9. On the law of the Energy Distribution in the Normal Spectrum; by Max Planck.

Translated from German as faithful as possible of Max Planck's original publication from 1901:

"Ueber das Gesetz der Energieverteilung im Normalspectrum; von Max Planck".

(Communicated in another form in the German Physical Society, Meeting on the 19th of October and December 14, 1900, negotiations 2nd p. 202 and p. 237. 1900.)

Introduction.

The more recent spectral measurements by 0. Lummer and E. Pringsheim¹) and even more strikingly those by H. Rubens and F. Kurlbaum²), which at the same time confirmed a result previously obtained by H. Beckmann³), have shown that W. Wien first did this from molecular kinetic considerations and the law of energy distribution in the normal spectrum, which I later derived from the theory of electromagnetic radiation, has no general validity.

The theory needs improvement in any case, and in the following, I will attempt to carry out such an improvement based on the theory of electromagnetic radiation that I have developed. For this purpose it will above all be necessary to, in the series of conclusions, which are: Wien's energy distribution law led to finding the link that is capable of modification; but then it will be a matter of removing this link from the series and creating a suitable replacement for it.

The physical foundations of the electromagnetic radiation theory, including the hypothesis of "natural radiation", also face sharper criticism. I explained in my last essay⁴) on this subject that we should stand our ground;

¹⁾ O. Lummer u. E. Pringsheim, Verhandl. der Deutsch. Physikal. Gesellsch. **2.** P. 163. 1900.

²⁾ H. Rubens, F. Kurlbaum. Sitzungsber. d. k. Akad. d. Wissench. zu Berlin vom 25. October 1900, p. 929.

³⁾ H. Beckmann. Inaug.-Dissertation, Tübingen 1898, *see also*: H. Rubens, Wied. Ann. **69.** p. 582. 1899.

⁴⁾ M. Planck, Ann. d. Phys. 1. p. 719. 1900.

and since, as far as I know, the calculations do not contain any errors, the theorem remains that the law of energy distribution in the normal spectrum is completely determined if it is possible to calculate the entropy S of an irradiated, monochromatically vibrating resonator as a function of its vibrational energy U. Because then you get from the relationship dS/dU=1/9 the dependence of the energy U on the temperature 9, and since on the other hand the energy U is linked by a simple relationship¹) to the radiation density of the corresponding vibration number and the dependence of this radiation density on the temperature. The normal energy distribution is then the one in which the radiation densities of all different vibration numbers have the same temperature.

The entire problem is therefore reduced to the one task of determining S as a function of U, and the most important part of the following investigation is dedicated to the solution of this task. In my first treatise on this subject, I presented S directly by definition, without further justification, as a simple expression of U, and contented myself with proving that this form of entropy satisfies all the requirements that thermodynamics places on it. At that time I believed that it was the only one of its kind and that Wien's law, which follows from it, necessarily had general validity. However, during a later, more detailed investigation²), it became clear to me that there must also be other expressions that do the same thing, and that a further condition is therefore required to be able to calculate S. I believed I had found such a condition in the statement, which seemed immediately plausible to me at the time, that with an infinitely small, irreversible change in a system of N identically constructed resonators located in the same stationary radiation field, which is almost in thermal equilibrium, the associated increase in their total entropy $S_N = NS$

¹⁾ Compare with equation (8).

²⁾ M. Planck, *l. c.* p. 730 ff.

only depends on its total energy $U_N = NU$ and its changes, but not on the energy U of the individual resonators. But since the latter is not confirmed by experience, one is forced to the conclusion that that sentence cannot be correct in its generality and must therefore be removed from the theory.¹)

So another condition must now be introduced that allows the calculation of S, and to accomplish this, a closer look at the meaning of the concept of entropy is necessary. The direction of the line of thought to be taken is given by the untenability of the previously made assumptions. In the following, a path is described in which a new, simple expression of entropy and thus a new radiation formula arises, which seems to be consistent with the facts established so far.

I. Calculating the entropy of a resonator as a function of its energy.

 \S 1. Entropy causes disorder, and according to the electromagnetic radiation theory, this disorder is based on monochromatic vibrations of a resonator, even if it is in a permanently stationary radiation field, in the irregularity with which it constantly changes its amplitude and phase if one considers clocks time are large compared to the time of vibration, but small compared to the time of measurement. If the amplitude and phase were constant, i.e. the vibrations were completely homogeneous, then no entropy could exist and the vibrational energy would have to be completely freely convertible into work. The constant Energy U of a single stationary vibrating resonator can then only be understood as a temporal average, or, what amounts to the same thing, as the simultaneous average of the energies of a large number N of identical Resonators,

¹⁾ Compare the criticisms this sentence has already found: by W. Wien (Report to the Paris Congress 2. p. 40.1900) and by 0. Lummer (1. c. 2. p. 92. 1900).

which are in the same stationary radiation field, far enough apart from each other so as not to directly influence each other. In this sense, in the future, we want to talk about the average energy U of an individual resonator. Then corresponds to the total energy

$$(1) U_N = NU$$

such a system of N resonators has a certain total entropy

$$(2) S_N = NS$$

of the same system, where S represents the average entropy of a single resonator, and this entropy S_N is due to the disorder with which the entire energy U_N is distributed among the individual resonators.

§ 2. We now set the entropy S_N of the system, up to an arbitrary additive constant, proportional to the logarithm of the probability W that the N resonators have a total of energy U_N , i.e.:

$$(3) S_N = k \log W + \text{const.}$$

In my opinion, this determination amounts to a definition of the stated probability W; for we have no basis in the assumptions on which the electromagnetic theory of radiation is based to speak of such a probability in a specific sense. The expediency of the determination made in this way can be cited from the outset by its simplicity and its close relationship to a theorem of the kinetic gas theory¹).

§ 3. It is now important to find the probability W that the N resonators have a total of vibrational energy U_N . For this, it is necessary to understand U_N not as a continuous, infinitely divisible quantity, but as a discrete quantity composed of a whole number of finite equal parts. If we call such a part an energy element ε , then we have to put:

(4)
$$U_N = P \cdot \varepsilon,$$

¹⁾ L. Boltzmann, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien (II) 76. p. 428. 1877.

where P means an integer, generally a large number, while we leave the value of ε open.

Now it is clear that the distribution of the P energy elements to the N resonators can only take place in a finite, specific number of ways. We call every such type of distribution a "complexion" after an expression used by L. Boltzmann for a similar term. The resonators are denoted by the numbers 1, 2, 3. . . N, write these next to each other in order and place under each resonator the number of energy elements that are allocated to it in any arbitrary distribution, then you get a symbol of the following form for each complexion:

Here N = 10, P = 100 is assumed. The number \Re of all possible complexions is equal to the number of all possible numerical images that can be obtained in this way, given certain N and P, for the bottom row. For clarity, it should be noted that two complexions are to be viewed as different if the corresponding number images contain the same numbers but in a different arrangement.

The number of all possible complexions results from the theory of combinations

$$\Re = \frac{N \cdot (N+1) \cdot (N+2) \cdot ... (N+P-1)}{1 \cdot 2 \cdot 3 \cdot ... P} = \frac{(N+P-1)!}{(N-1)! P!}$$

Now, according to Stirling's theorem, as a first approximation:

$$N! = N^N$$

consequently in a corresponding approximation

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

§ 4. The hypothesis, which we now want to base the further calculation, is as follows: The probability W that the N resonators have a total of vibrational energy U_N , is proportional to the number \Re

of all possible complexions when the energy U_N is distributed among the N resonators; or in other words: any particular complexion is as probable as any other particular complexion. Whether this hypothesis applies in nature can ultimately only be tested through experience. Conversely, suppose experience has decided in its favor. In that case, it will be possible to draw further conclusions from the validity of this hypothesis about the more special nature of the resonator's vibrations, namely on the character of the "indifferent and comparable in size original scope", in the expression of J. v. Kries. However, given the current status of the question, pursuing this line of thought further may seem premature.

§ 5. According to the introduced hypothesis in conjunction with equation (3), the entropy of the system of resonators under consideration when the additive constants are determined appropriately is:

(5)
$$\begin{cases} S_N = k \log \Re \\ = k \{ (N + P) \log (N + P) - N \log N - P \log P \} \end{cases}$$

and taking into account (4) and (1):

$$S_N = kN \{ (1 + \frac{U}{\varepsilon}) \log (1 + \frac{U}{\varepsilon}) - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} \}.$$

So according to (2) the entropy S of a resonator as a function of its energy U:

(6)
$$S = k \{ (1 + \frac{U}{\varepsilon}) \log (1 + \frac{U}{\varepsilon}) - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} \}.$$

II. Introduction of Wien's displacement law.

§ 6. Next to Kirchhoff's theorem of the proportionality of emission and absorption capacity is the so-called displacement law discovered by W. Wien²) and named after him,

¹⁾ Joh. v. Kries, Die Principien der Wahrscheinlichkeitsrechnung p. 36. Freiburg 1886.

²⁾ W. Wien, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, vom 9. Febr. 1893. p. 55.

which includes Stefan-Boltzmann's law of the dependence of total radiation on temperature as a special application, the most valuable component in the firmly established foundation of the theory of thermal radiation. The version given to him by Thiesen¹) reads:

$$E.d\lambda = \vartheta^5 \psi(\lambda \vartheta).d\lambda,$$

who λ denotes the wavelength, E $d\lambda$ the spatial density of the "black" radiation²) belonging to the spectral range λ to $\lambda + d\lambda$, ϑ the temperature, and $\psi(x)$ denotes a certain function of the single argument x.

 \S 7. We now want to investigate what Wien's displacement law says about the dependence of the entropy S of our resonator on its energy U and its natural period, in the general case that the resonator is in an arbitrarily diathermic medium. For this purpose, we first generalize Thiesen's form of the law to radiation in any diathermic medium with the speed of light propagation c. Since we do not have to consider the total radiation, but rather monochromatic radiation, when comparing different diathermic media it becomes necessary to introduce the vibration number v instead of the wavelength λ .

Let us, therefore, denote the spatial density of the radiant energy belonging to the spectral region v to v + dv by udv, this is how to write: udv instead of $Ed\lambda$, c/v instead of λ and cdv/v^2 instead of $d\lambda$. This results in:

$$u = \vartheta^5 \cdot \frac{c}{v^2} \cdot \psi(\frac{c\vartheta}{v})$$

Now, according to the well-known Kirchhoff-Clausius law, the energy of a certain temperature θ and a certain number of vibrations v

¹⁾ M. Thiesen, Verhandl. der Deutsch. Physikal. Gesellsch. 2. p. 66. 1900.

²⁾ One could perhaps even more appropriately speak of "white" radiation, in an appropriate generalization of what is already understood by completely white light.

emitted by a black surface per unit of time into a diathermic medium is inversely proportional to the square c^2 of the propagation speed; so the spatial energy density u is inversely proportional to c^3 , and we get:

$$u = \frac{\theta^5}{v^2 c^3} f(\frac{\theta}{v}),$$

where the constants of the function f are independent of c.

Instead, we can also write if f denotes a new function of a single argument every time, including in the following:

(7)
$$u = \frac{v^3}{c^3} f(\frac{\theta}{v})$$

and see, among other things, from this, as is well known, that the radiant energy contained in the cube of one wavelength of a certain temperature and number of vibrations: $u\lambda^3$ is the same for all diathermic media.

§ 8. To now move from the spatial radiation density u to the energy U of a stationary resonator located in the radiation field with the same number of vibrations v, we use the relationship expressed in equation (34) of my treatise on irreversible radiation processes¹):

$$\mathfrak{K} = \frac{v^2}{c^2} U$$

 $(\Re$ is the intensity of a monochromatic, rectilinearly polarized beam), which together with the well-known equation:

$$u = \frac{8\pi \Re}{c}$$

the relationship provides:

$$(8) u = \frac{8\pi v^2}{c^3} U$$

From this and from (7) it follows:

$$U = \nu f(\frac{\vartheta}{\nu}),$$

where c no longer occurs at all. Instead, we can also write:

$$\vartheta = \nu f(\frac{U}{\nu})$$

¹⁾ M. Planck, Ann. d. Phys. 1. p. 99. 1900.

 \S 9. Finally, we also introduce the entropy S of the resonator by setting:

$$\frac{1}{\vartheta} = \frac{dS}{dU}.$$

Then it happens:

$$\frac{dS}{dU} = \frac{1}{v} f(\frac{U}{v})$$

and integrated:

$$(10) S = f(\frac{U}{v}),$$

i.e. the entropy of the resonators vibrating in any diathermic medium depends on the single variable U/v and also only contains universal constants. This is the simplest version of Wien's displacement law that I know of.

§ 10. If we apply Wien's displacement law in the last version to the expression (6) of the entropy S, we see that the energy element ε must be proportional to the number of vibrations v, so:

$$\varepsilon = h.v$$

and thus:

$$S = k \{ (1 + \frac{U}{hv}) \log (1 + \frac{U}{hv}) - \frac{U}{hv} \log \frac{U}{hv} \}.$$

Here h and k are universal constants.

Substitution in (9) gives:

$$\frac{1}{\vartheta} = \frac{k}{h\nu} \log \left(1 + \frac{h\nu}{U}\right),\,$$

$$U = \frac{hv}{e^{\frac{hv}{k\theta}} - 1}.$$

and from (8), the required energy distribution law follows:

(12)
$$u = \frac{8\pi h v^3}{c^3} \cdot \frac{1}{e^{\frac{hv}{k\theta}} - 1}.$$

or also if one reintroduces the wavelength λ instead of the number of vibrations v with the substitutions given in § 7:

(13)
$$E = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda\theta}} - 1}.$$

I think that the expressions for the intensity and entropy of the radiation propagating in the diathermic medium, as well as the law for the increase of the total entropy in non-stationary radiation processes, can be derived elsewhere.

III. Numerical values.

§ 11. The values of the two natural constants h and k can be calculated quite precisely with the help of the available measurements. F. Kurlbaum¹) found that if one denotes by S_t the total energy that is radiated into the air in 1 second by 1 square cm of a black body at t° C:

$$S_{100} - S_0 = 0.0731 \frac{Watt}{cm^2} = 7.31.10^5 \frac{erg}{cm^2 sec}$$

This results in the spatial density of the total radiant energy in the air at absolute temperature 1:

$$\frac{4.7,31.10^5}{3.10^{10}.(373^4 - 273^4)} = 7,061.10^{-15} \frac{erg}{cm^3 grad^4}$$

On the other hand, according to (12), the spatial density of the total radiant energy for $\theta = 1$ is:

$$u = \int_{0}^{\infty} u \, dv = \frac{8\pi h}{c^{3}} \int_{0}^{\infty} \frac{v^{3} \, dv}{e^{\frac{hv}{k}} - 1}$$
$$= \frac{8\pi h}{c^{3}} \int_{0}^{\infty} v^{3} (e^{-\frac{hv}{k}} + e^{-\frac{2hv}{k}} + e^{-\frac{3hv}{k}} + ...) \, dv$$

and by term-by-term integration:

$$u = \frac{8\pi h}{c^3} \cdot 6 \left(\frac{k}{h}\right)^4 \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \ldots\right)$$
$$= \frac{48\pi k^4}{c^3 h^3} \cdot 1,0823.$$

If you set this = 7,061.10⁻¹⁵, it results, since $c = 3.10^{10}$,

(14)
$$\frac{k^4}{h^3} = 1,1682.10^{15}.$$

¹⁾ F. Kurlbaum, Wied. Ann. **65.** p. 759. 1898.

§ 12. 0. Lummer and E. Pringsheim¹) determined the product $\lambda_m \vartheta$, where λ_m is the wavelength of the maximum of E in the air at the temperature ϑ , to be 2940 μ degrees. So in absolute terms:

$$\lambda_m \vartheta = 0.294 \ cm \cdot grad.$$

On the other hand, it follows from (13), if one sets the differential quotient from E to λ equal to zero, whereby $\lambda = \lambda_m$:

$$(1 - \frac{ch}{5k\lambda_m \vartheta}). e^{\frac{ch}{k\lambda_m \vartheta}} = 1$$

and from this transcendent equation:

$$\lambda_m \vartheta = \frac{ch}{4,9651.k}$$

Consequently:

$$\frac{h}{k} = \frac{4,9651.0,294}{3.10^{10}} = 4,866.10^{-11}$$

From this and (14), the values of the natural constants result:

(15)
$$h = 6,55.10^{-27} erg.sec,$$

(16)
$$k = 1,346.10^{-16} \frac{erg}{grad}.$$

These are the same numbers, which I stated in my earlier communication.

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¹⁾ O. Lummer, E. Pringsheim, Verhandl. der Deutschen Physikal. Gesellsch. **2.** p. 176. 1900.