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The Kirchhoff-Planck Radiation Law

Considering Kirchhoff's law as it was initially meant may help us understand the rise of quantum theory.

Joseph Agassi

It is well known that Planck studied Kirchhoff's radiation law because he was attracted by its utter generality, and that he was thus led to his theory of the quantization of light. Why this stress on utter generality? Did Wien, for instance, in studying Kirchhoff's law, disregard its generality? Are not all laws of nature general, and attractive on account of their generality (*1*)?

Moreover, how general, precisely, is Kirchhoff's law? One may say it applies to all *thermal* radiation of all *black* bodies which are in *equilibrium* with their environments. The previous sentence contains three restrictions: the radiation has to be thermal, the radiating body black, and the setup that of thermal equilibrium. We may omit any one of these restrictions and obtain three different interpretations of the law; we may omit any two of these restrictions and obtain three more interpretations; and we may omit them all. Thus we can have at least eight (empirically) different interpretations of the law. I say at least eight different interpretations because we may also interpret terms like *thermal radiation* differently. The most radically narrow interpretation of this term will be (intentionally) circular: that radiation is thermal which obeys Kirchhoff's law. This interpretation is so narrow that, once we restrict the law to thermal radiation in this interpretation of the word, we obviously do not have to restrict the law any further; it becomes an immediate corollary to the definition and thus trivially a tautology. This is, indeed, how *Handbuch der Physik* introduces the law (*2,* p. 133). There is, however, an elaborate proof of the law (*3*), in which the second law of thermodynamics is used, and so, evidently those who accept the proof accept a different interpretation of the law. One might expect—quite a priori, indeed—to be able to read from the proof the right interpretation. In fact, however, all eight interpretations mentioned above are found in the introductory literature, even in the leading introductory literature (*4*), not to mention works which are ambiguous about this point, or even inconsistent. I do not speak of marginal works; I need not discuss the importance generally and

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The author is professor of philosophy, Boston University, Boston, Massachusetts, and Visiting Professor of Philosophy, Tel Aviv University, Tel Aviv, Israel.

quite rightly attached to Georg Joos's book (*5*), yet it is plainly inconsistent on the point of interpretation, or at least sufficiently ambiguous to be so read.

The reason for this diversity of interpretations and confusions may lie in the fact that the proof of Kirchhoff's law is not clear. Inasmuch as this is the case, I hope my present restatement of it will dispel some of the obscurity. I am afraid, however, that there is a little more to it than this. Young students are often bewildered not only by questions concerning the generality of Kirchhoff's law but also by the strange fact that the law is mentioned very seldom in the literature—that even Kirchhoff's emission and absorption coefficients are seldom mentioned—despite the fact that the law was proposed at so crucial a juncture as the time of the rise of quantum theory. Browsing through the literature, one may find an occasional use of Kirchhoff's law in some experimental physics, but the only place where it is treated at all seriously today is in the astrophysical literature. Thus, Chandrasakhar presents the Kirchhoff-Planck law very clearly though as a mere approximation to better laws (*6*). Here, indeed, is the crux of the difficulty. As I have said elsewhere (*7, 8*), often writers cannot repeat an idea which has been superseded without some tinkering; the tinkering does not improve matters, but it does often obscure the reasoning which underlay the old idea when it was proposed. (*Handbuch der Physik* at least claims that Kirchhoff's own presentation was unsatisfactory.) Historians, however, cannot allow themselves the luxury of improving upon history. Let me, then, present my view of the history of the case as briefly and schematically as I can.

Prevost's Law of Exchange

That radiation may be related to heat is ancient knowledge. Blacksmiths from time immemorial knew how to compare the temperature of metals by the color of their radiation. Yet it was Newton who declared *all* radiation to be a function of the temperature of the radiating body; he declared that fire is but radiating hot gas (*9*). To illustrate this he filled a glass tube with black smoke and heated it until the smoke glowed (*9*).

Newton's illustration was not conclusive, of course. In particular, the following objection may easily be imagined. It might be claimed that the smoke radiated in his experiment not from being heated by its environment but from some other environmental influence—for example, from being forced to absorb fire atoms. The claim that indeed Newton was mistaken may be supported by the observation that, once the heated glass tube is removed from the environment, it ceases to radiate after a very short period. It may be claimed that, though the tube is hardly cooled, it ceases to radiate because its environment has changed.

This objection to Newton's idea was answered by Prevost, who postulated, in 1809, that emission is cooling and absorption is heating (*10*). It follows from this postulate that, under obvious circumstances, one body may emit radiation and thereby cool and cease radiating, and that the radiation it has emitted may be absorbed by another body, which may thereby heat and start radiating light, which will be reabsorbed by the first body, and so on periodically. This idea is known as Prevost's law of exchange (*11*).

Thus far I have presented a crude idea concerning the relations between emission and absorption, one only incidentally related to the problem of the nature of fire. The problem of the relation between absorption and emission became significant with the discovery of absorption spectra and the rise of astrophysics—or, more precisely, solar physics (and solar chemistry).

Fraunhofer's Discovery of Spectroscopy

Spectral lines were observed a few times in the 18th century, but no significance was attached to these observations and they were not generally known. The real discovery of spectral lines is therefore attributed to Wollaston (1802), who thought they were boundaries between colors and who devised a method of observing them (*12*), and to Fraunhofer (1817), who is the father of astrospectroscopy (*13*). The story of its development goes this way.

Newton had thought that the spectrum contained seven colors, with ranges having arithmetic ratios corresponding to a Pythagorean scheme of harmony. He confessed his own inability to see borderlines between color ranges but claimed that an assistant of his could see them rather systematically (*14*). Next, Thomas Young started his studies by examining contemporary acoustic theories and trying to relate harmony to physiological acoustics (*15*). He turned to physiological optics as an afterthought and failed to develop a satisfactory physiological optics of seven colors. Most of the historical literature today criticizes Newton's corpuscular theory of light as defective, on the ground that it contains the postulate of an infinite variety of light particles, corresponding to the continuum of the wavelengths of the visible spectrum. This criticism is a hindsight. The proper presentation is this. Newton had postulated only seven kinds of light corpuscles, each having a *spread* over that part of the spectrum allotted to it. It was only when Young threw doubt on the existence of the seven colors that the choice was between (i) infinitely many (rather than seven) kinds of particles and (ii) one kind of wave with infinitely many different wavelengths. This is why the doubts concerning the seven colors became so crucial, and why Young turned to Huyghens (*16*).

Wollaston devised the first spectroscope, and with it discovered (1802) some of the solar dark lines. He thought these might be the boundaries between colors (*17*). This idea was soon destroyed by Fraunhofer's discovery (1817) of the multitude of these lines (see *13*). Wollaston also discovered the emission spectra, and the fact that, for sodium, the absorption spectrum may be the negative of the emission spectrum. On the hypothesis that all spectral lines of the sun are negatives of emission spectra of flames on earth, chemical analysis of the sun's composition could begin.

But the hypothesis is false. The history textbooks tell us of elements, such as helium, which were first identified in a solar spectrum; they omit mention of elements allegedly discovered on the sun and later declared nonexistent. The fact is that the relation between emission and absorption spectra is not always as simple as that between a negative and a positive photograph (*18*). Unless we realize this, the chief impetus for Kirchhoff's research is not noticed, and his results may seem mysterious.

Stewart's Law of Radiation

It would be very easy to complicate this study by considering all sorts of factors that destroy the symmetry between absorption and emission. Some of these factors—such as the Doppler effect—are very important for astrophysics but play almost no role, or none at all, in the present study of the relation between absorption and emission.

Other factors are more significant in this context—factors such as chains of emissions and absorptions which take place when two radiating elements interact but not when each one of them is excited separately. Let us ignore all such complications and center on one factor —temperature, with which we started. One thing we have noted already: that hot bodies emit and thereby cool, and that sometimes when they are absorbing they heat up enough to radiate (this is Prevost's law of exchange).

The simplest way to understand Prevost is to say that, although a body emits only when it is hot, it absorbs whenever it is exposed to light. That this is an oversimplification is common knowledge: ordinarily bodies absorb certain wavelengths, reflect others, and transmit still others. Indeed, the idea of the reciprocity between emission and absorption attempts to take these differences into account. So let us consider just one wavelength and the material which, when hot, emits it. Now one can read Prevost's law of exchange in the following manner: matter absorbs a wavelength which, when hot, it emits. This is Ångström's law (1853) (*19*). What about the wavelengths which the given body cannot emit? It cannot absorb them under any conditions. This is Stewart's law (1854) (*20*).

One corollary to Stewart's law may be pointed out at once. Suppose there exists a body which may, under some conditions (namely, when hot), emit white light—light of every wavelength of the spectrum. Then this body must also absorb all light—it is black. A black body is one which absorbs all light which falls on it; when cold, it appears black but, when hot, a black body may radiate light of different wavelengths, including white light, and thus appear to the eye not black at all. In any case, appearance to the eye is incidental. As Foucault had shown a little earlier (1849), a small flame located between the eye and a large flame of the same kind appears dark (because its absorption effect is stronger than its emission effect, and because the eye adjusts to the setup) (*21*).

A black body, then, is supposedly that body which absorbs all wavelengths, regardless of whether or not it looks black. This definition is not good enough, because even transparent bodies seem to absorb some portion, however minute, of any given wavelength. And so both Ångström's law and Stewart's law look either false or hopelessly inadequate. It is easy to correct the definition of a black body. Whereas, before, we spoke of blackness as the ability to absorb radiation of any wavelength and concluded that all bodies are black, we may now speak of blackness as the ability to absorb in its entirety any radiation of any wavelength. This definition will make blackness not too common but too rare to be a subject of study. Moreover, it raises the need to distinguish between various phenomena previously lumped together. Let us consider Foucault's experiment again, with a strong and a weak radiation source of the same material, and ask whether that material may be black. If, as Foucault thought, the weak source creates an absorption spectrum by dispersing light from the strong source through resonance, then the weak source cannot be made of black matter. Black matter cannot disperse light, since it must absorb all of it. It may, however, create an absorption spectrum by absorbing light from one direction, storing it for a while, and then emitting it in all directions. This is not resonance but resonance emission.

The existence of resonance emission proper, we have seen, contradicts Prevost's law of exchange. We must, therefore, declare seeming resonance emission to be really some other phenomenon: absorption raises the temperature of the weak source for the delay period, and this slight increase in the temperature causes the increase in radiation.

We thus see that both Ångström's and Stewart's laws raise more problems than they solve; they force us to speak of the degree of absorption and of the relation between absorption, emission, temperature, and so on.

This was the situation when Kirchhoff entered the scene, trying to take all these complications into account. This, indeed, was his first (1859) achievement (*22*). For simplicity's sake, I present it as follows.

Preliminaries to Kirchhoff's Law of Radiation

Let us take one unit of matter of a given chemical nature; the unit may be an arbitrary volume or mass, or it may be an atom. Let us use the following, rather loose, nomenclature concerning its emission, its absorption, and its disposition to emit and to absorb during a unit of time: E = actual emission; e = the disposition to emit; A = the actual absorption; a = the disposition to absorb.

Obviously, since A depends on the environment (there is no absorption when there is no surrounding radiation, for instance) in a manner different from that in which a depends on the environment, these terms cannot be equal. We may suggest that e and a are independent of the environment, and that E, too, in accord with Prevost's law, is not explicitly dependent on the environment. We postulate the following.

Functions e and a are explicit functions of internal variables only, such as the temperature of the material in question and its chemical composition. We also postulate,

$$E = e. \qquad (1)$$

Equation 1 is false, since it implies that there is no induced emission. However, it is an immediate corollary of Prevost's law, and so we shall pretend that it is true. Furthermore, we postulate

$$A = Ia, \qquad (2)$$

where I is the intensity of the incident beam or the density of the radiation in the immediate environment.

One immediate corollary from Eqs. 1 and 2 is of supreme importance, and takes much of the mystery out of the dimension of Planck's constant, as we see later. (Dimensions are denoted here by square brackets.) We have seen that, by definition, $[E] = [A]$; and from this we can deduce, with the aid of Eqs. 1 and 2, that

$$[e]/[a] = [E]\,[I]/[A] = [I]$$

which is the dimension of the density of light passing through a unit of area in a unit of time t, or the dimension of energy divided by l^5t.

Equation 2 is false, too, since it assumes that excited atoms have the same disposition to absorb as unexcited ones. But the merit of Eq. 2 is its simplicity—that is, its linearity—and so it is a good approximation in weak fields; we shall accept it for the time being as true.

Up to now we have been very imprecise, speaking of e, a, and so on without paying heed to wavelengths at all. So let us correct this and speak from now on of e_λ, a_λ, E_λ, A_λ of the given unit of matter; we shall retain Eqs. 1 and 2 with this modification. Equation 1, now $E_\lambda = e_\lambda$, has changed its meaning in a somewhat unintended way: it now denies not only the possibility of induced emission but also the possibility of resonance emission. Similarly, Eq. 2, which becomes $A_\lambda = I_\lambda\, a_\lambda$, now denies not only saturation but also secondary absorption. Still, we shall accept both equations as true. Now, Stewart's law becomes:

$$e_\lambda \equiv 0 \rightarrow a_\lambda \equiv 0 \qquad (3)$$

—in other words, what a body cannot emit (when hot) it cannot absorb (when hot or cold); we may rewrite Eq. 3 thus:

$$e_\lambda = K_\lambda\ a_\lambda;\ K_\lambda \geqq 0 \qquad (3a)$$

for all wavelengths, where K_λ is a still undefined coefficient, except in that it is nonnegative.

Both Eqs. 3 and 3a contradict our observation that every body will absorb some portion of any incident radiation, that no body is utterly unable to absorb any given wavelength. From the viewpoint of the old quantum theory it is quite clear that some quanta will not be absorbed by some systems under any conditions; but in the old quantum theory the term *absorption* is much more rigorously defined than the term *absorb* is in the observation that any matter will absorb some portion, however small, of any incident radiation. The situation here is much more baffling than it looks, and we must, in desperation, declare Eq. 3a to be true and turn a blind eye to many common observations as being too complex to handle as yet. So, back to Eq. 3a.

Since e_λ and a_λ are both explicit functions of internal variables only, so is K_λ. For, by the very use of Eq. 3a, K may be construed as an explicit function of internal variables. To put it differently, if K were an explicit function of an environmental variable, then, obviously, we might, by varying that variable, alter e/a.

To take care of Ångström's law, we must view a_λ as larger than or equal to e_λ at low temperatures and the reverse at high temperatures, or else view both e_λ and a_λ as 0. In the latter case, it does not matter what value we assign K_λ. Otherwise, we can write

$$K = e/a, \qquad (3b)$$

remembering that the arguments of this equation are all internal variables.

The standard way of writing Eq. 3b is

$$e\ (\lambda, T, \ldots)/a\ (\lambda, T, \ldots) = K\ (\lambda, T, \ldots) \qquad (3c)$$

where the dots stand for the unspecified internal variables, such as chemical constitution, specific gravity, or specific heat. The change from e to e_λ was viewed as an increase in precision; the change from $e_\lambda\ (T, \ldots)$ to $e\ (\lambda, T, \ldots)$ is viewed as mere change of nomenclature. But Eq. 3c may somehow have smuggled in the hypothesis that K for any single wavelength is independent of K for any other wavelength—that a body's absorption-emission mechanisms for one wavelength (the energy levels for one wavelength) bear no relation to those for another wavelength. The Bohr model already assures us that this hypothesis simply is not valid. But we have not advanced thus far yet. Also, we may say that if there really is any interdependence between mechanisms for absorption and emission of different wavelengths, the dots in Eq. 3c will register that difference. Moreover, the dependence of the quantities in Eq. 3c on temperature may take care of the point at issue: remembering Prevost's law we may say that the body in question, when absorbing wavelength 1, is heated, and so it may thus change its pattern with respect to wavelength 2. Are there other internal variables significant in this way, and, if so, what are they? If not, how does the dependence on temperature reflect the absorption-emission mechanism?

Kirchhoff's Law and Its Proof

Kirchhoff's most important step was to prove the following formula:

$$K\ (\lambda, T, \ldots) = K\ (\lambda, T), \qquad (4)$$

where, again, the dots stand for unspecified internal variables.

The proof can be given in two steps. First, imagine that, under some external conditions,

$$K\ (\lambda, T, \ldots) = K\ (\lambda, T). \qquad (5)$$

Since K is independent of external variables, Eq. 4 follows Eq. 5. (Eq. 4 may read, "under *all* external conditions, etc.," whereas Eq. 5 reads, "under *some* external conditions, etc." Yet the stronger Eq. 4 follows here from the weaker Eq. 5!)

The second step is to prove Eq. 5. Take two bodies amalgamated with a cavity between them, both having temperature T and both emitting a wavelength λ. If K is not the same for both under such equilibrium conditions, radiation may be used to destroy the equilibrium, contrary to the second law of thermodynamics. For, this law implies that a system does not by itself move away from thermal equilibrium. Hence, under equilibrium conditions, K is the same for both bodies, and so Eq. 5 is true and thus our proof is complete.

There are various more precise versions (*3, 22*) of the proof of Eq. 5; what is objectionable in the proof, however, is not its imprecision but the assumption it rests on, which is much more stringent than appears to be the case. The assumption is that any two bodies at any temperature may radiate any given wavelength, which we may filter and allow to be emitted and absorbed by both bodies in isolation from any other wavelength, interference from the filter (in terms of temperature and of emission of its own radiation), and so on.

Let us accept the proof, nonetheless—namely, accept

$$e/a = K\ (\lambda, T)$$

as a universally true equation. Notice that we have no reason to accept $e = e\ (\lambda, T)$ or $a = a\ (\lambda, T)$; indeed, were e independent of other variables, spectroscopy would be impossible. To estimate K we may choose a black body. By definition, a body is black if, for it, $a \equiv 1$; thus, for a black body,

$$e = e\ (\lambda, T) = K\ (\lambda, T).$$

Are there any black bodies? Can we assume that any exist? If the assumption that they do leads to a theoretical difficulty, the difficulty may be used as proof for the nonexistence of black bodies (*23*). We shall, therefore, have to avoid all theoretically significant corollaries to the hypothesis that black bodies exist; the use of black bodies is either a simplification of a discussion for the sake of convenience or an asymptotic ideal case considered for the sake of empirical investigation. Let us assume the existence of a black body and the presence of a cavity in it, under equilibrium conditions. We can easily see that, for any given wavelength, there is in the cavity a constant energy density ε of waves of that length, and that, in each time unit, each part of the walls of the cavity absorbs this amount of energy multiplied by c, the speed of light, and emits the same amount of energy. That is,

$$E_\lambda = A_\lambda = I_\lambda = \varepsilon \cdot c = e/a = e = K.$$

If we fix T, make in the black body a very small hole leading to the cavity, and place in the hole a filter for light of fixed λ, we can measure I, provided our interference with the system is negligible. We may consider an alternative setup. Einstein has envisaged a perfectly white cavity ($a \equiv 0$) with a piece of a black body inserted for a while to arrange the energy distribution in the cavity to equal K. For this white cavity (with the black body eliminated), K is of no interest, since, if a equals 0, e also equals 0 and K has no physical significance; yet this white cavity will give us a way to measure K and then use the results on ordinary bodies where K is of great significance, especially where we are trying to deduce emission spectra from absorption spectra.

Between Kirchhoff and Planck

The Stefan-Boltzmann (*24*) law (1879) is as follows:

$$I(T) = \int_0^\infty K\,(\lambda,\,T)\,d\lambda = \sigma\,T^4. \qquad (6)$$

Boltzmann derived it (*25*) from the Maxwellian assumption that radiation causes pressure, and from the two laws of thermodynamics. It is nowadays considered valid for black bodies only, since, now, K is viewed as being less universal than Kirchhoff thought it was; but Boltzmann's considerations are not thereby impaired.

The same thing may be said of Wien's theorem (1893) (*26, 27*),

$$K\,(\lambda,\,T) = \lambda^{-5}\,f\,(\lambda\cdot T), \qquad (7)$$

where f is a still undetermined function of the one variable $\lambda \cdot$T. Equation 6 follows from Eq. 7, as it should.

Also, by considering a parallel between the radiation pressure and the pressure of a Maxwellian gas, Wien further determined the relationship known as Wien's law (1896) (*27*):

$$f\,(\lambda\cdot T) = e^{-a/\lambda T}. \qquad (8)$$

This parallel was made complete in Einstein's famous paper of 1905, where radiation was itself treated as a gas proper (quantized).

From considerations of degrees of freedom and the Boltzmann distribution, Lord Rayleigh concluded (1900) (*28, 29*), however, that

$$f\,(\lambda\,T) = A\,\lambda\,T. \qquad (9)$$

That Eq. 9 violates the idea of equilibrium between radiation and the walls of the cavity is obvious; this follows from the assumption of a Boltzmann distribution for infinitely many degrees of freedom, as Jeans pointed out in 1901 and 1904 (*30*), on quite general grounds. He even quoted Maxwell to say that the introduction of degrees of freedom for radiation brings in infinitely many new degrees of freedom, and that hence any distribution which takes them into account will lead to a catastrophe. Jeans himself thought that, if the time required for its occurrence were very long, the catastrophe would not matter overmuch (*31*).

Planck was quite ignorant of this difficulty and even of Rayleigh's formula (*32, 33*)—for reasons mentioned below—whereas Rayleigh was well aware of Planck's formula and, in a note published in 1902, refers to it and to the simple relation between the Planck and the Rayleigh formulas (*29*). That he did not follow Planck's reasoning, then or later (as he confessed in 1911 in a letter to Ehrenfest) (*33*) is a different matter. Planck's reasoning still requires some clarification.

Planck's Studies Prior to His Quantization

Enter Planck.

Planck's initial interest was in thermodynamics. He interpreted (*34*) Helmholtz's view on the law of conservation of energy in a very interesting manner, as follows. Given the forces acting in a system, we can examine them, or the potentials from which they may derive, and deduce the law of conservation of energy. We may assume, quite generally, even if we do not know the forces in a system, that these forces are conservative. It may be argued that such an approach is defective, since it is based on ignorance; not so, says Helmholtz according to Planck; the law of conservation of energy is philosophically deeper than any law of force of any system; conservation of energy is the primary law of nature. Planck greatly admired Helmholtz, and he intended to apply to the second law of thermodynamics the same mode of reasoning he thought Helmholtz had applied to the first law. Whereas others would view the application of these laws as a kind of shortcut to circumvent our ignorance, Plank viewed these laws as primary. Whereas others preferred, when possible, to deduce the two laws from specific conditions of given systems—whether laws of force, models, distributions, or other conditions—Planck preferred to deduce his results from the laws without specific assumptions (which he called "models" or "mechanisms," in this generalized sense) whenever possible. Whereas Lorentz derived the theory of oscillators from this theory of the electron, Planck tried to deduce it from Maxwell's equations and from general considerations only. He said later that he was unfamiliar with Lorentz's work, but that he would have rejected it anyway as being based on a specific mechanism (*35*). And he refused to assume the Maxwell-Boltzmann distribution throughout his work; he did assume it in the last stage of his work, but he never viewed this as anything but a symptom of a defeat (*36*).

Planck's interest in Kirchhoff's law derived from its utter universality, which suggested that it depended on no specific mechanism (*37*). He was dissatisfied with Wien's derivation of the value of $f\,(\lambda\cdot T)$, which, we remember, was based on an analogy with a Boltzmann gas—a dual violation of Planck's fundamental principles (since it was an analogy, and an analogy to a model).

Planck's first contribution was to correlate the average energy of an electrodynamic (Maxwellian) oscillator and the average energy of the field with which it is in equilibrium, for a given frequency, or, rather, for the frequency range $(\nu,\,\nu + d\,\nu)$. His formula, which Lorentz had arrived at by other means, is

$$E_\nu = \frac{8\,\pi\,\nu^2}{c^3}\,U_\nu\,d\,\nu \qquad (10)$$

where U is the average energy of the oscillator for the given frequency range and E is the energy density of the field for the same range. (Note that $[E_\nu] = [U_\nu]/l^3$.)

Planck's second step was in line with exercises which he performed, and described in his *Treatise on Thermodynamics,* for various systems: he searched for an arbitrary function S such that the second law of thermodynamics would be characterized by its asymmetry and such that S would help describe the behavior of the system under consideration—in the context of this discussion, would help in the derivation of Wien's law. First we have to translate Wien's theorem and Wien's law from a function of λ to a function of ν, remembering that

$$d\,\nu = d\,(c/\lambda) = (-c/\lambda^2)\,d\,\lambda$$

or

$$d\,\lambda = -\,\frac{\lambda^2}{c}\,d\nu.$$

Equation 7 then becomes

$$K\,(\nu,\,T) = \nu^3\,f\,(\nu/T) \qquad (7a)$$

where we write $f\,(\nu/T)$ in preference to $f\,(T/\nu)$, because this makes it easier to write

$$f(\nu/T) = e^{-a\nu/T}. \qquad (8a)$$

According to Wien's law, the energy density in a black cavity is

$$E_\nu = a\, \nu^3\, e^{-\beta\nu/T}\, d\nu \qquad (11)$$

and, from Eq. 10, we have

$$U_\nu = \gamma\, \nu\, e^{-\beta\nu/T} \qquad (12)$$

From thermodynamics we have

$$dS = dU/T$$

or

$$dS/dU = 1/T,$$

and from Eq. 12 we have

$$\frac{1}{T} = \frac{1}{\beta\,\nu} \ln \frac{U}{\gamma\,\nu} \qquad (12a)$$

so that

$$dS = \frac{dU}{T} = \frac{dU}{\beta\,\nu} \ln \frac{U}{\gamma\,\nu}$$

and

$$\frac{d^2S}{dU^2} = \frac{\delta}{U}. \qquad (13)$$

Under the force of experience, which refuted Wien's law (see *38*), Planck changed his Eq. 13 to

$$\frac{d^2S}{dU^2} = \frac{a}{U\ (b+U)}, \qquad (14)$$

from which he concluded, with the aid of Wien's theorem and his own law for the relation between the energies of the oscillators and the cavity (Eq. 10) that

$$U_\nu = h\nu\ (e^{-h\nu/kT} - 1)^{-1} \qquad (15)$$

and

$$E_\nu = \frac{8\pi h\nu^3}{c^3}\ (e^{-h\nu/kT} - 1)^{-1} d\nu. \qquad (16)$$

It is a strange fact that Planck's discovery of the constants h and k was made prior to his quantization of radiation, and that he himself, as well as tradition, has obscured this fact (*39*). Planck himself was so impressed by these constants and their dimensions that, even before he introduced quantization, he spoke of the new possibilities that he himself had opened toward a theory of natural constants and natural units.

Einstein's Version of Kirchhoff's Law

Planck's work on the entropy of oscillators has been, of course, entirely superseded by the work of others. Its historical importance is that it enabled him to modify Wien's formula (Eq. 9) by modifying Eq. 13 into Eq. 14 by the use of Eq. 10. The strange dimension of h in Eq. 16 looks strange only in retrospect; there was nothing puzzling about it before Planck's postulation of his famous quantization of energy.

Planck set out to solve one problem and ended up with three. His original problem of explaining Kirchhoff's law was one; the nature of quanta and the explanation of the distribution of radiation in the cavity are the two new ones. All too often people confuse Kirchhoff's law with the law of distribution of radiation in black cavities under equilibrium conditions, because of the numerical equivalence of these two laws. In any case, it is well known that Planck thought he had explained the black-cavity radiation distribution by quantization plus Boltzmann distribution. These postulations lead to Wien's law, not to Planck's (*40–42*); replacing Boltzmann's distribution by the Bose-Einstein distribution will lead to Planck's law of distribution. But Kirchhoff's law of emission and absorption is still unexplained; though Planck's distribution does provide the estimate for the correlation between emission and absorption, it does not explain it. The next development of quantum theory was divorced from all thermal considerations and all statistical considerations, but it did throw immense light both on quantization and on the relations between emission and absorption; I am referring to Bohr's theory, of course, which needs no discussion here. But the step following it deserves some mention, since it is all too often neglected, and since, when represented, its logic is not made clear (*43*). I refer to Einstein's theory of Kirchhoff's law of 1916 (*41, 44*).

Whether because of the studies of induced emission (resonance radiation, fluorescence) of Wood and of others (*45*) or *ad hoc,* Einstein, in order to arrive at Planck's distribution, assumed the existence of induced emission. Further, he considered the dispositions of matter to emit and absorb definite quanta to be in accord with Bohr's theory. Thus, instead of speaking of E_ν, he spoke of $E_{m,n}$, the disposition of matter to emit by a quantum jump from energy level m to energy level n, and, similarly, replaced A_ν with $A_{m,n}$; but he did not assume $E_{m,n}$ to equal $e_{m,n}$, as $e_{m,n}$ depends on internal variables alone, whereas $E_{m,n}$ depends on the field, too, since induced emission is allowed.

Again, let us consider a black cavity under equilibrium conditions (see *46*).

Due to the equilibrium conditions, the probability of an oscillator's attaining the energy state U_m is

$$p\ (U_m) = e^{-\varepsilon_m/kT} \qquad (17)$$

The probability of emission $\nu_{m,n}$ when the state m occurs is denoted as $A_{m,n}$; the probability of emission $e_{m,n}$, then, is

$$e_{m,n} = e^{-\epsilon_n/kT} A_{m,n}. \qquad (18)$$

The absorption coefficient $a_{m,n}$ is likewise defined, so that

$$a_{m,n} = e^{-\varepsilon_n/kT} B_{m,n}, \qquad (19)$$

where $B_{m,n}$ denotes the probability of absorption of $\nu_{m,n}$ when the state n occurs and $\nu_{m,n}$ is present.

In line with the linear Eq. 2 above, let us assume that

$$A_{m,n} = a_{m,n}\, E\ (\nu_{m,n}, T) \qquad (20)$$

where E is the field-energy distribution, as above.

The third factor to consider now is induced emission, where, instead of $E = e$, as postulated above, we postulate $E = e + i$, where i denotes induced emission and

$$i_{m,n} = e^{-\varepsilon_m/kT}\, C_{m,n} \cdot E\ (\nu_{m,n}, T), \qquad (21)$$

where $C_{m,n}$ denotes the probability for induced emission of $\nu_{m,n}$ when the state m occurs and when $\nu_{m,n}$ is present. Since, in equilibrium, $A_{m,n} = E_{m,n}$,

$$e^{-\varepsilon_n/kT} B_{m,n} \cdot E\ (\nu_{m,n}, T) = e^{-\varepsilon_m/kT} A_{m,n} + e^{-\varepsilon_m/kT} C_{m,n} \cdot E\ (\nu_{m,n}, T). \qquad (22)$$

It is nice to note that the linearity in the various equations, though used more extensively than in the original considerations, is now very natural, since it follows from assumptions of stochastic independence which are quite natural. We now introduce a new assumption, which is physically appealing, though it may be less neat. It is the assumption that when T goes to infinity, E does too. Eddington has shown that this assumption is unnecessarily strong—that monotony will do (*47*). Nonetheless we shall make the strong assumption, which reduces Eq. 22 with T going to infinity to the case

$$B_{m,n} = C_{m,n}. \qquad (23)$$

From Eqs. 22 and 23 we easily deduce that, under equilibrium conditions,

$$E\ (\nu_{m,n}, T) = (A_{m,n}/B_{m,n})\ [e^{-(\varepsilon_m - \varepsilon_n/kT)} - 1]^{-1}. \qquad (24)$$

Postulating, with Bohr, $\varepsilon_m - \varepsilon_n = h\nu_{m,n}$, and, further,

$$A_{m,n} = \frac{8\,\pi\, h\, \nu^3}{c^3}\, B_{m,n}, \qquad (25)$$

we can identify Eq. 24 with Planck's distribution (Eq. 16). It should be noted that the only distribution assumed concerned the oscillators, not the field, and that the general assumption was that of equilibrium conditions. But Eq. 25 as well as the corollary, Eq. 23, may be generalized, because they contain no explicit reference to the equilibrium conditions. In this respect Einstein was using Kirchhoff's techniques; but we have thus far not achieved anything like Kirchhoff's law.

It is true that Eq. 25 entails a modern version of Stewart's law, but we do not need Einstein's theory for that; Einstein takes for granted Bohr's theory of energy levels, from which that version of Stewart's law follows. The question may rise, now, How do we formulate Kirchhoff's law with the aid of Einstein's coefficients? In the first place, Einstein's formula for Planck's distribution evidently does not necessarily hold for non-black bodies or for nonequilibrium systems. Moreover, the ratio $A_{m,n}/B_{m,n}$, which equals the ratio $e_{m,n}/a_{m,n}$, is very far from being e_λ/a_λ, and, as $E_{m,n}/A_{m,n}$ tends, under equilibrium conditions, with strong fields, to approach $A_{m,n}/B_{m,n}$, it is a poor substitute for e_λ/a_λ.

To be precise, we should sum overall m and n, so that $\varepsilon_m - \varepsilon_n$ has the same value $h\nu$ for any given ν. Thus,

$$K = \frac{\sum E_{m,n}}{\sum A_{m,n}} = \frac{\sum p\,(U_m)\,[A_{m,n} + B_{m,n}\,p\,(\nu)]}{\sum p\,(U_n)\,B_{m,n}\,p\,(\nu)} \tag{26}$$

where $p\,(U_m)$ is the probability of an oscillator's being in energy state ε_m, and is an explicit function of T, and $p\,(\nu)$ is the probability that a quantum of frequency ν is sufficiently near to the oscillator to interact with it, and is a function of the field distribution and intensity.

We do not yet know how to assess these probabilities under any conditions other than those of a black cavity and equilibrium. At all events,

$$K = \sum \frac{p\,(U_m)\,A_{m,n}\,[1 + \alpha\,p\,(\nu)]}{p\,(U_n)\,\alpha\,A_{m,n}\,p\,(\nu)} \tag{26a}$$

where

$$1/\alpha = 8\,\pi\,h\,\nu^3/c^3$$

as in Eq. 25, or

$$K = \sum \frac{p\,(U_m)}{p\,(U_n)} \left[\frac{1}{\alpha\,p\,(\nu)} + 1\right]; \tag{26b}$$

and, assuming equilibrium conditions and applying Eq. 17,

$$K = e^{-h\nu/kT} \left[\frac{1}{\alpha\,p\,(\nu)} + 1\right]. \tag{26c}$$

And so, again, Einstein's coefficients are eliminated from the Kirchhoff formula, as they were from the Planck formula. So long as $p\,(\nu)$ is very large, we may view K as dependent solely on the probability that the oscillators attain energy states U_m and U_n; these probabilities may be functions of the temperature alone, in collisions, or of $p\,(\nu)$ in resonance radiation. Still, it is quite obvious that here K is not in the least universal even when $p\,(\nu)$ does not enter the picture at all.

What has become of the proof that, in equilibrium, K must be universal or else the second law of thermodynamics is violated? This proof is still valid, but only as an approximation for equilibrium conditions. According to Einstein's theory, less of the equilibrium theory can be generalized than could be generalized under Kirchhoff's, since the division into internal and external variables—indeed, Prevost's law of exchange—has long since been dropped.

References and Notes

1. For generality in science, see K. R. Popper, *The Logic of Scientific Discovery* (Basic Books, New York, 1959), sect. 18. For Planck's stress on the generality of Kirchhoff's law, see his Nobel Prize lecture, *The Origins and Development of Quantum Theory* (Oxford Univ. Press, New York, 1922), p. 3, and his *Scientific Autobiography* (Philosophical Library, New York, new ed., 1949), p. 34. The stress is repeated by Klein [M. J. Klein, *Arch. Hist. Exact Sci.*, **1**, 460 (1962); ———, in *The Natural Philosopher*, D. E. Gershenson and D. Greenberg, Eds. (Blaisdell, New York, 1963), vol. 1, p. 96]. It is also often repeated in the introductory physics literature [see, for example, F. K. Richtmyer and E. H. Kennard, *Introduction to Modern Physics* (McGraw-Hill, New York, ed. 5, 1956), p. 147].
2. S. Flügge, Ed., *Handbuch der Physik*, vol. 26 (Springer, Berlin, 1958).
3. J. H. Poynting and J. J. Thomson, *A Textbook of Physics*, vol. 3, *Heat* (London, 1904), chap. 15; E. Pringsheim, *Verhandl. Deut. Phy. Ges.* **3**, 81 (1901); L. Dunoyer, *Ann. Chim. Phys.* **8**, 30 (1906); G. C. Evans, *Proc. Amer. Acad.* **46**, 97 (1910); D. Hilbert, *Z. Physik* **13**, 1057 (1912); discussion between Pringsheim and Hilbert, *ibid.* **14**, 589 (1913); *ibid.*, p. 592; *ibid.*, p. 847.
4. For the most restricted interpretation, see M. Born, *Optik* (Berlin, 1933), p. 460, and F. K. Richtmyer and E. H. Kennard, *Introduction to Modern Physics* (McGraw-Hill, New York, ed. 5, 1956). For the unrestricted interpretation, see S. Flügge, Ed., *Handbuch der Physik*, vol. 20 (Springer, Berlin, 1928), p. 122 ff., and F. A. Jenkins and H. E. White, *Fundamentals of Optics* (McGraw-Hill, New York, ed. 3, 1957), p. 430. The equilibrium condition alone is commonest, its *locus classicus* for general physics being M. Planck, *Introduction to Theoretical Physics, Theory of Heat* (London, 1932), p. 185, as well as Planck's *Vorlesungen uber die Theorie der Wärmstrahlung* (Leipzig, ed. 5, 1923); or, for astrophysics, S. Chandrasakhar, *An Introduction to the Study of Stellar Structures* (Chicago, 1939), p. 203. See also Einstein's scientific autobiography in P. A. Schilpp, Ed., *Albert Einstein: Philosopher-Scientist* (Cambridge Univ. Press, New York, 1950), p. 37. The restriction to thermal radiation only is common in texts on luminescence, fluorescence, and phosphorescence; also, in E. T. Whittaker, *A History of Theories of Aether and Electricity* (Philosophical Library, New York, 1953), vol. 2, p. 78, where, however, "thermal" and "blackbody" seem to be used as synonyms. For the restriction to both thermal radiation and equilibrium conditions, see M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill, New York, ed. 4, 1957), pp. 101–104. Other restrictions occur in the literature, such as the one imposed by G. Joos, *Theoretical Physics* (Hafner, London, ed. 3, 1958), p. 620—namely, that the medium be uniform. (For the redundancy of this constraint, see A. Cotton, *Eclairage Electrique* **14**, 405 (1898), ———, *ibid.*, p. 540, and S. Chandrasakhar, *An Introduction to the Study of Stellar Structures* (Chicago, 1939), pp. 202, 203. Finally, astrophysicists, following Wiedemann, tend to define local (color) temperature as that which fits Kirchhoff's law in equilibrium; see S. Chandrasakhar, *Radiation Transfer* (Oxford Univ. Press, New York, 1950), pp. 7, 8.
5. G. Joos, *Theoretical Physics* (Hafner, London, ed. 3, 1958), pp. 620, 621. See also E. Mach, *Die Prinzipien der Wärmelehre* (Leipzig, ed. 2, 1900), where Kirchhoff's law seems to be utterly unrestricted at first (p. 140) but then, in view of Wiedemann's refutation, is claimed to be restricted to equilibrium conditions (p. 142).
6. See S. Chandrasakhar, *Radiation Transfer* (Oxford Univ. Press, New York, 1950), chaps. 10–12, where Kirchhoff's law is shown to be an approximation for gray atmospheres. Contrast this with A. B. Pippard [*The Elements of Classical Thermodynamics* (Cambridge Univ. Press, New York, 1961)]: "The success of thermodynamics in these circumstances [of cavity radiation] is perhaps the strongest evidence we possess for regarding the laws as valid in all physical situations to which they can be applied." Another strange phenomenon is the proof of Kirchhoff's law given in A. Sommerfeld's *Thermodynamics and Statistical Mechanics* (Academic Press, New York, 1956), p. 135. There is no follow-up on it that I know of.
7. See J. Agassi, *Towards an Historiography of Science* (Mouton, The Hague, 1963).
8. Note that in exceptional cases the tinkering goes too far rather than not far enough, when writers apply the "conventional twist" [see K. R. Popper, *The Logic of Scientific Discovery* (Basic Books, New York, 1959)], and turn the law into a tautology. In our example the "conventional twist" is given by *Handbuch der Physik* (*2*), which renders Kirchhoff's law a definition of thermal radiation. However, "in practice, the luminescence emissions and thermal radiations of phosphorus are readily distinguishable because there are large differences between their . . . characteristics" [H. W. Leverenz, *An Introduction to Luminescence of Solids* (Wiley, New York, 1950)]. Hence the definition is quite redundant and, with it, the law, as used by *Handbuch der Physik*.
9. I. Newton, *Opticks* (1704).
10. P. Prevost, *Essai sur le calorique rayonant* (Geneva, 1809). For extracts, see D. B. Brace, Ed., *The Laws of Radiation and Absorption*, vol. 15 of *Harper's Scientific Memoirs* (New York, 1901).
11. The idea is adumbrated in Newton's *Opticks*.
12. *Phil. Trans.* **92**, 365 (1802).
13. *Ann. Physik* **56**, 264 (1817) [for English translation see J. S. Ames, Ed., *Prismatic and Diffraction Spectra*, vol. 2 of *Harper's Scientific Memoirs* (New York, 1898)]. Note that solar chemistry is impossible without at least some stellar spectroscopy. Hence Fraunhofer's great effort in procuring the spectrum of Sirius and his justified pride in having achieved it.
14. See I. Newton, *Opticks:* "whilst an Assistant, whose Eyes for distinguishing Colours were more critical than mine, did by Right Lines . . . note the Confines of the Colours. . . . And this operation being divers times repeated . . . I found that the Observations agreed well enough with one another, and that the Rectilinear Sides . . . were . . . divided after the manner of a Musical Chord."
15. T. Young, *A Course of Lectures on Natural Philosophy* (London, 1807), vol. 1, pp. 367, 378, 389; see also, *Miscellaneous Works of the Late Th. Young* (London, 1855), vol. 1. Note in the latter work (pp. 82–3) the new theory of harmony of colors (in Newton's rings) as a new link between acoustics and optics—only to be given up in 1817 (pp. 280–82). See also (p. 35) the beautifully simple relation between ocular biophysics and spectroscopy.
16. Mach [*The Principles of Physical Optics* (London, 1926)] is the only writer, I think, who suggests that Young's optical studies

developed from acoustics, through search for an optical analogue to sound interference. But Mach cannot say why the analogy is important. Mach is impressed with Young's study of Newton's rings and with Young's employment of acoustic analogies there, but he fully ignores Young's view of optical harmony in the rings. Also, as a consequence, Mach fails to attribute to Young the idea that, though physically there are infinitely many colors, biologically there are only a few. Peacock, one of Young's two chief biographers, considers the trigger to Young's revolutionary attempt to have been the alleged publication, in 1790, of a nonexistent book by Huygens [see G. Peacock, *Life of Th. Young* (London, 1855)]. Alexander Wood considers the trigger to have been the failure of attempts to detect light pressures [see his *Thomas Young, Natural Philosopher* (Cambridge Univ. Press, New York, 1954)]. This failure was viewed at the time as neither conclusive nor relevant.

17. *Phil. Trans. Roy. Soc. London Ser. A* **92**, 378 (1802). The discovery was in some accord with Young's view, but it also demanded modification of that view, as Young admits (*ibid.*, p. 395). Note that here Wollaston and Young see a physical basis for a biological theory of color; but they insist that there are only a few biological colors yet infinitely many physical colors. Young gave Wollaston credit for this discovery, though he himself had predicted it earlier.
18. See C. A. Young, *The Sun* (New York, 1895, 1896, 1898) for plates presenting absorption and emission spectra as negatives and positives; see A. Cotton's impressive "The present state of Kirchhoff's law," *Astrophys. J.* **9**, 237 (1899). A list of difficulties in astrospectroscopy is given in *Smithsonian Inst. Ann. Rep. to July 1898* (1900). Concerning the discovery of alleged new elements on the sun, this could not go on indefinitely, in view of Mendeléeff's periodic table, as noted by Sir William Crookes, who, commenting on his own (alleged) new element, considers the game near to a close [*Smithsonian Inst. Ann. Rep. to July 1899* (1901)]. But the problem of identification remained serious for a while. In the strict sense, the problem of identifying solar spectral lines is still not totally solved.
19. *Stockholm Acad. Handl.* (1852–53), p. 229; *Phil. Mag.* **9**, 327 (1855).
20. *Trans. Roy. Soc. Edinburgh* **22**, 1 (1858). For the priority dispute, see G. R. Kirchhoff, *Phil. Mag.* **25**, 258 (1863) and J. W. S. Rayleigh, *ibid.* **1**, 98 (1901). See also A. Cotton, *Astrophys. J.* **9**, 237 (1899), and H. Roscoe, *Smithsonian Inst. Ann. Rept. to July 1899* (1901), especially p. 621.
21. *Ann. Chim. Phys.* **58**, 476 (1860).
22. *Berlin Monatsber.* **1859**, 783 (1859); *Poggendorff's Ann.* **109**, 275 (1860); *Abhandl. Berlin Akad.* **1861**, 63 (1861); *Phil. Mag.* **19**, 193 (1860); *ibid.* **21**, 260 (1861); D. B. Brace, Ed., *The Laws of Radiation and Absorption*, vol. 15 of *Harper's Scientific Memoirs* (New York, 1901).
23. The question of the importance of the hypothesis of the existence of black bodies was seldom raised; see, however, *Sci. Abstr.* **1**, 383 (1898).
24. *Wien. Ber.* **79**, 391 (1879).
25. *Wien. Ann.* **22**, 291 (1884).
26. *Berlin. Sitzber.* (9 Feb. 1893), p. 55.
27. *Ann. Physik* **58**, 662 (1896).
28. *Phil. Mag.* **49**, 539 (1900).
29. J. W. S. Rayleigh, *Scientific Papers* (Dover, New York, new ed., 1964), vol. **4**, p. 483.
30. *Phil. Mag.* **10**, 91 (1905); *Nature* **72**, 243 (1905); *ibid.*, p. 293.
31. *Proc. Roy. Soc. London Ser. A* **76**, 295 (1905); *ibid.*, p. 545; see H. A. Lorentz, *The Theory of Electrons and its Applications to the Phenomena of Light and Radiant Heat* (Dover, New York, ed. 2, 1952).
32. M. J. Klein, in *The Natural Philosopher* (Blaisdell, New York, 1963).
33. J. W. S. Rayleigh, *Scientific Papers* (Dover, New York, new ed., 1964), vol. 6, p. 45. See also note added in 1911 to vol. 5, p. 253. See also R. J. Strutt, *John William Strutt, 3rd Baron Rayleigh* (Arnold, London, 1924), for this and for Nernst's reply to Rayleigh's letter. In his letter to Nernst, Rayleigh claims priority for having raised a serious problem, and Nernst most agreeably endorses the claim, but carefully prevents the interpretation that Rayleigh's discovery of a problem guided Planck. Even in J. H. Jeans, *Report on Radiation and The Quantum Theory* (London, ed. 2, 1924), where the development begins with the Rayleigh-Jeans formula and the ultraviolet catastrophe and proceeds through Planck's solution to Bohr's theory, it is not quite alleged that Planck solved Rayleigh's problem.
34. M. Planck, *Das Prinzip der Erheltung der Energie* (Berlin, ed. 5, 1924); *Treastise on Thermodynamics* (Dover, New York, ed. 3, 1945), preface to first ed. and pt. 3.
35. ———, *The Origins and Development of Quantum Theory* (Oxford Univ. Press, New York, 1922).
36. ———, *ibid.*, p. 19, and all later philosophical works.
37. This answers the question raised in the opening paragraph of this article. Kirchhoff's law was refuted by Wiedemann [*Wiedemanns Ann.* **37**, 180 (1893)], before Planck began his studies, by observations of cold flames (cold from the viewpoint of Kirchhoff's law). This raises the question, Which part of the presuppositions of Kirchhoff should be abandoned? It seems that the question was systematically avoided (see *3*). For Planck, however, the situation must have looked very different, since he had a special version of the second law of thermodynamics [see his *Treatise on Thermodynamics* (Dover, New York, ed. 3, 1945), pt. 3]. He could easily accept the proof of Kirchhoff's law, with the added constraint that none of the internal variables were employed in an irreversible process. For, when they are, the second law as he understood it need not be violated together with the violation of Kirchhoff's law. Consequently, the restriction of the law of thermal equilibrium was, at the time, neither necessary nor sufficient; hence Planck's later presentation of the law with this restriction (see *4*) resulted from later considerations.
38. O. Lummer and E. Pringsheim, *Verhandl. Deut. Physik Ges. Berlin* **1**, 215 (1899); *ibid.* **2**, 174 (1900); *Ann. Physik* **3**, 159 (1900).
39. See, for instance *35*. In his *Scientific Autobiography* (Philosophical Library, New York, new ed., 1949), p. 42, Planck speaks ambiguously, saying that in 1900 "it was necessary to introduce a universal constant which I called *h*." Similarly the comment of Max von Laue (*ibid.*, p. 41) is puzzling. "This finding . . . was reported by Max Planck again [!] on December 14, 1900. That was the birthday of Quantum Theory." In a paper submitted for publication in November 1899 [*Ann. Physik* **1**, 69 (1900)], Planck estimates $h = 6.885 \cdot 10^{-27}\ \mathrm{cm}^2 \times \mathrm{g} \times \mathrm{sec}^{-1}$ and mentions its importance for a future theory of natural constants. In a paper submitted in March 1900 [*Ann. Physik* **1**, 717 (1900)] the estimate is repeated. Planck's estimate on 14 December 1900 is $6.55 \cdot 10^{-27}$ erg × sec. Most latter-day restatements of Planck's findings are encumbered with typographical complications which obscure the fact that *h* came before quantum theory. It is incredible how much of the abundant transcription and restatement in textbooks and histories is so very mechanical as to preserve even typographical clumsiness. See however, N. J. Klein, *Phys. Today* **19**, 23 (1966), especially p. 26.
40. A. Einstein, *Ann. Physik* **17**, 132 (1905).
41. D. ter Haar, *Selected Readings in Physics: The Old Quantum Theory* (Oxford Univ. Press, New York, 1967).
42. For the claim that Einstein's work leads to Wien's law, see E. T. Whittaker, *A History of Theories of Aether and Electricity* (Philosophical Library, New York, 1953), vol. 2, pp. 89, 100–105.
43. See, for example, E. T. Whittaker, *ibid.*, vol. 2, p. 198. A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, New York, 1934), skip the derivation. Max Born, *Optik* (Berlin, 1933), gives a much too cursory one. It is customary to add half-life factors to Einstein's formulas [see, for example, *Handbuch der Physik* (*2*); E. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge Univ. Press, New York, 1951)]. This is hardly permissible [see D. ter Haar (*41*), pp. 64, 65]. Finally, a piquant item: P. Jordan, *Anschauliche Quantumtheorie* (Berlin, 1936), introduces Einstein's conclusions as empirical results. Even in places where the derivation is correct [for example, in D. ter Haar (*41*) and M. J. Klein, in *The Natural Philosopher* (Blaisdell, New York, 1963)], the point of our interest is not explicitly stated: the estimate of the Einstein coefficients is for equilibrium conditions, but, since these coefficients are constants, the estimate is quite universal. The constancy of Einstein's coefficients is, as far as I know, stressed only by Einstein himself [see D. ter Haar (*41*), p. 171].
44. *Mitt. Physik Ges. Zurich* **18** (1916); *Verhandl. Deut. Physik Ges.* **18**, 318 (1916); *Z. Physik* **18**, 121 (1917). Einstein's chief concern was the problem of recoil, which is of no interest in the present study.
45. *Phil. Mag.* **8**, 293 (1904); *Proc. Roy. Soc. London* **84**, 209 (1910). Since Einstein does not refer to Wood but refers only to K. von Mosengeil's study of recoil, it is unlikely that he knew of Wood's work.
46. Einstein himself deduces from Eq. 24 plus Wien's theorem (Eq. 7) both Bohr's $\epsilon_m - \epsilon_n = h\nu$ and $A_{m,n} = \zeta\nu^3 B_{m,n}$, leaving the determination of h and ζ to empirical investigation. This is attractive, since Wien's theorem, as Einstein points out, is purely thermodynamical. Also, this is suspect, since this treatment leaves it as a mere empirical fact that $\zeta/h = 8\pi/c^3$. All this calls for further investigation. Einstein's insistence on the fundamental nature of Eq. 7 is Planckian, though Planck would not approve, since Wien's considerations were statistical. For the relations between Planck and Einstein, see M. J. Klein, in *The Natural Philosopher,* vols. 2 and 3 (Blaisdell, New York, 1963, 1964). See also N. Bohr, H. A. Kramers, J. C. Slater, *Phil. Mag.* **47**, 785 (1924); P. Franck, *Rev. Mod. Phys.* **21**, 394 (1949); R. A. Millikan, *ibid.*
47. A. S. Eddington, *Phil. Mag.* **1**, 803 (1925).
48. An early version of the core of this article was given at a progress-report session of the History of Science convention held in Philadelphia in December 1963. I am indebted to A. Shimony and M. J. Klein for their comments and to Boston University and Tel Aviv University for technical assistance.