A NEW EQUATION FOR THE DISTRIBUTION OF RADIANT ENERGY

BY GILBERT N. LEWIS

CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA

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From certain considerations based on Einstein's theory of light quanta, I have recently deduced an equation for the entropy of radiation, as a function of energy density and frequency, which is identical with the one obtained by Planck. From this expression it would seem possible to proceed immediately to Planck's equation for the distribution of radiant energy, by using a method which has hitherto been regarded as unquestionably valid. The deduction, however, rests upon a certain tacit assumption, as may be seen by a brief review of the method used in Planck's "Theory of Heat Radiation."

Using the same notation as in the preceding article, \( U \) and \( S \) are the total energy and entropy of a hollow containing radiation, \( u \) and \( s \) are the corresponding densities, and \( u_\nu \) and \( s_\nu \) represent the rate of change of these densities with the frequency, as we proceed through the spectrum. Thus, in the total volume \( V \)

\[
U = V \int_0^\infty u_\nu \, d\nu \\
S = V \int_0^\infty s_\nu \, d\nu
\] (1) (2)

If the radiation is in thermal equilibrium the entropy is at a maximum. In other words, if we consider a slight variation in the distribution of energy, produced by increasing infinitesimally the energy in some parts of the spectrum and decreasing that in other parts, then the total change in entropy produced by this variation will be zero (to the same order of infinitesimals). That is,

\[
\delta S = 0.
\] (3)

If the variation is subject to the conditions that volume and total energy are fixed,

\[
\delta V = 0, \\
\delta U = 0.
\] (4) (5)

From the preceding equations, bearing in mind that the operations indicated by "\( d \)" and "\( \delta \)" are independent, we find that

\[
\int_0^\infty \delta u_\nu \, d\nu = 0,
\] (6)
\[
\int_0^\infty \delta s, d\nu = 0, \tag{7}
\]
and the last equation may also be written in the form,
\[
\int_0^\infty \frac{\partial s}{\partial u_\nu} \delta u_\nu d\nu = 0. \tag{8}
\]

It is a well-known theorem of calculus that if
\[
\int_{x_1}^{x_2} \varphi(x)\psi(x)dx = 0
\]
for all values of \(\psi(x)\) which are compatible with the condition that
\[
\int_{x_1}^{x_2} \psi(x)dx = 0,
\]
then \(\varphi(x)\) must be a constant. Applying this theorem to equations (6) and (8) it follows that \(\delta s/u_\nu\) is a constant, and from this point Planck proceeds by methods of undoubted validity to derive his distribution formula.

The whole proof rests upon the unstated assumption that the only restriction upon \(u_\nu\) is given by equation (6). This is equivalent to assuming that every state of thermal equilibrium is completely determined by a single variable, such as density of radiant energy or temperature. This assumption that underlies the whole classical thermodynamics of radiation as developed by Wien and Planck is based upon no experimental or theoretical evidence.

It is obvious that if the law of conservation of photons be accepted, the state of a system in equilibrium will be determined only when the density of energy and the concentration of photons are both given; but this law may at present, seem too radical for general acceptance. I shall, therefore, attempt to show that, without any further assumptions than those which have already been fully accepted, we may deduce the existence of states of true thermal equilibrium which are not comprised in the "thermodynamics" of Wien and Planck (cf. the equilibrium states discussed by Einstein to which he applies the terms "aussergewöhnlich" and "improprement dit").

As in my preceding paper, we may define a function \(n_\nu\) by the equation
\[
n_\nu = u_\nu/\hbar \nu, \tag{9}
\]
and thence define two other quantities by the equations
\[
n = \int_0^\infty n_\nu dv; \quad N = Vn. \tag{10}
\]
We may also for convenience and without any implications call $N$ the number of photons. We then find, by introducing these quantities into the classical equations for the thermodynamics of radiation, that whenever radiation is completely enclosed by perfectly reflecting walls, whether these be stationary or movable, the quantity $N$ remains constant, whatever process may be considered. Thus if the process be one of free expansion from a smaller into a larger enclosure, neither $u$, nor $v$ changes, while in case the walls move, as in a Wien displacement, the Doppler effect produces for each type of light the same relative change in $u$, and $v$.

Let us now consider radiation enclosed within mirror walls, one of which is so thin that, owing to random fluctuations in the pressure of the light, it acquires a sort of Brownian movement, until a stationary state is reached such that no further average exchange of energy between the thin wall and the radiation occurs. Even if the original radiation were monochromatic it would not remain so, but, owing to the Doppler effect produced by the vibrating wall, would become distributed over all frequencies from zero to infinity.

It remains to show that this stationary state is a state of true thermal equilibrium. Suppose that the outside of this wall is in contact with a gas which also by itself would give a Brownian movement to the wall. If the temperature of the gas is very high it will give to the wall more energy than it receives, and this in turn will be imparted to the radiation within the enclosure. If the temperature is very low the opposite process will occur. There will be one temperature of the gas when neither process will occur, on the average, and this may be defined as also the temperature of the radiation. We then evidently have a condition of thermal equilibrium such that by raising slightly the temperature of the gas we raise also that of the radiation, and this may be done in a perfectly reversible manner.

Thus the radiation may have any number of different states of equilibrium, all at the same temperature, according to the amount of energy originally in the enclosure, and only one of these states coincides with the state of black body radiation, which is alone considered in the classical thermodynamics of radiation.

It would seem that the only escape from the conclusion that more true equilibrium states really exist than have hitherto been considered would be to deny even the theoretical possibility of ideal mirror walls. But even this mode of escape fails, for we might consider a hollow of such enormous extent that it would take a very long time for any occurrence at the wall to affect the interior. If in such an enclosure we start with nearly monochromatic radiation and some free electrons, then there will be that interchange of energy and momenta between the electrons and the light which is known as the Compton effect, and this will result again in a stationary state in which the radiant energy is distributed between all frequencies.
from zero to infinity. The temperature of such a state could be measured by the average kinetic energy of the electrons. Here also the process of reaching the equilibrium state will occur without change in the number of photons.

In all of these equilibrium states in which the number of photons is fixed we have in addition to equations (6) and (8),

$$\delta N = 0 \text{ or } \int_0^\infty \delta \left( \frac{u_\nu}{h\nu} \right) d\nu = 0.$$  \hspace{1cm} (11)

If we now employ simultaneously equations (6), (8) and (11), the calculus of variations no longer shows that $\partial s_\nu/\partial u_\nu$ is a constant, but rather that

$$\frac{\partial s_\nu}{\partial u_\nu} = \lambda_1 + \frac{\lambda_2}{h\nu},$$  \hspace{1cm} (12)

where $\lambda_1$ and $\lambda_2$ are two undetermined coefficients which in a given thermal distribution are constant over the whole range of frequencies.

Instead of pursuing these purely mathematical methods to evaluate $\lambda_1$ and $\lambda_2$ we may treat the problem with greater simplicity by utilizing the fact that the thermal distribution in any system of radiation approaches as a limit, at high frequencies, the general equation first obtained by Wien (using an asterisk to denote equations true only in the limiting case of high frequency),

$$u_\nu = \text{const. } \nu^2 e^{-\frac{h\nu}{kT}}.$$  \hspace{1cm} (13)*

The constant of this equation was evaluated by Planck as $8\pi h/c^3$, but this gives only the particular kind of equilibrium known as that of black body radiation. In order to include all of our new types of equilibrium we may introduce a new quantity $\gamma$ which is constant only when the number of photons is constant. If $\gamma = 1$ for the case of black body radiation, then in general $\gamma$ will give the ratio, at any high frequency, between the actual energy density and the energy density in a black hollow at the same temperature. The general equation of the Wien type may then be written as

$$u_\nu = \frac{\gamma 8\pi h^3}{c^3} e^{-\frac{h\nu}{kT}}.$$  \hspace{1cm} (14)*

The expression for the entropy of radiation, which was obtained in the preceding paper, and which is essentially identical with that of Planck, is

$$s_\nu = \frac{k_{\nu_\nu}}{h\nu} \ln \frac{1}{8\pi \beta e} + \frac{8\pi k^2}{c^3} \left[ \left( 1 + \frac{c^2 u_\nu}{8\pi h^2} \right) \ln \left( 1 + \frac{c^2 u_\nu}{8\pi h^2} \right) - \frac{c^2 u_\nu}{8\pi h^2} \ln \frac{c^2 u_\nu}{8\pi h^2} \right]$$  \hspace{1cm} (15)
from which, by differentiation and slight rearrangement, we find

$$\frac{\partial s_r}{\partial u_r} = \frac{k}{\hbar\nu} \ln \frac{1}{8\pi\beta\varepsilon} + \frac{k}{\hbar\nu} \ln \left(\frac{8\pi\hbar\nu}{c^3u_r} + 1\right).$$  \hspace{1cm} (16)

For the limiting case of high frequencies this becomes

$$\frac{\partial s_r}{\partial u_r} = \frac{k}{\hbar\nu} \ln \left(\frac{1}{8\pi\beta\varepsilon} \frac{8\pi\hbar\nu}{c^3u_r}\right).$$  \hspace{1cm} (17)*

Combining (14)* and (17)* we have

$$\frac{\partial s_r}{\partial u_r} = \frac{k}{\hbar\nu} \ln \frac{1}{\gamma 8\pi\beta\varepsilon} + \frac{1}{T},$$  \hspace{1cm} (18)

where we may dispense with the asterisk since this equation has the same form as (12) and since \(\lambda_1\) and \(\lambda_2\), being constant, have now been determined by finding their values in the range of high frequency.

Our problem is now solved, for we can equate the values \(\partial s_r/\partial u_r\) given in equations (16) and (18), and find as our general expression for the distribution law

$$u_r = \frac{8\pi\hbar\nu^3}{c^3} \frac{1}{\frac{\hbar\nu}{kT} \frac{1}{e^\gamma} - 1}.$$  \hspace{1cm} (19)

In the special case where \(\gamma = 1\) this reduces to the familiar formula of Planck, but it also includes all the other states of true thermodynamic equilibrium that we have dealt with in this paper. We may note that for any value of \(\hbar\nu/kT\), as \(\gamma\) becomes smaller, equation (19) approaches equation (14)*, hence that generalized form of the Wien equation may be regarded as the universal law of radiation at small densities, just as the simple gas law is the limiting law for all gases at small densities.

All that I have attempted to show in this paper—and this I think I have shown beyond question—is that there are many states of radiation in thermal equilibrium which are not included in the classical thermodynamics of radiation, and that in these states the distribution of radiant energy with respect to frequency may be considered by methods similar to those that have been employed in the more limited fields previously studied.

It is true that I have been led to the discovery of these new equilibrium states through an attempt to find a law of conservation of photons, but their existence does not yet prove that such a law obtains. If it later proves possible to show that in absorption and emission of light the photon acts as an indestructible and uncreatable atom, then we shall find, not only in the thermodynamics of radiation, but also in the thermodynamics
of all substances, great fields of equilibria hitherto unsuspected, in which the individual states differ from one another with respect to the new variable, the number of photons. If such a necessity arises and the law of conservation of photons can be established, it may be necessary to revise still further our ideas of thermal radiation, for in that case it would be doubtful whether what is known as black body radiation is as definite a thing as has been supposed.

1 Lewis, these PROCEEDINGS, 13, 307 (1927).
3 Einstein, Ann. Physik, 38, 881 (1921); J. Physique, 3, 277 (1913).

THE HYDROGEN ATOM WITH A SPINNING ELECTRON IN WAVE MECHANICS

BY C. F. RICHTER

CALIFORNIA INSTITUTE OF TECHNOLOGY

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In this paper it is shown that the Schrödinger wave mechanics, plus the Uhlenbeck-Goudsmit spinning electron, completely represents the fine structure of hydrogen-like spectra.

The Hamiltonian function of the system in classical mechanics is taken as

\[
H = \frac{1}{2m} \left[ \frac{p_r^2}{r^2} + \frac{p_\theta^2}{r^2 \sin^2 \theta} + \frac{p_\phi^2}{r^2} \right] + \frac{1}{2I} \left[ p_\theta^2 + \frac{1}{\sin^2 \theta} (p_\phi^2 + p_\psi^2 - 2p_\phi p_\psi \cos \theta) \right] - \frac{Ze^2}{r} + \frac{Q}{r^3} \left[ \cos \alpha p_\theta p_\theta - \cot \theta \sin \alpha p_\theta p_\psi + \csc \theta \sin \alpha p_\theta p_\theta + \cot \theta \sin \alpha p_\phi p_\phi \right] + \left( 1 + \cot \theta \cot \theta \cos \alpha \right) p_\psi p_\psi - \cot \theta \csc \theta \cos \alpha p_\phi p_\phi \right)
\]

in which \( r, \theta, \varphi \) are polar coordinates of the center of the electron, referred to the nucleus (of atomic number \( Z \)); \( \theta, \psi, \Phi \) are Eulerian angles of the (spherical) electron referred to a parallel polar axis and initial plane; \( m \) is the mass of the electron, \( I \) its moment of inertia, \( e \) its charge, while \( Q = \frac{Ze^2}{2mc^2} \), and \( \alpha \) is an abbreviation for \( \psi - \varphi \).

The writer has made use of the above expression for the quantization of the system on the old quantum theory;\(^1\) the results were identical with those of other investigators.\(^2\) It should be remarked that this form is valid only to terms of order \( v^2/c^2 \), where \( v \) is the velocity of the electron.