

H. Konen, "das Leuchten der Gase und Dämpfe," Braunschweig, 1913, pp. 302 ff. Besides many papers by other authors not mentioned in Mr. Jolly's summary.

From the experience gained in our Münster Laboratory it seems necessary:

- (1) to make use of tubes with a *continuous flow of gas*;
- (2) to make use of *continuous electric current* in all measurements of intensity or energy of spectral lines in order to avoid complications that make it impossible to draw any reliable conclusions either from radiometric or photometric measurements. That it is possible to fulfil both conditions, by means of special tubes described in the first of the papers mentioned above, is, in my opinion, conclusively shown by Mr. J. Schwedes.

Yours very truly,
H. KONEN.

Münster i/W, physikalisches Institut
der Universität, Jan. 25, 1914.

LVI. *The Theory of Photoelectric and Photochemical Action.*
By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics, University of London, King's College**.

FOR many reasons and especially on account of the complexity which recent experimental investigations † have shown to characterize the relation between the number of electrons emitted by bodies and the intensity and frequency of the radiation used to stimulate them, it seems desirable to consider the theory of these effects from as many points of view as possible. I have therefore amplified the discussion of some of the points raised in my previous papers dealing with these questions. I shall consider first the amount of energy which is abstracted from the radiation when one electron or atom is liberated. In what follows immediately I shall use the term atom to include electrically charged particles, *i. e.* ions and electrons, since the argument is exactly the same whether the particles are supposed electrically charged or not.

* Communicated by the Author. A paper read before the American Physical Society at the Chicago Meeting, Nov. 28, 1913.

† Pohl and Pringsheim, numerous papers in recent volumes of the *Verhandlungen der Deutschen Physik. Gesellschaft.* Compton and Richardson *Phil. Mag.* vol. xxvi. p. 549 (1913).

The Energy abstracted per Atom liberated.

Consider any condensed form of any substance, bounded by a surface, which emits any monatomic gas under the influence of illumination.

Let ξ = the mean internal kinetic energy of these atoms, *i. e.* the kinetic energy they possess when in the condensed form.

W = the average work done by each atom in escaping from the substance.

w = the average change of total energy which accompanies the escape of a single atom.

Then $\frac{3}{2} RT$ is the mean external kinetic energy (*i. e.* after escaping) of an atom at temperature T and

$$w = \frac{3}{2} RT - \xi + W. \quad \dots \dots \dots (1)$$

Let $\phi(\nu)$ denote the mean energy which each atom, liberated under the influence of monochromatic radiation of frequency ν , has acquired from the radiation at the moment of liberation. The kinetic energy of each atom immediately before emission is thus $\phi(\nu) + \xi$, if the contribution to ξ arising from the radiation is treated as negligible (see last paragraph), and the mean kinetic energy each atom carries away from the surface of the substance is

$$T_\nu = \phi(\nu) + \xi - W = \phi(\nu) + \frac{3}{2} RT - w. \quad \dots \dots (2)$$

If the substance is enclosed by an isolating boundary, so that the space between the substance and the boundary is initially vacuum, there will ultimately be equilibrium characterized by some constant temperature, let us say T . The body will be emitting atoms under the influence of the complete radiation characteristic of T , and these will be returning to the body on account of their kinetic motions. The two processes balance, so that the state is invariable. By moving a piston transparent to radiation, the quantity of emitted gas can be varied without changing the quantity of radiation, so that, as before*, if n is the number of liberated atoms per unit volume,

$$n = A_0 e^{\int \frac{w}{RT^2} dT}, \quad \dots \dots \dots (3)$$

where A_0 is a quantity which is characteristic for the substance but is independent of T . The number N_1 of liberated

* O. W. Richardson, *Phil. Mag.* vol. xxiii. p. 619 (1912).

atoms which are returned to each unit area of the substance in unit time is

$$N_1 = n \beta T^{\frac{3}{2}} = A T^{\frac{3}{2}} e^{\int_{\nu_0}^{\infty} \frac{w}{RT^2} dT}, \dots (4)$$

where β is a constant readily calculated from the kinetic theory of gases and A is thus still independent of T and characteristic for the substance.

Let $\epsilon F(\nu)$ be the number of atoms emitted from unit area of the substance in unit time in the presence of unit energy density of frequency between ν and $\nu + d\nu$, and assume that the number of atoms emitted in the presence of the whole spectrum characteristic of T is, using Planck's formula,

$$N_2 = \frac{C}{4} \frac{8\pi}{C^3} \int_{\nu_0}^{\infty} \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu. \dots (5)$$

This equation contains the important assumption, which does not yet seem to have tested experimentally, that the number of atoms emitted by a given amount of light is the same whether the light is undecomposed or is broken up, without loss of energy, into its spectral constituents. In other words, it assumes that the photochemical substance acts as its own grating. This may be justified as being the simplest assumption which is consistent with the conclusions drawn from experiments on photoelectric action, that the number of emitted electrons is simply proportional to the intensity of light of definite spectral composition but varies greatly when equal energies of light of different frequencies are compared.

In (5) we have taken the lower limit of the integral to be finite and equal to ν_0 . This is to cover the possibility, which appears to be demanded by the results of photoelectric experiments, that $\epsilon F(\nu)$ is a function which takes the value zero when $\nu = \nu_0$ and does not exist for values of ν between 0 and ν_0 . If $\epsilon F(\nu)$ is a function which extends over the whole spectrum the case can be provided for by simply putting $\nu_0 = 0$.

Now consider the kinetic energy which is carried away from the substance by the atoms liberated under the influence of the radiation. If $\epsilon F(\nu)$ has the properties we have attributed to it, this amount of kinetic energy is, by virtue of (2) and (5),

$$E_2 = \frac{2\pi}{c^3} \int_{\nu_0}^{\infty} \left\{ \phi(\nu) + \frac{3}{2} RT - w \right\} \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu. (6)$$

$$= \frac{2\pi}{c^3} \int_{\nu_0}^{\infty} \phi(\nu) \epsilon F(\nu) \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu - N_2 \left(w - \frac{3}{2} RT \right). (7)$$

We have also from (5)

$$RT^2 \frac{\partial N_2}{\partial T} = \frac{2\pi}{c^2} \int_{\nu_0}^{\infty} \left\{ \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}} - 1} + RT^2 \frac{\partial \log \epsilon F(\nu)}{\partial T} \right\} \frac{\epsilon F(\nu) h\nu^3}{e^{\frac{h\nu}{RT}} - 1} d\nu, (8)$$

since $\epsilon F(\nu) = 0$ when $\nu = \nu_0$.

Differentiating (4) by T , we have

$$RT^2 \frac{\partial N_1}{\partial T} = N_1 \left(\frac{3}{2} T + w_T \right), \\ = E_1 + N_1 \left(w_T - \frac{3}{2} RT \right), \dots (9)$$

where $E_1 = 2N_1RT$ is the kinetic energy returned to the substance by the motion of thermal agitation of the gas. In the steady state $E_1 = E_2$ and $N_1 = N_2$. This is true, so far as the present use of these equations is concerned, even if there is scattering or reflexion of atoms at the surface of the substance. For by a well-known principle in atomic statistics there are as many deflexions of returning atoms outwards, of a given class, as there are deflexions inwards of escaping atoms of the same class. Substituting for E_1 and N_1 in (9) the values given by (7) and (8) we get

$$\int_{\nu_0}^{\infty} \frac{\epsilon F(\nu) h\nu^3}{e^{\frac{h\nu}{RT}} - 1} \left\{ \phi(\nu) - \frac{h\nu e^{\frac{h\nu}{RT}}}{e^{\frac{h\nu}{RT}} - 1} - RT^2 \frac{\partial \log \epsilon F(\nu)}{\partial T} \right\} d\nu = 0. (10)$$

This equation is true for all values of ν_0 and T and for all the admissible forms of $\epsilon F(\nu)$ characteristic of different substances. In general it appears from (10) that $\phi(\nu)$ may be dependent not only on ν but may also involve the properties of the substance, through $\epsilon F(\nu)$ and ν_0 and the temperature T . The experimental evidence all goes to show that at sufficiently low temperatures photoelectric action is approximately independent of the temperature of the substance for light of a given intensity; so that at low temperatures (such for example as are employed in ordinary laboratory experiments on these effects) equation (10) reduces to

$$\int_{\nu_0}^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} \{ \phi(\nu) - h\nu \} d\nu = 0. \dots (11)$$

If photochemical and photoelectric actions are (fundamentally) independent of temperature at low temperatures then $\epsilon F(\nu)$ and $\phi(\nu)$ will be functions of ν and ν_0 only and will not involve T . In that case either $\epsilon F(\nu) = 0$ or $\phi(\nu) = h\nu$

for every value of ν . For it is easy to show that the only regular function of ν not involving T which satisfies the equation

$$\int_{\nu_0}^{\infty} \chi(\nu) e^{-\frac{h\nu}{RT}} d\nu = 0, \dots \dots \dots (12)$$

if ν_0 is also independent of T , is $\chi(\nu) = 0$. For let

$$\chi(\nu) = a_0 + \sum_{s=1}^{\infty} a_s \nu^s + b_s \nu^{-s}$$

over the range $\nu_0 < \nu < \infty$. By repeated integration of (12) with respect to dT from 0 to T or repeated differentiation with respect to T , we see that for every integer p

$$\int_{\nu_0}^{\infty} \nu^{\pm p} \chi(\nu) e^{-\frac{h\nu}{RT}} d\nu = 0. \dots \dots \dots (13)$$

Multiplying the integrals (13) by the corresponding constants $a_0 a_1 a_2 \dots b_1 b_2 \dots$ and adding we get

$$\int_{\nu_0}^{\infty} [\chi(\nu)]^2 e^{-\frac{h\nu}{RT}} d\nu = 0.$$

Since $e^{-\frac{h\nu}{RT}}$ and ν_0 are always positive it follows that $\chi(\nu) = 0$ for $\nu_0 < \nu < \infty$. Applying this result to (11) it follows that

$$\phi(\nu) = h\nu. \dots \dots \dots (14)$$

Thus the quantity of energy which an atom abstracts from the radiation before it is liberated, under the influence of light of frequency ν , is $h\nu$.

This result has only been shown to be valid at low temperatures. It appears to follow from the following assumptions:—

- (1) That the distribution of energy in the radiation is given by Planck's formula.
- (2) That such a function as $\epsilon F(\nu)$ exists and the effects of the spectral components of mixed light are additive.
- (3) That photochemical actions are fundamentally independent of temperature at low temperatures and that they do not contravene the second law of thermodynamics.
- (4) That the part of ξ which comes from the radiation is negligible.

This demonstration shows that the considerations about the specific heat of electricity and electron reflexion which entered into proofs * I have given of this and related formulæ

* Phys. Rev. vol. xxxiv. p. 146 (1912); Phil. Mag. vol. xxiii. p. 624 (1912), vol. xxiv. p. 570 (1912).

were not really essential. Equation (14) has also been obtained by Einstein *, who bases his demonstration on the assumption that radiation of the same frequency and equal amount as that absorbed during emission is given out on recombination. This hypothesis seems to be of a restrictive character and results in the existence of states of radiation in equilibrium with matter which are different from the complete radiation characteristic of that temperature. The justification urged for the existence of such states of equilibrium between matter and radiation is that they would not violate the second law of thermodynamics. It appears, however, from the foregoing considerations that the particular limitation set up by Einstein is not really essential.

In a recent paper Planck † has considered the equilibrium between radiation and matter which liberates electrons under its influence. He arrives thus at a consistent system which includes Planck's law of distribution for the radiant energy and Maxwell's law for the energy of the electrons. The law which Planck finds to govern the amount of energy abstracted from the radiation by the liberated electrons agrees with that found above in that it approaches $h\nu$ as the temperature approaches zero. This follows from equations (12) and (28) of Planck's paper.

Einstein's demonstration leads to (14) as a limit which is true for small radiation densities. This may be regarded as analogous to the result obtained above, according to which (14) is necessarily valid only at low temperatures; since low temperatures correspond to small radiation densities.

It is evident from what has been said that the functions $\chi(\nu, \nu_0, T)$ which satisfy the equation

$$\int_{\nu_0}^{\infty} \frac{\nu^3}{e^{\frac{h\nu}{RT}} - 1} \chi(\nu, \nu_0, T) d\nu = 0 \dots \dots \dots (15)$$

are of great interest in the theory of photochemical action.

It will be observed that we have not proved that (14) is not true at all temperatures. All we have proved is that if photochemical action is fundamentally independent of temperature at low temperatures, then at such temperatures (14) is true. I shall show in a moment that a consistent

* Ann. der Physik, vol. xxxvii. p. 832 (1912); Journ. de Physique, 1913.
 † Sitzungsber. der k. Preuss. Akad. der Wiss., Physik.-Math. Classe, xviii. p. 350 (1913).

scheme of relations may be framed whereby

$$\phi(\nu) = h\nu.$$

universally, at all temperatures. The deduction will depend on assumptions (1), (2), and (4) but not on the first part of assumption (3).

The Amount of Decomposition.

The function $eF(\nu)$ is of great interest. The experiments on photoelectric action show that it may be very complicated, and the simple solutions of the equations which I have so far been able to consider exhibit only a rough correspondence with the experimental results*. It is, however, important to know whether they are affected by the considerations about the specific heat of electricity which I have previously made use of.

$eF(\nu)$ is a function of ν_0 as well as ν . Let us denote it by $F(\nu_0, \nu)$. Then from (4) and (5),

$$\frac{2\pi}{c^2} \int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} F(\nu_0, \nu) d\nu = AT^{\frac{1}{2}} e^{\int_{RT}^T \frac{w}{RT^2} dT} = N. \quad (16)$$

This equation may be varied by giving to w a small increment η (independent of T) and a corresponding increment ξ to ν_0 , the other quantities being unchanged. This variation is admissible because it can be realized physically by making use of a layer of attracting matter or an electrical double layer. Hence

$$\int_{\nu_0 + \xi}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} F(\nu_0 + \xi, \nu) d\nu = e^{-\frac{\eta}{RT}} \int_{\nu_0}^{\infty} \frac{h\nu^3 F(\nu_0, \nu)}{e^{\frac{h\nu}{RT}} - 1} d\nu.$$

Neglecting squares and higher powers of the small quantities ξ, η , and remembering that $F(\nu_0, \nu) = 0$ when $\nu = \nu_0$, this gives

$$\int_{\nu_0}^{\infty} \frac{h\nu^3}{e^{\frac{h\nu}{RT}} - 1} \left\{ \frac{\eta}{RT} F(\nu_0, \nu) + \xi \frac{\partial F(\nu_0, \nu)}{\partial \nu_0} \right\} d\nu = 0. \quad (17)$$

Equation (17) is solved by

$$\frac{\eta}{\xi} = h, \text{ and } F(\nu_0, \nu) = \frac{\text{const}}{\nu^p} \left(1 - e^{-\frac{h\nu}{RT}} \right) \times (\nu - \nu_0)^p. \quad (18)$$

where p is any positive number. This solution includes the

* Compton and Richardson (*loc. cit.*).

one previously discussed*, viz:—

$$\frac{\eta}{\xi} = h, \text{ and } F(\nu_0, \nu) = \frac{\text{const}}{\nu^3} (\nu - \nu_0). \quad (19)$$

as the particular case $p=1$ restricted in validity to small values of T .

Now consider the equation (16), which we may write

$$I = \int_{\nu_0}^{\infty} \frac{\nu^3 F(\nu_0, \nu)}{1 - e^{-\frac{h\nu}{RT}}} e^{-\frac{h\nu}{RT}} h d\nu = \Phi(T) e^{-\frac{h\nu_0}{RT}}, \quad (20)$$

where
$$\Phi(T) = AT^{\frac{1}{2}} e^{\frac{h\nu_0}{RT}} + \int_{RT}^T \frac{w}{RT^2} dT. \quad (21)$$

This may be regarded as defining $\Phi(T)$. Equation (18) suggests putting

$$F(\nu_0, \nu) = \frac{1}{\nu^3} (1 - e^{-\frac{h\nu}{RT}}) \psi(\nu - \nu_0), \quad (22)$$

where ψ is an undetermined function of $\nu - \nu_0$ only and does not involve T . It follows from (18) that ψ can include every function of the argument which is regular between $\nu = \nu_0$ and $\nu = \infty$ and still be a solution of (17). By changing the variable to $z = \frac{h(\nu - \nu_0)}{RT}$,

$$I = RT e^{-\frac{h\nu_0}{RT}} \int_0^{\infty} \psi\left(\frac{RT}{h} z\right) e^{-z} dz,$$

and by successive integration by parts

$$RT \left\{ \psi(0) + \frac{RT}{h} \psi'(0) + \left(\frac{RT}{h}\right)^2 \psi''(0) + \dots + \left(\frac{RT}{h}\right)^n \psi^n(0) + \dots \right\} = \Phi(T). \quad (23)$$

Since, by hypothesis $\psi(\nu - \nu_0)$ does not depend on T , $\psi(0), \psi'(0) \dots \psi^n(0) \dots$ &c. are all independent of T . If the solution we are seeking exists, equation (23) must be true for all real positive values of T . The solution therefore will only exist if $\Phi(T)$ can be expanded as a series of positive integral powers of T . By Maclaurin's theorem, if such an expansion is possible,

$$\Phi(T) = \Phi(0) + T\Phi'(0) + \frac{T^2}{2!} \Phi''(0) + \dots + \frac{T^n}{n!} \Phi^n(0) + \dots \quad (24)$$

* Phil. Mag. vol. xxiv. p. 570 (1912).

Hence by comparing coefficients, $\Phi(0)=0$ and

$$\begin{aligned} \psi(0) &= \frac{1}{R} \Phi'(0), & \psi'(0) &= \frac{h}{R^2 2!} \Phi''(0), \dots \\ \psi^{n-1}(0) &= \frac{h^{n-1}}{R^n n!} \Phi^n(0), \text{ \&c.} \dots \dots \dots \end{aligned} \quad (25)$$

Since

$$\psi(x) = \psi(0) + x\psi'(0) + \frac{x^2}{2!}\psi''(0) + \dots \quad (26)$$

the relations (25) are sufficient to determine $\psi(\nu-\nu_0)$ if it exists.

Let us now consider the equation which expresses the balance of kinetic energy between the outgoing and returning streams of atoms. This may be written, using (2), (6), and (16), since $E=2NRT$,

$$J = \int_{\nu_0}^{\infty} \frac{\nu^3 T_\nu F(\nu_0, \nu)}{e^{\frac{h\nu}{RT}} - 1} h d\nu = \frac{c^2}{\pi} NRT = 2RT\Phi(T)e^{-\frac{h\nu_0}{RT}}, \dots \quad (27)$$

or

$$J = \int_{\nu_0}^{\infty} \chi(\nu-\nu_0) e^{-\frac{h\nu}{RT}} h d\nu = 2RT\Phi(T)e^{-\frac{h\nu_0}{RT}}, \dots \quad (28)$$

if

$$\chi(\nu-\nu_0) \equiv T_\nu \psi(\nu-\nu_0) \dots \dots \dots \quad (29)$$

is a function only of $(\nu-\nu_0)$. This assumption is suggested since the form of (28) is the same as that of (20). Thus, by the same treatment as in dealing with (20),

$$\begin{aligned} \chi(0) + \frac{RT}{h} \chi'(0) + \left(\frac{RT}{h}\right)^2 \chi''(0) + \dots + \left(\frac{RT}{h}\right)^n \chi^n(0) + \dots &= 2\Phi(T) \\ = 2RT \left\{ \psi(0) + \left(\frac{RT}{h}\right) \psi'(0) + \left(\frac{RT}{h}\right)^2 \psi''(0) + \dots + \left(\frac{RT}{h}\right)^n \psi^n(0) + \dots \right\} \end{aligned}$$

whence $\chi(0)=0$ and

$$\chi'(0)/\psi(0) = \chi''(0)/\psi'(0) = \dots = \chi^n(0)/\psi^{n-1}(0) = \dots = 2h. \quad (30)$$

Since $\chi(x) = \chi(0) + x\chi'(0) + \frac{x^2}{2!}\chi''(0) + \dots$

$$= 2h \left(x\psi(0) + \frac{x^2}{2!}\psi'(0) + \frac{x^3}{3!}\psi''(0) + \dots \right)$$

$$= 2h \int_0^x \psi(x) dx = T_x \psi(x), \text{ from (29),}$$

we see that

$$T_x = \frac{2h}{\psi(x)} \int_0^x \psi(x) dx. \dots \dots \dots \quad (31)$$

Now turn to the equation (21) which defines $\Phi(T)$. Differentiate both sides by T and divide each side of the resulting equation by the corresponding side of (21). This gives

$$w = h\nu_0 - \frac{RT}{2} + RT^2 \frac{\Phi'(T)}{\Phi(T)}. \dots \dots \quad (32)$$

But, from equation (2),

$$\begin{aligned} T_\nu &= \phi(\nu) + \frac{3}{2}RT - w \\ &= \phi(\nu) - h\nu_0 + 2RT - RT^2 \frac{\Phi'(T)}{\Phi(T)}, \dots \dots \quad (33) \end{aligned}$$

and since T_ν is from (29) a function of $\nu-\nu_0$ only, it follows from (33) that

$$\phi(\nu) = h\nu - 2RT + RT^2 \frac{\Phi'(T)}{\Phi(T)} + f(\nu-\nu_0)$$

where $f(\nu-\nu_0)$ is an arbitrary function of $\nu-\nu_0$ only. But f must be zero because ϕ cannot involve ν_0 which depends on the properties of a distant surface. Thus

$$\phi(\nu) = h\nu - 2RT + RT^2 \frac{\Phi'(T)}{\Phi(T)}. \dots \dots \quad (34)$$

Substituting the value of $F(\nu_0, \nu)$ given by (22) in (10) we have

$$\int_{\nu_0}^{\infty} \psi(\nu-\nu_0) \{ \phi(\nu) - h\nu \} e^{-\frac{h\nu}{RT}} d\nu = 0,$$

and, from (34),

$$\left\{ RT^2 \frac{\Phi'(T)}{\Phi(T)} - 2RT \right\} \int_{\nu_0}^{\infty} \psi(\nu-\nu_0) e^{-\frac{h\nu}{RT}} d\nu = 0.$$

Since $\psi(\nu-\nu_0) \neq 0$,

$$RT^2 \frac{\Phi'(T)}{\Phi(T)} - 2RT = 0 \dots \dots \dots \quad (35)$$

From this

$$\Phi(T) = AT^2, \dots \dots \dots (36)$$

where A is a constant, and from (34)

$$\phi(\nu) \equiv h\nu, \dots \dots \dots (37)$$

for every substance and at all temperatures. Thus the restriction to low temperatures which might have been required for (37) to satisfy (10) is not really necessary. Equation (33) now reduces to

$$T_\nu = h(\nu - \nu_0), \dots \dots \dots (38)$$

and, putting $\nu - \nu_0 = x$, (31) becomes

$$x\psi(x) = 2 \int_0^x \psi(x) dx, \dots \dots \dots (39)$$

or

$$x \frac{\partial \psi(x)}{\partial x} + \psi(x) = 2\psi(x). \dots \dots \dots (40)$$

Thus

$$\psi(\nu - \nu_0) = A_1(\nu - \nu_0), \dots \dots \dots (41)$$

where A_1 is a constant. The values of Φ and ψ given by (36) and (41) respectively satisfy the relations (25), since

$$\psi'(0) = A_1, \quad \Phi''(0) = 2A,$$

and all the other coefficients vanish. Incidentally, from (32),

$$w = h\nu_0 + \frac{3}{2} RT. \dots \dots \dots (42)$$

The results of this investigation may be summarized as follows:—Considering the equation

$$\int_{\nu_0}^{\infty} \frac{\nu^3 T_\nu F(\nu_0, \nu)}{e^{\frac{h\nu}{RT}} - 1} h d\nu = 2RT\Phi(T) e^{-\frac{h\nu_0}{RT}} = 2ART^{3/2} \int_0^{\infty} \frac{w}{T^2} dT,$$

which contains most of the quantities under discussion. This equation and equations (10), (16), and (17), all of which involve independent relationships, are all satisfied

by the following consistent scheme of mutually related functions:—

$$\left. \begin{aligned} \phi(\nu) &= h\nu, & 0 < \nu < \infty, \\ F(\nu_0, \nu) &= \frac{Ah}{R^2} \left(1 - e^{-\frac{h\nu}{RT}}\right) \frac{\nu - \nu_0}{\nu^3}, & \nu_0 < \nu < \infty, \\ T_\nu &= h(\nu - \nu_0), & \nu_0 < \nu < \infty, \\ hv_0 &= w - \frac{3}{2} RT, \\ \Phi(T) &= AT^2. \end{aligned} \right\} (43)$$

So far as I have been able to discover, this is the only set of functions involving only a single critical frequency which will satisfy all the relations as laid down (see below) without contradiction. No use whatever has been made of the value of the specific heat of electricity or any other specifically electrical property of the materials, so that the results will be just as valid for photochemical as for photoelectric actions.

A certain amount of caution is necessary in the application of these formulæ to compare with the results of experiments. In carrying out the calculations we have entirely neglected the part played by electron reflexion in the electrical case, and by the corresponding deflexions of the atoms in the types of photochemical action which are more generally regarded as such. From the principle of statistical equivalence referred to on p. 479, it follows that this neglect will not affect the equilibrium values, so that the equations (43) will express the relations which are inherent in the phenomena so far as the action of the radiation on the molecules is concerned. But in photoelectric experiments at any rate we have to deal, not with a state of equilibrium, but with the rate of emission under given illumination. This is less than the ideal emission by an amount which represents the number of electrons deflected back into the interior. An exactly similar difficulty arises in the application of the equilibrium theory of the thermionic emission of electrons to the experimental measurements of the maximum rate of thermionic emission at a given temperature*.

More serious limitations are introduced by the assumption that the contribution to the mean internal kinetic energy ξ arising from the radiation is negligible. It is, in fact, possible that the whole of ξ may arise in this way. To

* O. W. Richardson, Phil. Mag. vol. xxiii. p. 604 (1912).

include the possibility that the part of ξ thus arising is not negligible we might have defined $\phi(\nu)$ rather differently as the excess at emission of the internal kinetic energy over the mean value ξ . In that case some of the other conclusions would require reconsideration. Also, the results which have been given are not easily harmonized with the values of the specific heats of bodies at low temperatures. For these reasons, the formulation outlined above is to be taken as illustrative rather than final. Another direction in which it is practically certain that the foregoing theory is too much simplified is in the assumption of only one critical frequency ν_0 . I hope to be able to return to the discussion of these questions later.

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LVII. *The Structure of the Atom.* By SIR ERNEST RUTHERFORD,
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THE present paper and the accompanying paper by Mr. C. Darwin deal with certain points in connexion with the "nucleus" theory of the atom which were purposely omitted in my first communication on that subject (Phil. Mag. May 1911). A brief account is given of the later investigations which have been made to test the theory and of the deductions which can be drawn from them. At the same time a brief statement is given of recent observations on the passage of α particles through hydrogen, which throw important light on the dimensions of the nucleus.

In my previous paper (*loc. cit.*) I pointed out the importance of the study of the passage of the high speed α and β particles through matter as a means of throwing light on the internal structure of the atom. Attention was drawn to the remarkable fact, first observed by Geiger and Marsden †, that a small fraction of the swift α particles from radioactive substances were able to be deflected through an angle of more than 90° as the results of an encounter with a single atom. It was shown that the type of atom devised by Lord Kelvin and worked out in great detail by Sir J. J. Thomson was unable to produce such large deflexions unless the diameter of the positive sphere was exceedingly small. In order to account for this large angle scattering of α particles, I supposed that the atom consisted of a positively charged nucleus of small dimensions

* Communicated by the Author.

† Proc. Roy. Soc. A. lxxxii. p. 495 (1909).

in which practically all the mass of the atom was concentrated. The nucleus was supposed to be surrounded by a distribution of electrons to make the atom electrically neutral, and extending to distances from the nucleus comparable with the ordinary accepted radius of the atom. Some of the swift α particles passed through the atoms in their path and entered the intense electric field in the neighbourhood of the nucleus and were deflected from their rectilinear path. In order to suffer a deflexion of more than a few degrees, the α particle has to pass very close to the nucleus, and it was assumed that the field of force in this region was not appreciably affected by the external electronic distribution. Supposing that the forces between the nucleus and the α particle are repulsive and follow the law of inverse squares, the α particle describes a hyperbolic orbit round the nucleus and its deflexion can be simply calculated.

It was deduced from this theory that the number of α particles falling normally on unit area of a surface and making an angle ϕ with the direction of the incident rays is proportional to

- (1) $\text{cosec}^4 \phi/2$ or $1/\phi^4$ if ϕ be small;
- (2) the number of atoms per unit volume of the scattering material;
- (3) thickness of scattering material t provided this is small;
- (4) square of the nucleus charge Ne ;
- (5) and is inversely proportional to $(mu^2)^2$, where m is the mass of the α particle and u its velocity.

From the data of scattering on α particles previously given by Geiger*, it was deduced that the value of the nucleus charge was equal to about half the atomic weight multiplied by the electronic charge. Experiments were begun by Geiger and Marsden † to test whether the laws of single scattering of α particles were in agreement with the theory. The general experimental method employed by them consisted in allowing a narrow pencil of α particles to fall normally on a thin film of matter, and observing by the scintillation method the number scattered through different angles. This was a very difficult and laborious piece of work involving the counting of many thousands of particles. They found that their results were in very close accord with the theory. When the thickness of the scattering film was very small, the amount of scattering was directly proportional

* Proc. Roy. Soc. A. lxxxiii. p. 492 (1910).

† Geiger and Marsden, Phil. Mag. xxv. p. 604 (1913).