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ON THE THEORY OF LIGHT PRODUCTION AND LIGHT ABSORPTION

by A. Einstein

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[2] In a study published last year¹ I showed that the Maxwell theory of electricity in conjunction with the theory of electrons leads to results that contradict the evidence on black-body radiation. By a route described in that study, I was led to the view that light of frequency ν can only be absorbed or emitted in quanta of energy $(R/N)\beta\nu$, where R denotes the absolute constant of the gas equation applied to one gram-molecule, N the number of actual molecules in one gram-molecule, β the exponential coefficient of Wien's (and Planck's) radiation formula, and ν the frequency of the light in question. This relationship was developed for a range that corresponds to the [3] range of validity of Wien's radiation formula.

At that time it seemed to me that in a certain respect Planck's theory of radiation² constituted a counterpart to my work. New considerations, which are being reported in §1 of this paper, showed me, however, that the theoretical foundation on which Mr. Planck's radiation theory is based differs from the one that would emerge from Maxwell's theory and the theory of electrons, precisely because Planck's theory makes implicit use of the aforementioned hypothesis of light quanta.

In §2 of this paper I shall make use of the hypothesis of light quanta to derive a relationship between the Volta effect and photoelectric diffusion.

§1. *Planck's theory of radiation and the light quanta*

In §1 of my paper cited above I have shown that the molecular theory of heat combined with the Maxwell theory of electricity and the theory of

[1] ¹A. Einstein, *Ann. d. Phys.* 17 (1905): 132.

[4] ²M. Planck, *Ann. d. Phys.* 4 (1901): 561.

electrons lead to a formula for black-body radiation that contradicts experience

$$(1) \quad \rho_\nu = \frac{R}{N} \frac{8\pi\nu^2}{L^3} T .$$

Here ρ_ν denotes the density of radiation at temperature T and at a frequency between ν and $\nu + 1$.

What is the reason that Mr. Planck did not arrive at the same formula, but obtained instead the expression

$$(2) \quad \rho_\nu = \frac{a\nu^3}{\frac{\beta\nu}{e^{\frac{\nu}{T}} - 1}} \quad ? \quad [5]$$

Mr. Planck derived¹ the mean energy E_ν of a resonator of proper frequency ν situated in a space filled with disordered radiation as given by the equation

$$(3) \quad E_\nu = \frac{L^3}{8\pi\nu^2} \rho_\nu . \quad [8]$$

This reduced the problem of black-body radiation to the problem of determining E_ν as a function of temperature. The latter problem will have been solved if one can calculate the entropy of one of many similarly constituted, mutually interacting resonators of proper frequency ν that are in dynamic equilibrium.

Let us envision the resonators as ions that could perform rectilinear sinusoidal vibrations about an equilibrium position. The fact that the ions have electrical charges is irrelevant in the calculation of this entropy; we simply have to conceive these ions as mass points (atoms) whose momentary state is completely determined by their instantaneous deviation x from the equilibrium position and by their instantaneous velocity $dx/dt = \xi$.

¹M. Planck, *Ann. d. Phys.* 1 (1900): 99.

For the distribution of states of these resonators to be uniquely determined in thermodynamic equilibrium, one has to assume that there exists an arbitrarily small number of freely moving molecules besides the resonators, which by virtue of their collisions with the ions can transmit energy from resonator to resonator; we will not take into account these molecules in our calculation of entropy.

We could determine \bar{E}_ν as a function of temperature from the Maxwell-Boltzmann distribution law and would thereby obtain the invalid radiation formula (1). One arrives at the route taken by Mr. Planck in the following manner.

Let p_1, \dots, p_n be appropriately chosen state variables¹ that completely determine the state of a physical system (e.g., in our case the values x and ξ of all the resonators). At the absolute temperature T , the entropy S of this system is represented by the equation²

$$S = \frac{\bar{H}}{T} + \frac{R}{N} \lg \int e^{-\frac{N}{RT} H} dp_1 \dots dp_n,$$

where \bar{H} denotes the energy of the system at temperature T , H denotes the energy as a function of p_1, \dots, p_n , and the integral is to be extended over all possible combinations of the values of p_1, \dots, p_n .

If the system consists of a very large number of molecular structures--and the formula has meaning and validity only in this case--then only those combinations of values of the $p_1 \dots p_n$ whose H differs very little from \bar{H} contribute significantly to the value of the integral appearing in S .³ If this is taken into account, it is easily seen that, except for negligible quantities, one can put

$$S = \frac{R}{N} \lg \int_H^{H+\Delta H} dp_1 \dots dp_n,$$

[11] ¹A. Einstein, *Ann. d. Phys.* 11 (1903): 170.

²*loc. cit.* §6.

³Follows from §3 and §4 *loc. cit.*

where ΔH should be chosen very small, yet large enough to make $R \lg(\Delta H)/N$ a negligible quantity. S is then independent of the value of ΔH .

If one substitutes the variables x_α and ξ_α of the resonators instead of dp_1, \dots, dp_n in the equation and takes into account that the equation holding for the α -th resonator is

$$\int_{E_\alpha}^{E_\alpha + dE_\alpha} dx_\alpha d\xi_\alpha = \text{const. } dE_\alpha$$

(because E_α is a quadratic, homogeneous function of x_α and ξ_α), one obtains the following expression for S :

$$(5) \quad S = \frac{R}{N} \lg W,$$

where one has put

$$(5a) \quad W = \int_H^{H+\Delta H} dE_1 \dots dE_n.$$

If one would calculate S according to this formula, one would again arrive at the invalid radiation formula (1). To arrive at Planck's formula, one has to postulate that, rather than assume any value whatsoever, the energy E_α of a resonator can only assume values that are integral multiples of ϵ , where

$$\epsilon = \frac{R}{N} \beta \nu.$$

This is because, on setting $\Delta H = \epsilon$, one immediately sees from equation (5a) that, except for an inconsequential factor, W turns into the very quantity that Mr. Planck named "the number of complexions."

Hence, we must view the following proposition as the basis underlying Planck's theory of radiation:

The energy of an elementary resonator can only assume values that are integral multiples of $(R/N)\beta\nu$; by emission and absorption, the energy of a resonator changes by jumps of integral multiples of $(R/N)\beta\nu$.

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SEVEN YEARS BEFORE THE 'BOHR ATOM'**

However, this assumption involves yet a second one, because it contradicts the theoretical basis from which equation (3) is developed. For if the energy of a resonator can only change in jumps, then the mean energy of a resonator in a radiation space cannot be obtained from the usual theory of electricity, because the latter does not recognize *distinguished* energy values of a resonator. Thus, the following assumption underlies Planck's theory:

[17] Although Maxwell's theory is not applicable to elementary resonators, nevertheless the *mean* energy of an elementary resonator in a radiation space is equal to the energy calculated by means of Maxwell's theory of electricity.

This proposition would be immediately plausible if, in all those parts of the spectrum that are relevant for observation, $\epsilon = (R/N)\beta\nu$ were small compared with the mean energy \bar{E}_ν of a resonator; however, this is not at all the case, for within the range of validity of Wien's radiation formula, $e^{\beta\nu/T}$ is large compared with 1. It is easy to prove that according to Planck's theory of radiation, within the range of validity of Wien's radiation formula, \bar{E}_ν/ϵ has the value $e^{-\beta\nu/T}$, thus, \bar{E}_ν is much smaller than ϵ . Therefore only a few resonators have energies different from zero.

In my opinion the above considerations do not at all disprove Planck's theory of radiation; rather, they seem to me to show that with his theory of radiation Mr. Planck introduced into physics a new hypothetical element: the hypothesis of light quanta.

§2. *An expected quantitative relationship between photoelectric diffusion and the Volta effect*

[18] It is well known that if metals are ordered according to their photo-
[19] electric sensitivity, one obtains the Volta electric potential series, in which a metal is the more photosensitive the closer it is to the electro-positive end of the electric potential series.

To a certain degree, this fact can be understood by assuming only that the forces (which are not to be examined here) that produce the active double layers reside on the metal-gas interface rather than on the metal-metal interface.

Let these forces produce an electric double layer on the surface of a piece of metal M that borders on a gas, and a corresponding potential difference V between metal and gas, taken as positive when the metal has the higher potential.

Let V_1 and V_2 be the potential differences between metals M_1 and M_2 in electrostatic equilibrium if they are insulated from each other. If the two metals are brought into contact, the electric equilibrium is disturbed and complete¹ voltage equalization of the metals takes place. Thereby, simple layers will be superposed on the aforementioned double layers at the metal-gas interfaces; to these corresponds an electrostatic field in the air space whose line integral equals the voltage difference.

If V_{ℓ_1} and V_{ℓ_2} denote the electric potentials at points of the gas space directly adjacent to the metals in contact, and V' denotes the potential in the interior of the metals, we have

$$V' - V_{\ell_1} = V_1 ,$$

$$V' - V_{\ell_2} = V_2 ,$$

and thus

$$V_{\ell_2} - V_{\ell_1} = V_1 - V_2 .$$

Thus, the electrostatically measurable Volta difference is numerically equal to the difference of the potentials assumed by the metals in the gas if they are insulated from each other.

If one ionizes the gas, the electric forces present in the gas space will cause a migration of the ions, to which there corresponds a current in the metals which, at the place of contact of the metals, is directed from the metal with the higher V (less electropositive) to the metal with the lower V (more electropositive). [20]

[21]

Suppose a metal M is insulated in a gas. Let V be its potential difference with respect to the gas that corresponds to the double layer. In order to move a unit of negative electricity from the metal into the gas, an amount of work numerically equal to the potential V has to be performed. Hence, the greater the V , i.e., the less electropositive the metal, the more [22]

¹We disregard the effect of thermoelectric forces.

energy is needed for the photoelectric diffusion, i.e., the smaller the photoelectric sensitivity of the metal.

So far we have considered the facts without making assumptions about the nature of photoelectric diffusion. However, the hypothesis of light quanta also yields a quantitative relationship between the Volta effect and photoelectric diffusion. Thus, to move a negative elementary quantum (charge ϵ) from the metal into the gas, it has to be supplied with at least an energy $V\epsilon$. Then, a light species will be able to remove negative electricity from the metal only when the "light quantum" of that light species has at least the value $V\epsilon$. We thus obtain

$$V\epsilon \leq \frac{R}{N} \beta\nu$$

or

$$V \leq \frac{R}{A} \beta\nu ,$$

where A denotes the charge of one gram-molecule of a univalent ion.

If we now assume that some of the absorbing electrons are able to leave the metal as soon as the energy of the light quanta exceeds $V\epsilon^1$ — which is a very plausible assumption — we obtain

$$V = \frac{R}{A} \beta\nu ,$$

where ν denotes the lowest photoelectrically effective frequency.

Thus, if ν_1 and ν_2 are the lowest light frequencies acting on the metals M_1 and M_2 , the following equation will hold for the Volta potential difference V_{12} of the two metals:

$$-V_{12} = V_1 - V_2 = \frac{R}{A} \beta(\nu_1 - \nu_2),$$

or, if V_{12} is measured in volts:

$$V_{12} = 4.2 \times 10^{-15}(\nu_2 - \nu_1) .$$

¹The thermal energy of electrons is disregarded.

This formula contains the following, at least by and large valid, proposition: The more electropositive a metal, the smaller the lowest light frequency that is effective for that metal. It would be of great interest to know whether this formula expresses the facts in a quantitative way as well.

[23]

[24]

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