldots$ will correspond to a definite number R of all possible complexions which is evaluated in the above manner. Among all energy distributions which are possible for a constant $E_0 = E + E' + E'' + \ldots$ there is one well-defined one for which the number of possible complexions R_0 is larger than for any other distribution. We look for this distribution, if necessary by trial, since this will just be the distribution taken up by the resonators in the stationary radiation field, if they together possess the energy E_0. The quantities E, E', E'', ... can then be expressed in terms of E_0. Dividing E by N, E' by N', ... we obtain the stationary value of the energy U_ν, $U'_{\nu'}$, $U''_{\nu''}$, ... of a single resonator of each group, and thus also the spatial density of the corresponding radiation energy in a diathermic medium in the spectral range ν to $\nu+d\nu$,

$$u_\nu \, d\nu = \frac{8\pi\nu^2}{c^3} \, . \, U_\nu \, d\nu,$$

so that the energy of the medium is also determined.

Of all quantities which occur only E_0 seems now still to be arbitrary. One sees easily, however, how one can finally evaluate E_0 from the total energy E_t, since if the chosen value of E_0 leads, for instance, to too large a value of E_t, we must decrease it, and the other way round.

After the stationary energy distribution is thus determined using a constant h, we can find the corresponding temperature ϑ in degrees absolute† using a second constant of nature $k = 1{\cdot}346 \times 10^{-6}$ erg degree^{-1} through the equation

$$\frac{1}{\vartheta} = k \frac{d \ln R_0}{dE_0}.$$

The product $k \ln R_0$ is the entropy of the system of resonators; it is the sum of the entropy of all separate resonators.

It would, to be sure, be very complicated to perform explicitly the above-mentioned calculations, although it would not be without some interest to test the truth of the attainable degree of approximation in a simple case. A more general calculation which is performed very simply, using the above prescriptions shows much more directly that the normal energy distribution determined in this way for a medium containing radiation is

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† The original states "degrees centigrade" which is clearly a slip [D. t. H.].

given by the expression

$$u_\nu d\nu = \frac{8\pi\nu^3}{c^3}\frac{d\nu}{e^{h\nu/k\vartheta}-1},$$

which corresponds exactly to the spectral formula which I gave earlier

$$E_\lambda d\lambda = \frac{c_1\lambda^{-5}}{e^{c_2/\lambda\vartheta}-1}d\lambda.$$

The formal differences are due to the differences in the definitions of u_ν and E_λ. The first equation is somewhat more general inasfar as it is valid for an arbitrary diathermic medium with light velocity c. The numerical values of h and k which I mentioned were calculated from that equation using the measurements by F. Kurlbaum and by O. Lummer and E. Pringsheim.†

I shall now make a few short remarks about the question of the necessity of the above given deduction. The fact that the chosen energy element ε for a given group of resonators must be proportional to the frequency ν follows immediately from the extremely important Wien displacement law. The relation between u and U is one of the basic equations of the electromagnetic theory of radiation. Apart from that, the whole deduction is based upon the theorem that the entropy of a system of resonators with given energy is proportional to the logarithm of the total number of possible complexions for the given energy. This theorem can be split into two other theorems: (1) The entropy of the system in a given state is proportional to the logarithm of the probability of that state, and (2) The probability of any state is proportional to the number of corresponding complexions, or, in other words, any definite complexion is equally probable as any other complexion. The first theorem is, as far as radiative phenomena are concerned, just a definition of the probability of the state, insofar as we have for energy radiation no other *a priori* way to define the probability than the definition of its entropy. We have here a distinction from

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† F. Kurlbaum[4] gives $S_{100}-S_0 = 0{\cdot}0731$ Watt cm^{-2}, while O. Lummer and E. Pringsheim[5] give $\lambda_m\vartheta = 2940\,\mu$ degree.

the corresponding situation in the kinetic theory of gases. The second theorem is the core of the whole of the theory presented here: in the last resort its proof can only be given empirically. It can also be understood as a more detailed definition of the hypothesis of natural radiation which I have introduced. This hypothesis I have expressed before[6] only in the form that the energy of the radiation is completely "randomly" distributed over the various partial vibrations present in the radiation.† I plan to communicate elsewhere in detail the considerations, which have only been sketched here, with all calculations and with a survey of the development of the theory up to the present.

To conclude I may point to an important consequence of this theory which at the same time makes possible a further test of its reliability. Mr. Boltzmann[7] has shown that the entropy of a monatomic gas in equilibrium is equal to $\omega R \ln P_0$, where P_0 is the number of possible complexions (the "permutability") corresponding to the most probable velocity distribution, R being the well known gas constant ($8{\cdot}31 \times 10^7$ for $\mathrm{O} = 16$), ω the ratio of the mass of a real molecule to the mass of a mole, which is the same for all substances. If there are any radiating resonators present in the gas, the entropy of the total system must according to the theory developed here be proportional to the logarithm of the number of all possible complexions, including both velocities and radiation. Since according to the electromagnetic theory of the radiation the velocities of the atoms are completely independent of the distribution of the radiation energy, the total number of complexions is simply equal to the product of the number

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† When Mr. W. Wien in his Paris report about the theoretical radiation laws did not find my theory on the irreversible radiation phenomena satisfactory since it did not give the proof that the hypothesis of natural radiation is the only one which leads to irreversibility, he surely demanded, in my opinion, too much of this hypothesis. If one could prove the hypothesis, it would no longer be a hypothesis, and one did not have to formulate it. However, one could then not derive anything new from it. From the same point of view one should also declare the kinetic theory of gases to be unsatisfactory since nobody has yet proved that the atomistic hypothesis is the only one which explains irreversibility. A similar objection could with more or less justice be raised against all inductively obtained theories.

relating to the velocities and the number relating to the radiation. For the total entropy we have thus

$$f \ln (P_0 R_0) = f \ln P_0 + f \ln R_0,$$

where f is a factor of proportionality. Comparing this with the earlier expressions we find

$$f = \omega R = k,$$

or $$\omega = \frac{k}{R} = 1{\cdot}62 \times 10^{-24},$$

that is, a real molecule is $1{\cdot}62 \times 10^{-24}$ of a mole, or, a hydrogen atom weighs $1{\cdot}64 \times 10^{-24}$ g, since H = 1·01, or, in a mole of any substance there are $1/\omega = 6{\cdot}175 \times 10^{23}$ real molecules. Mr. O. E. Mayer[8] gives for this number 640×10^{21} which agrees closely.

Loschmidt's number L, that is, the number of gas molecules in 1 cm^3 at 0°C and 1 atm is

$$L = \frac{1\,013\,200}{R\,.\,273\,.\,\omega} = 2{\cdot}76 \times 10^{19}.$$

Mr. Drude[9] finds $L = 2{\cdot}1 \times 10^{19}$.

The Boltzmann–Drude constant α, that is, the average kinetic energy of an atom at the absolute temperature 1 is

$$\alpha = \tfrac{3}{2}\omega R = \tfrac{3}{2}k = 2{\cdot}02 \times 10^{-16}.$$

Mr. Drude[9] finds $\alpha = 2{\cdot}65 \times 10^{-16}$.

The elementary quantum of electricity e, that is, the electrical charge of a positive monovalent ion or of an electron is, if ε is the known charge of a monovalent mole,

$$e = \varepsilon\omega = 4{\cdot}69 \times 10^{-10} \text{ e.s.u.}$$

Mr. F. Richarz[10] finds $1{\cdot}29 \times 10^{-10}$ and Mr. J. J. Thomson[11] recently $6{\cdot}5 \times 10^{-10}$.

If the theory is at all correct, all these relations should be not approximately, but absolutely, valid. The accuracy of the calculated numbers is thus essentially the same as that of the relatively worst known, the radiation constant k, and is thus much better than all determinations up to now. To test it by more direct methods should be both an important and a necessary task for further research.

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