

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

*Max Planck's original 1901 publication was translated from German as faithfully
as possible by Patrick MARC (patrick.marc@2newton.fr):*

**“Ueber das Gesetz der Energieverteilung im Normalspectrum;
von Max Planck.”**

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2. p. 202 and p. 237. 1900.)

Introduction.

The most recent spectral measurements by O. Lummer and E. Pringsheim¹⁾ and, even more strikingly, those of H. Rubens and F. Kurlbaum²⁾, confirming at the same time a result previously obtained by H. Beckmann³⁾, show that the considerations of molecular kinetics first stated by W. Wien and the law of energy distribution in the normal spectrum, subsequently derived from the theory of electromagnetic radiation, have no general validity.

One must improve the theory in any case, trying to achieve this based on the theory of electromagnetic radiation developed previously. For this purpose, it is necessary to draw a series of conclusions: Wien's energy distribution law led to finding the link capable of modification; it is, therefore, a matter of creating a suitable replacement for it.

The physical foundations of the electromagnetic radiation theory, including the hypothesis of “natural radiation,” also face sharper criticism. In the last essay⁴⁾ on this subject, one explained to 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.

Since, as far as one knows, the calculations do not contain any errors, the theorem remains that the law of energy distribution in the normal spectrum is wholly determined if it is possible to calculate the entropy S of an irradiated, monochromatically vibrating resonator as a function of its vibrational energy U . The relationship $dS/dU=1/\vartheta$ gives the dependence of the energy U on the temperature ϑ . However, one links the energy U by a simple relationship¹⁾ to the radiation density of the corresponding vibration number and the dependence of this radiation density on the temperature. The expected energy distribution is when 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 one dedicates the essential part of the following investigation to the solution of this task. In the first treatise on this subject, one presented S directly by definition, without further justification, as a simple expression of U , and one contented with proving that this form of entropy satisfies all the requirements that thermodynamics places on it. At that time, one believed 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 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 . One believed to have found such a condition in the statement, which seemed immediately plausible 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 $S_N = NS$ only depends on its total energy $U_N = NU$ and its changes, but not on the energy U of the individual resonators.

1) Compare with equation (8).

2) M. Planck, l. c. p. 730 ff.

This sentence, in turn, necessarily leads to Wien's energy distribution law. However, as experience does not confirm the latter, one must conclude that that sentence cannot be correct in its generality and remove it from the theory.¹⁾

So, one must introduce another condition allowing the calculation of S . To accomplish this, a closer look at the meaning of the concept of entropy is necessary. The untenability of the previously made assumptions gives the direction to take. In the following, one describes a path that yields a new, more straightforward expression of entropy and, thus, provides a new radiation formula consistent with the facts established so far.

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

§ 1. Entropy causes disorder, and according to the electromagnetic radiation theory, the monochromatic vibrations of a resonator cause this disorder, even if it is in a stationary radiation field and changes amplitude and phase irregularly; if clocks time is considerable 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 utterly homogeneous, no entropy could exist, and the vibrational energy would have to be entirely freely convertible into work. One can only understand that the constant Energy U of a single stationary vibrating resonator is a temporal average, or, what amounts to the same thing, is the simultaneous average of the energies of a large number N of identical Resonators, which are in the same stationary radiation field, far enough apart from each other so as not to influence each other directly.

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

In this sense, one talks about the average energy U of an individual resonator in the future. Then, it corresponds to the total energy:

$$(1) \quad U_N = NU,$$

such a system of N resonators has a specific total entropy

$$(2) \quad S_N = NS,$$

of the same system, where S represents the average entropy of a single resonator, and this entropy S_N is due to the disorder that distributes the entire energy U_N 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 energy U_N , so:

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

This determination amounts to a definition of the stated probability W , for one has no basis in the assumptions to base the electromagnetic theory of radiation to speak of such a probability in any specific sense. One qualifies it by its simplicity and its close relationship with a theorem of the kinetic theory of gases.¹⁾

§ 3. Finding the probability W that the N resonators have total vibrational energy U_N is essential. For this, one must understand U_N as a discrete quantity composed of an integer number of finite equal parts, not a continuous, infinitely divisible amount. Calling this part the energy element ε , it gives:

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

where P is a large integer, and the value of ε is open.

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

Then, the distribution of the P energy elements to the N resonators can only take place in a finite, specific number of ways. One calls every such type of distribution a “complexion” after an expression used by L. Boltzmann for a similar term. The resonators are denoted by 1, 2, 3,..., N . One writes these side by side and allocates the energy elements under each resonator in any arbitrary distribution. So, one gets a table of the following form for each complexion:

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

Here, considering $N=10$ and $P=100$. The number \mathfrak{R} of all possible complexions equals the number of all possible numerical images that can be obtained in this way, given specific N and P , for the bottom row. For clarity, notice that two complexions are different if the corresponding number images contain the same numbers in a different arrangement.

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

$$\mathfrak{R} = \frac{N \cdot (N + 1) \cdot (N + 2) \cdots (N + P - 1)}{1 \cdot 2 \cdot 3 \cdots P} = \frac{(N + P - 1)!}{(N - 1)! P!}$$

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 based on 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 \mathfrak{R} of all possible complexions, distributing the energy U_N among the N resonators.

In other words, any particular complexion is as probable as any other one. Whether this hypothesis applies in nature can ultimately only be tested through experience. Conversely, suppose experience has decided in its favor. It will be possible to draw further conclusions from the validity of this hypothesis about the more special nature of the resonator oscillations, namely, the character "original amplitude indifferent and comparable in size" expressed by J. v. Kries¹). 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 appropriately determining the additive constants is

$$(5) \quad \left\{ \begin{array}{l} S_N = k \log \mathfrak{R} \\ = k\{(N + P) \log (N + P) - N \log N - P \log P\} \end{array} \right.$$

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

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

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

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

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.

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

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

who λ denotes the wavelength, $E \cdot d\lambda$ 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 particular function of the single argument x .

§ 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 . However, we do not have to consider the total radiation but rather monochromatic radiation; one must introduce the vibration number ν instead of the wavelength λ to compare different diathermic media.

Therefore, designate the spatial density of the energy of the radiation belonging to the spectral region ν to $\nu + d\nu$ by $u \cdot d\nu$. One must write $u \cdot d\nu$ instead of $E \cdot d\lambda$, c/ν instead of λ , and $c \cdot d\nu/\nu^2$ instead of $d\lambda$. This results in

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

According to Kirchhoff-Clausius law, the energy of a temperature ϑ and the number of vibrations ν , when 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.

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.

So the spatial energy density u is inversely proportional to c^3 , and one gets:

$$u = \frac{\vartheta^5}{v^2 c^3} f\left(\frac{\vartheta}{v}\right)$$

So, constants of the function f are independent of c .

Instead, one can write if f denotes a new single-argument function each time, including in the following:

$$(7) \quad u = \frac{v^3}{c^3} f\left(\frac{\vartheta}{v}\right)$$

Therefore, $u \cdot \lambda^3$ for the radiation energy, in the cube of one wavelength of a specific temperature and number of vibrations, is the same for all diathermic media.

§ 8. Next, for a stationary resonator located in the radiation field with the same number of vibrations ν , to move from the spatial radiation density u to the energy U , one uses the relationship expressed in equation (34) of the treatise on irreversible radiation processes¹):

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

(\mathfrak{R} is the intensity of a monochromatic, rectilinearly polarized beam), which, together with the well-known equation:

$$u = \frac{8 \pi \mathfrak{R}}{c}$$

The relationship provides:

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

From this and from (7) it follows:

$$U = v f\left(\frac{\vartheta}{v}\right)$$

Where c no longer occurs at all. Instead, one can also write

$$\vartheta = v f\left(\frac{U}{v}\right)$$

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

§ 9. Finally, one also introduces the entropy S of the resonator by this setting:

$$(9) \quad \frac{1}{\vartheta} = \frac{dS}{dU}.$$

Then it happens:

$$\frac{dS}{dU} = \frac{1}{\nu} f\left(\frac{U}{\nu}\right)$$

And integrated:

$$(10) \quad S = f\left(\frac{U}{\nu}\right),$$

i.e., the entropy of the resonators vibrating in any diathermic medium depends on the single variable U/ν and only contains universal constants. That is the simplest version of Wien's displacement law that one knows.

§ 10. Applying Wien's displacement law in the last version to the expression (6) of the entropy S , one sees that the energy element ε must be proportional to the number of vibrations ν , so:

$$\varepsilon = h \cdot \nu$$

and thus:

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

Here, h and k are universal constants.

Substitution in (9) gives:

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

$$(11) \quad U = \frac{h\nu}{e^{\frac{k\vartheta}{h\nu}} - 1}$$

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

$$(12) \quad u = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{k\vartheta}{h\nu}} - 1}$$

Or also, if one reintroduces the wavelength λ instead of the number of vibrations ν with the substitutions given in § 7:

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

The expressions for the intensity and entropy of the radiation propagating in the diathermic medium and the law for increasing 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 precisely using the available measurements. F. Kurlbaum¹⁾ found that if one denotes by S_t the total energy radiated into the air in 1 second by 1 square cm of a black body at $t^\circ \text{C}$, then one has:

$$S_{100} - S_0 = 0.0731 \frac{\text{Watt}}{\text{cm}^2} = 7.31 \cdot 10^5 \frac{\text{erg}}{\text{cm}^2 \text{ sec}}$$

This results in the spatial density of the total radiation energy in the air at absolute temperature $\mathbf{1}$:

$$\frac{4.731 \cdot 10^5}{3 \cdot 10^{10} \cdot (373^4 - 273^4)} = 7,061 \cdot 10^{-15} \frac{\text{erg}}{\text{cm}^3 \text{ degree}^4}$$

On the other hand, from (12), the spatial density of the total radiation energy for $\mathfrak{J} = \mathbf{1}$ is:

$$\begin{aligned} u &= \int_0^\infty u dv = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3 dv}{e^{\frac{hv}{k}} - 1} \\ &= \frac{8\pi h}{c^3} \int_0^\infty v^3 (e^{-\frac{hv}{k}} + e^{-\frac{2hv}{k}} + e^{-\frac{3hv}{k}} + \dots) dv \end{aligned}$$

Integrating term-by-term, one obtains:

$$\begin{aligned} u &= \frac{8\pi h}{c^3} \cdot 6 \left(\frac{k}{h}\right)^4 \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \dots\right) \\ &= \frac{48\pi k^4}{c^3 h^3} \cdot 1,0823 \end{aligned}$$

As $c = 3 \cdot 10^{10}$ cm/sec, setting this = $7,061 \cdot 10^{-15}$ results in

$$(14) \quad \frac{k^4}{h^3} = 1,1682 \cdot 10^{15}$$

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

§ 12. 0. Lummer and E. Pringsheim¹⁾ determined that the product $\lambda_m \vartheta$, where λ_m is the wavelength of the maximum of E in the air at temperature ϑ , was **2940** $\mu \cdot \text{degrees}$. So, in absolute terms:

$$\lambda_m \vartheta = 0.294 \text{ cm} \cdot \text{degree}$$

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

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

And, from this transcendental equation:

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

Consequently:

$$\frac{h}{k} = \frac{4,9651 \cdot 0,294}{3 \cdot 10^{10}} = 4,866 \cdot 10^{-11}$$

Then, from this and from (14), one obtains the values of the natural constants:

$$(15) \quad h = 6,55 \cdot 10^{-27} \text{ erg} \cdot \text{sec}$$

$$(16) \quad k = 1,346 \cdot 10^{-16} \frac{\text{erg}}{\text{degree}}$$

These are the same numbers indicated in a previous communication.

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

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