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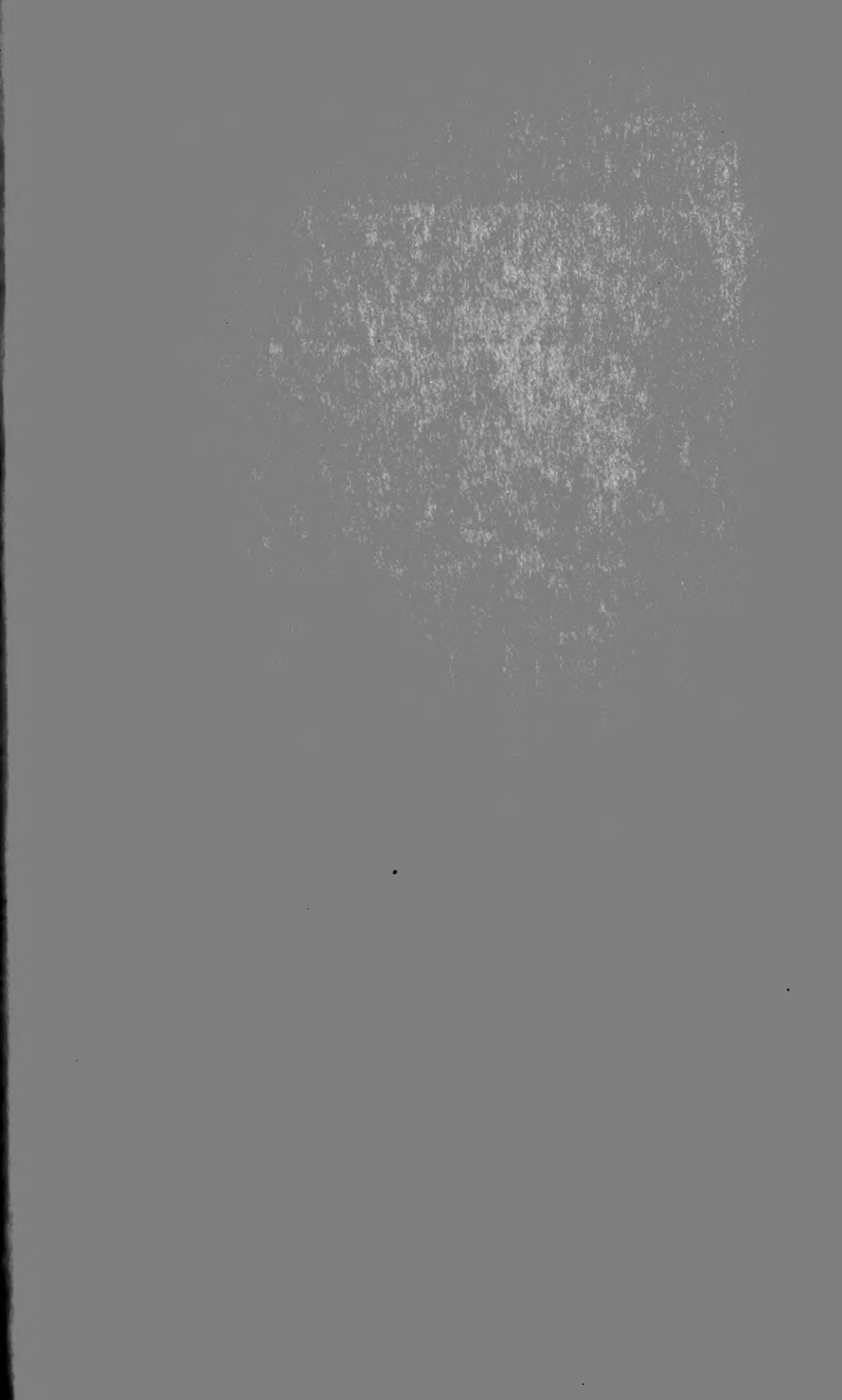
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CONDUCTED BY

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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

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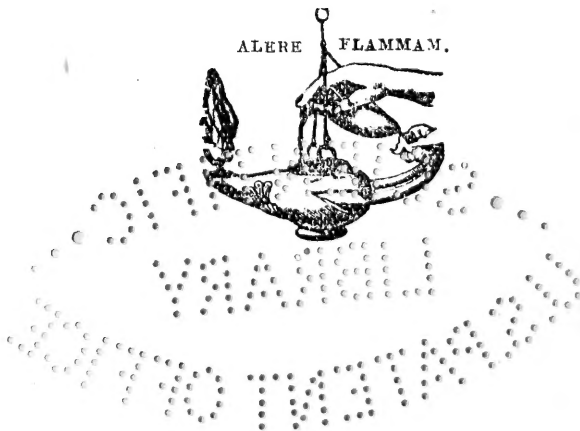
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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.



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THE
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[SIXTH SERIES.]

JANUARY 1913.

I. *The Correction to the Length of Terminated Rods in Electrical Problems.* By Lord RAYLEIGH, O.M., F.R.S.*

IN a short paper "On the Electrical Vibrations associated with thin terminated Conducting Rods"† I endeavoured to show that the difference between the half wave-length of the gravest vibration and the length (l) of the rod (of uniform section) tends to vanish relatively when the section is reduced without limit, in opposition to the theory of Macdonald which makes $\lambda = 2.53 l$. Understanding that the argument there put forward is not considered conclusive, I have tried to treat the question more rigorously, but the difficulties in the way are rather formidable. And this is not surprising in view of the discontinuities presented at the edges where the flat ends meet the cylindrical surface.

The problem assumes a shape simpler in some respects if we suppose that the rod of length l and radius a is surrounded by a cylindrical coaxial conducting case of radius b extending to infinity in both directions. One advantage is that the vibrations are now *permanently maintained*, for no waves can escape to infinity along the tunnel, seeing that l is supposed great compared with b ‡. The greatness of l secures also the independence of the two ends, so that the whole correction to the length, whatever it is, may be regarded as

* Communicated by the Author.

† Phil. Mag. vol. viii. p. 105 (1904); Scientific Papers, vol. v. p. 198.

‡ Phil. Mag. vol. xliii. p. 125 (1897); Scientific Papers, vol. iv. p. 276.
The conductors are supposed to be *perfect*.

simply the double of that due to the end of a rod infinitely long.

At an interior node of an infinitely long rod the electric forces, giving rise (we may suppose) to potential energy, are a maximum, while the magnetic forces representing kinetic energy are evanescent. The end of a terminated rod corresponds, approximately at any rate, to a node. The complications due to the end thus tell mainly upon the electric forces*, and the problem is reduced to the electrostatical one of finding the *capacity* of the terminated rod as enclosed in the infinite cylindrical case at potential zero. But this simplified form of the problem still presents difficulties.

Taking cylindrical coordinates z, r , we identify the axis of symmetry with that of z , supposing also that the origin of z coincides with the flat end of the interior conducting rod which extends from $-\infty$ to 0. The enclosing case on the other hand extends from $-\infty$ to $+\infty$. At a distance from the end on the negative side the potential V , which is supposed to be unity on the rod and zero on the case, has the form

$$V_0 = \frac{\log b/r}{\log b/a}, \quad (1)$$

and the *capacity* per unit length is $1/(2 \log b/a)$.

On the plane $z=0$ the value of V from $r=0$ to $r=a$ is unity. If we knew also the value of V from $r=a$ to $r=b$, we could treat separately the problems arising on the positive and negative sides. On the positive side we could express the solution by means of the functions appropriate to the complete cylinder $r < b$, and on the negative side by those appropriate to the annular cylindrical space $b > r > a$. If we assume an arbitrary value for V over the part in question of the plane $z=0$, the criterion of its suitability may be taken to be the equality of the resulting values of dV/dz on the two sides.

We may begin by supposing that (1) holds good on the negative side throughout; and we have then to form for the positive side a function which shall agree with this at $z=0$. The general expression for a function which shall vanish when $r=b$ and when $z=+\infty$, and also satisfy Laplace's equation, is

$$A_1 J_0(k_1 r) e^{-k_1 z} + A_2 J_0(k_2 r) e^{-k_2 z} + \dots, \quad . (2)$$

where k_1, k_2 , &c. are the roots of $J_0(kb)=0$; and this is to

* Compare the analogous acoustical questions in 'Theory of Sound,' §§ 265, 317.

be identified when $z=0$ with (1) from a to b and with unity from 0 to a . The coefficients A are to be found in the usual manner by multiplication with $J_0(kr)$ and integration over the area of the circle $r=b$. To this end we require

$$\int_0^a J_0(kr) r dr = -\frac{a}{k} J_0'(ka), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\int_a^b J_0(kr) r dr = -\frac{1}{k} \left\{ b J_0'(kb) - a J_0'(ka) \right\}, \quad . \quad (4)$$

$$\begin{aligned} \int_a^b \log r J_0(kr) r dr = & -\frac{1}{k} \left\{ b \log b J_0'(kb) \right. \\ & \left. - a \log a J_0'(ka) \right\} - \frac{1}{k^2} J_0(ka). \quad . \quad (5) \end{aligned}$$

Thus altogether

$$\frac{J_0(ka)}{k^2 \log b/a} = A \int_0^b J_0^2(kr) r dr = \frac{1}{2} b^2 A J_0'^2(kb). \quad . \quad (6)$$

For $J_0'^2$ we may write J_1^2 ; so that if in (2) we take

$$A = \frac{2J_0(ka)}{k^2 b^2 J_1^2(kb) \log b/a}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

we shall have a function which satisfies the necessary conditions, and at $z=0$ assumes the value 1 from 0 to a and that expressed in (1) from a to b . But the values of dV/dz are not the same on the two sides.

If we call the value, so determined on the positive as well as upon the negative side, V_0 , we may denote the true value of V by $V_0 + V'$. The conditions for V' will then be the satisfaction of Laplace's equation throughout the dielectric (except at $z=0$), that on the negative side it make $V'=0$ both when $r=a$ and when $r=b$, and vanish at $z=-\infty$, and on the positive side $V'=0$ when $r=b$ and when $z=+\infty$, and that when $z=0$ V' assume the same value on the two sides between a and b and on the positive side the value zero from 0 to a . A further condition for the exact solution is that dV/dz , or $dV_0/dz + dV'/dz$, shall be the same on the two sides from $r=a$ to $r=b$ when $z=0$.

Now whatever may be in other respects the character of V' on the negative side, it can be expressed by the series

$$V' = H_1 \phi(h_1 r) e^{h_1 z} + H_2 \phi(h_2 r) e^{h_2 z} + \dots, \quad . \quad (8)$$

where $\phi(h_1 r)$ &c. are the normal functions appropriate to the symmetrical vibrations of an annular membrane of radii

a and b , so that $\phi(hr)$ vanishes for $r=a$, $r=b$. In the usual notation we may write

$$\phi(hr) = \frac{J_0(hr)}{J_0(ha)} - \frac{Y_0(hr)}{Y_0(ha)}, \quad . \quad . \quad . \quad (9)$$

with the further condition

$$Y_0(ha) J_0(hb) - J_0(ha) Y_0(hb) = 0, \quad . \quad . \quad . \quad (10)$$

determining the values of h . The function ϕ satisfies the same differential equation as do J_0 and Y_0 .

Considering for the present only one term of the series (8), we have to find for the positive side a function which shall satisfy the other necessary conditions and when $z=0$ make $V'=0$ from 0 to a , and $V'=H\phi(hr)$ from a to b . As before, such a function may be expressed by

$$V' = B_1 J_0(k_1 r) e^{-k_1 z} + B_2 J_0(k_2 r) e^{-k_2 z} + \dots, \quad (11)$$

and the only remaining question is to find the coefficients B . For this purpose we require to evaluate

$$\int_a^b \phi(hr) J_0(kr) r dr.$$

From the differential equation satisfied by J_0 and ϕ we get

$$k^2 \int_a^b J_0(kr) \phi(hr) r dr = - \left[r \cdot \phi \cdot \frac{dJ_0}{dr} \right]_a^b + \int_a^b \frac{d\phi}{dr} \frac{dJ_0}{dr} r dr,$$

and

$$h^2 \int_a^b J_0(kr) \phi(hr) r dr = - \left[r \cdot J_0 \cdot \frac{d\phi}{dr} \right]_a^b + \int_a^b \frac{d\phi}{dr} \frac{dJ_0}{dr} r dr;$$

so that

$$\begin{aligned} (k^2 - h^2) \int_a^b J_0(kr) \phi(hr) r dr &= \left[r J_0 \frac{d\phi}{dr} - r \frac{dJ_0}{dr} \phi \right]_a^b \\ &= -ha J_0(ka) \phi'(ha), \quad . \quad (12) \end{aligned}$$

since here $\phi(ha) = \phi(hb) = 0$, and also $J_0(kb) = 0$. Thus in (11), corresponding to a single term of (8),

$$B = \frac{2haH J_0(ka) \phi'(ha)}{(h^2 - k^2)b^2 J_1^2(kb)} \quad . \quad . \quad . \quad (13)$$

The exact solution demands the inclusion in (8) of all the

admissible values of h , with addition of (1) which in fact corresponds to a zero value of h . And each value of h contributes a part to each of the infinite series of coefficients B , needed to express the solution on the positive side.

But although an exact solution would involve the whole series of values of h , approximate methods may be founded upon the use of a limited number of them. I have used this principle in calculations relating to the potential from 1870 onwards*. A potential V , given over a closed surface, makes

$$\frac{1}{4\pi} \iiint \left\{ \left(\frac{dV}{dx} \right)^2 + \left(\frac{dV}{dy} \right)^2 + \left(\frac{dV}{dz} \right)^2 \right\} dx dy dz, \quad (14)$$

reckoned over the whole included volume, a minimum. If an expression for V , involving a finite or infinite number of coefficients, is proposed which satisfies the surface condition and is such that it necessarily includes the true form of V , we may approximate to the value of (14), making it a minimum by variation of the coefficients, even though only a limited number be included. Every fresh coefficient that is included renders the approximation closer, and as near an approach as we please to the truth may be arrived at by continuing the process. The true value of (14) is equal by Green's theorem to

$$\frac{1}{4\pi} \iint V \frac{dV}{dn} dS, \quad \dots \dots (15)$$

the integration being over the surface, so that at all stages of the approximation the calculated value of (14) exceeds the true value of (15). In the application to a *condenser*, whose armatures are at potentials 0 and 1, (15) represents the *capacity*. A calculation of capacity founded upon an approximate value of V in (14) is thus always an over-estimate.

In the present case we may substitute (15) for (14), if we consider the positive and negative sides separately, since it is only at $z=0$ that Laplace's equation fails to receive satisfaction. The complete expression for V on the right is given by combination of (2) and (11), and the surface of integration is composed of the cylindrical wall $r=b$ from $z=0$ to $z=\infty$, and of the plane $z=0$ from $r=0$ to $r=b$ †. The

* Phil. Trans. clxi. p. 77 (1870); Scientific Papers, vol. i. p. 33. Phil. Mag. xlv. p. 328 (1872); Scientific Papers, vol. i. p. 140. Compare also Phil. Mag. xlvii. p. 566 (1899), xxii. p. 225 (1911).

† The surface at $z=+\infty$ may evidently be disregarded.

cylindrical wall contributes nothing, since V vanishes along it. At $z=0$

$$V = \Sigma(A+B)J_0(kr), \quad -dV/dz = \Sigma k(A+B)J_0(kr);$$

and

$$(15) = \frac{1}{4}b^2 \Sigma k(A+B)^2 J_1^2(kb). \quad . \quad . \quad . \quad (16)$$

On the left the complete value of V includes (1) and (8). There are here two cylindrical surfaces, but $r=b$ contributes nothing for the same reason as before. On $r=a$ we have $V=1$ and

$$-\frac{dV}{dr} = \frac{1}{a \log b/a} - \Sigma h H \phi'(ha) e^{hz};$$

so that this part of the surface, extending to a great distance $z=-l$, contributes to (15)

$$\frac{l}{2 \log b/a} - \frac{a}{2} \Sigma H \phi'(ha). \quad . \quad . \quad . \quad (17)$$

There remains to be considered the annular area at $z=0$. Over this

$$V = \frac{\log b/r}{\log b/a} + \Sigma H \phi(hr), \quad . \quad . \quad . \quad (18)$$

$$dV/dz = \Sigma h H \phi(hr). \quad . \quad : \quad . \quad . \quad . \quad (19)$$

The integrals required are

$$\int_a^b \phi(hr) r dr = -h^{-1} \{b \phi'(hb) - a \phi'(ha)\}, \quad . \quad . \quad (20)$$

$$\int_0^a \log r \phi(hr) r dr = -h^{-1} \{b \log b \phi'(hb) - a \log a \phi'(ha)\}, \quad (21)$$

$$\int_a^b \{\phi(hr)\}^2 r dr = \frac{1}{2}b^2 \{\phi'(hb)\}^2 - \frac{1}{2}a^2 \{\phi'(ha)\}^2; \quad . \quad . \quad (22)$$

and we get for this part of the surface

$$\frac{1}{2}a \Sigma H \{\phi'(ha)\} + \frac{1}{4} \Sigma h H^2 [b^2 \{\phi'(hb)\}^2 - a^2 \{\phi'(ha)\}^2]. \quad (23)$$

Thus for the whole surface on the left

$$(15) = \frac{l}{2 \log b/a} + \frac{1}{4} \Sigma h H^2 [b^2 \phi'^2(hb) - a^2 \phi'^2(ha)], \quad (24)$$

the simplification arising from the fact that (1) is practically a member of the series ϕ .

The calculated capacity, an overestimate unless all the coefficients H are correctly assigned, is given by addition o

(16) and (24). The first approximation is obtained by omitting all the quantities H , so that the B 's vanish also. The additional capacity, derived entirely from (16), is then $\frac{1}{4}b^2 \sum kA^2 J_1^2(kb)$, or on introduction of the value of A ,

$$\frac{b}{\log^2 b/a} \sum \frac{J_0^2(ka)}{k^3 b^3 J_1^2(kb)}, \quad \dots \quad (25)$$

the summation extending to all the roots of $J_0(kb)=0$. Or if we express the result in terms of the correction δl to the length (for one end), we have

$$\delta l = \frac{2b}{\log b/a} \sum \frac{J_0^2(ka)}{k^3 b^3 J_1^2(kb)}, \quad \dots \quad (26)$$

as the first approximation to δl and an overestimate.

The series in (26) converges sufficiently. $J_0^2(ka)$ is less than unity. The m th root of $J_0(x)=0$ is $x=(m-\frac{1}{2})\pi$ approximately, and $J_1^2(x)=2/\pi x$, so that when m is great

$$\frac{1}{x^3 J_1^2(x)} = \frac{8}{\pi(4m-1)^2} \cdot \dots \quad (27)$$

The values of the reciprocals of $x^3 J_1^2(x)$ for the earlier roots can be calculated from the tables* and for the higher roots from (27). I find

$m.$	$x.$	$\pm J_1(x).$	$x^{-3} \div J_1^2(x).$
1	2.4048	.51915	.2668
2	5.5201	.34027	.0513
3	8.6537	.27145	.0209
4	11.7915	.23245	.0113
5	14.9309	.20655	.0070

The next five values are .0048, .0035, .0026, .0021, .0017. Thus for any value of a the series in (26) is

$$\cdot 2668 J_0^2(2.405 a/b) + \cdot 0513 J_0^2(5.520 a/b) + \dots ; \quad (28)$$

it can be calculated without difficulty when a/b is given. When a/b is very small, the J 's in (28) may be omitted, and we have simply to sum the numbers in the fourth column of the table and its continuation. The first ten roots give .3720. The remainder I estimate at .015, making in all .387. Thus in this case

$$\delta l = \frac{\cdot 774 b}{\log b/a} \cdot \dots \quad (29)$$

* Gray & Mathews, Bessel's Functions, pp. 244, 247.

It is particularly to be noticed that although (29) is an over-estimate, it vanishes when a tends to zero.

The next step in the approximation is the inclusion of H_1 corresponding to the first root h_1 of $\phi(hb)=0$. For a given k , B has only one term, expressed by (13) when we write h_1 , H_1 for h , H . In (16) when we expand $(A+B)^2$, we obtain three series of which the first involving A^2 is that already dealt with. It does not depend upon H_1 . Constant factors being omitted, the second series depends upon

$$\Sigma \frac{J_0^2(ka)}{k(h_1^2 - k^2) J_1^2(kb)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (30)$$

and the third upon

$$\Sigma \frac{k J_0^2(ka)}{(h_1^2 - k^2)^2 J_1^2(kb)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (31)$$

the summations including all admissible values of k . In (24) we have under Σ merely the single term corresponding to H_1 , h_1 . The sum of (16) and (24) is a quadratic expression in H_1 , and is to be made a minimum by variation of that quantity.

The application of this process to the case of a very small leads to a rather curious result. It is known ('Theory of Sound,' § 213 *a*) that k_1^2 and h_1^2 are then nearly equal, so that the first terms of (30) and (31) are relatively large, and require a special evaluation. For this purpose we must revert to (10) in which, since ha is small,

$$Y_0(ha) = \log ha J_0(ha) + 2J_2(ha), \quad \cdot \quad \cdot \quad \cdot \quad (32)$$

so that nearly enough

$$J_0(hb) = (h-k)b J_0'(kb) = \frac{Y_0(hb)}{\log ha} = \frac{Y_0(kb)}{\log ka},$$

and

$$k-h = \frac{Y_0(kb)}{b J_1(kb) \log ka} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

Thus, when a is small enough, the first terms of (30) and (31) dominate the others, and we may take simply

$$(30) = - \frac{b \log k_1 a}{2 k_1^2 Y_0(k_1 b) J_1(k_1 b)}, \quad \cdot \quad \cdot \quad \cdot \quad (34)$$

$$(31) = \frac{b^2 \log^2 k_1 a}{4 k_1 Y_0^2(k_1 b)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (35)$$

Also

$$\phi'(k_1a) = -\frac{1}{k_1a \log k_1a}, \quad \phi'(k_1b) = \frac{Y_1(k_1b)}{\log k_1a}. \quad (36)$$

Using these, we find from (16) and (24)

$$\begin{aligned} \frac{b}{\log^2 b/a} \sum \frac{1}{k^3 b^3 J_1^2(kb)} + \frac{H_1}{k_1^2 b \log b/a \cdot Y_0(k_1b) J_1(k_1b)} + \frac{H_1^2}{4k_1 Y_0^2(k_1b)} \\ + \frac{l}{2 \log b/a} + \frac{k_1 H_1^2}{4 \log^2 k_1a} \left\{ b^2 Y_1^2(k_1b) - k_1^{-2} \right\}, \quad (37) \end{aligned}$$

as the expression for the capacity which is to be made a minimum. Comparing the terms in H_1^2 , we see that the two last, corresponding to the negative side, vanish in comparison with the other in virtue of the large denominator $\log^2 k_1a$. Hence approximately

$$H_1 = -\frac{2Y_0(k_1b)}{k_1b \log b/a \cdot J_1(k_1b)}, \quad (38)$$

and (37) becomes

$$\frac{l}{2 \log b/a} + \frac{b}{\log^2 b/a} \sum \frac{1}{k^3 b^3 J_1^2(kb)} - \frac{b}{\log^2 b/a} \frac{1}{k_1^3 b^3 J_1^2(k_1b)} \quad (39)$$

when made a minimum by variation of H_1 . Thus the effect of the correction depending on the introduction of H_1 is simply to wipe out the initial term of the series which represents the first approximation to the correction.

After this it may be expected that the remaining terms of the first approximation to the correction will also disappear. On examination this conjecture will be found to be verified. Under each value of k in (16) only that part of B is important for which h has the particular value which is nearly equal to k . Thus each new H annuls the corresponding member of the series in (39), so that the continuation of the process leaves us with the first term of (39) isolated. The inference is that the correction to the capacity vanishes in comparison with $b \div \log^2 b/a$, or that δl vanishes in comparison with $b \div \log b/a$. It would seem that δl is of the order $b \div \log^2 b/a$, but it would not be easy to find the numerical coefficient by the present method.

In any case the correction δl to the length of the rod vanishes in the electrostatical problem when the radius of the rod is diminished without limit—a conclusion which I extend to the vibrational problem specified in the earlier portion of this paper.

II. *On the Theory of the Decrease of Velocity of Moving Electrified Particles on passing through Matter.* By N. BOHR, Dr. phil. Copenhagen*.

WHEN cathode-rays or α - and β -rays penetrate through matter their velocity decreases. A theory of this phenomena was first given by Sir J. J. Thomson†. In the calculation of this author the cathode- and β -rays are assumed to lose their velocity by collisions with the electrons contained in the atoms of the matter. The form of the law, found by this calculation, connecting the velocity of the particles and the thickness of matter traversed, has been recently shown by Whiddington‡ to be in good agreement with experiments. Somewhat different conceptions are used in the calculation of Sir J. J. Thomson on the absorption of α -rays, as the latter, on account of their supposed greater dimensions, are assumed to lose their velocity by collisions, not with the single electrons but with the atoms of the matter considered as entities.

According to the theory given by Professor Rutherford§ of the scattering of α -rays by matter, the atoms of the matter are supposed to consist of a cluster of electrons kept together by attractive forces from a nucleus. This nucleus, which possesses a positive charge equal to the sum of the negative charges on the electrons, is further supposed to be the seat of the essential part of the mass of the atom, and to have dimensions which are exceedingly small compared with the dimensions of the atom. According to this theory an α -particle consists simply of the nucleus of a helium atom. We see that after such a conception there is no reason to discriminate materially between the collisions of an atom with an α - or β -particle—apart of course from the differences due to the difference in their charge and mass.

An elaborate theory of the absorption and scattering of α -rays, based on Professor Rutherford's conception of the constitution of atoms, was recently published by C. G. Darwin||. In the theory of this author the α -particles simply penetrate the atoms and act upon the single electrons contained in them, by forces varying inversely as the square

* Communicated by Prof. E. Rutherford, F.R.S.

+ J. J. Thomson, 'Conduction of Electricity through Gases,' pp. 370-382.

‡ R. Whiddington, Proc. Roy. Soc. A. lxxxvi. p. 360 (1912).

§ E. Rutherford, Phil. Mag. xxi. p. 669 (1911).

|| C. G. Darwin, Phil. Mag. xxiii. p. 907 (1912).

of the distance apart*. By help of some further simple assumptions about the distribution of the electrons in the atoms and the effect of the forces acting upon them, Darwin obtained results for the scattering as well as for the absorption of the rays, which agree approximately with the experiments.

The above theories make use, however, of some special assumptions which seem to me to be open to objections of a principal character, and I have in this paper made an attempt to treat the problem in a somewhat different manner. The theory in question assumes that the loss of velocity of a moving electrified particle in passing through matter is due to a transfer of kinetic energy to the electrons of the atoms with which it collides. If we assume that the effect of the forces which keep the electrons in their position—or their orbits—inside the atoms can be neglected during the very short collisions between the electrons and the particles, we can very simply calculate the orbits of the electrons during the collisions, and consequently the energy transferred to them and the loss of velocity of the particle. If, however, we integrate the total loss of energy due to all the electrons in the matter, we get in this way an infinitely great value for the absorption. Sir J. J. Thomson, in his above mentioned theory of the decrease of velocity of cathode-rays, avoids this difficulty by introducing, as an effective limit for the action of the electrons on the velocity of the particles, a distance comparable in size with the distance apart of the single electrons in the atoms. This limit is chosen from the consideration that for distances greater than this, the effect of the different electrons on the moving particles will mutually disturb each other. The simultaneous influence of the different electrons on the particles will, as it will be seen, highly affect the deflexions of the particles for the distances in question, and the limit mentioned will therefore hold for the calculation of the scattering of the rays. The limit will, however, not hold for the calculation of the decrease of velocity of the particles; for, on account of the great velocity, the motion of the particles will be very slightly affected by collisions in which the distance of the electrons from the path of the particle is of the order of magnitude assumed for the distance apart of the electrons in the atoms. The forces exerted by a particle on an electron, and consequently the energy transferred to the

* Corresponding assumptions are also used by Sir J. J. Thomson in a recent paper on the ionization of moving electrified particles, *Phil. Mag.* xxiii. p. 449 (1912).

latter by the collision, will therefore be very nearly independent of the simultaneous effect of other electrons on the particle.

Darwin, in his theory of absorption of α -rays, proceeds in another way and avoids the difficulty by assuming that the forces on the electrons from the side of the atoms can be neglected during the very short and violent collisions between an electron and an α -particle, which occur when the particle traverses the same atom to which the electron belongs ; and further, that the velocity of the α -particle will be unaltered if the particle during its path does not enter the atom. Using these assumptions and comparing the theory with the experiments, Darwin finds values for the diameter of the atoms which decrease for increasing atomic weight, and which for the lightest elements are several times greater than the generally adopted values for this quantity, and for the heaviest elements several times smaller. It seems, however, to me not to be justifiable to take the surface of the atoms as the limit of the effect of the electrons in the atoms on the particles. Outside an atom the forces on the particle from the electrons and the central positive charge will certainly very nearly neutralize each other ; but the decrease of velocity of the particles depends only on the motion of the electrons during the collision, and not on the total force exerted on the particle by the whole atom, the latter force producing only the scattering of the rays.

We can, however, get a natural limit for the effect of the electrons on the velocity of the moving particles by taking into account the forces by which the electrons are kept in their positions in the atoms. Under the influence of these forces the electrons will have a sort of vibratory motion if they are disturbed by an impulse from outside. We see immediately that the forces in question will materially alter the motion of the electrons during the collision, and consequently the loss of energy of the particle, if the time of vibration of the electrons is of the same order of magnitude as the time of collision, *i. e.*, the time which the particle takes to travel through a distance of the same order of magnitude as the shortest distance apart of the electron from the path of the particle *. We see, further, that the effect of the electrons on the velocity of the particle will decrease very rapidly with the distance of the electrons from the particle, if this distance is so great that the time of collision is great compared with the time of vibration. The effective

* Compare J. J. Thomson, *loc. cit.* Phil. Mag. xxiii. p. 454 (1912).

limit for the action of the electrons on the velocity of the particles—and consequently the value of the absorption of the rays—which we get in this way will depend purely on the frequency of the electrons and the velocity of the particles, and may for the same velocity of the particles be very different for the different electrons inside the same atom, according to their different frequencies. The limit in question will, at least for some of the electrons in elements of high atomic weight, in which elements the existence of vibrations with very high frequencies is observed, be much smaller than for the electrons in the elements of low atomic weight. This circumstance seems, as it will be shown, to account for the comparatively much smaller absorption of such elements for the same weight of matter per cm.²

It will be perceived that the theory of the decrease of velocity of moving electrified particles on passing through matter in this form bears a great analogy to the ordinary electromagnetic theory of dispersion; the different times of vibration for the different wave-lengths considered in the theory of dispersion is here replaced by the different times of collision of particles of different velocities and at different distances from the electrons. In fact it will be shown, that the information about the number and the frequency of the electrons in the atoms, which we get from the theory of dispersion, will enable us to calculate values for the absorption of α -rays for the lightest elements which are in very close agreement with the observed values. Since, however, the decrease in the effect of the electrons corresponding to an increase in their frequency is much more rapid for the dispersion than for the loss of velocity of moving particles, it seems possible by considering the latter to get more information about the higher frequencies in the atoms, and from this some more information about the internal structure of the atoms.

In considering the collisions between the electrons and the particles we shall at first neglect the forces from the side of the atoms. Let E and M be the charge and the mass of a particle, and e and m be corresponding quantities for an electron. Let us further assume that the electron is at rest, and that the particle has a velocity V before the collision, and let the distance apart of the electron from the path of the particle before the collision be p ; then the calculation

14 Dr. N. Bohr : *Theory of Decrease of Velocity of*
of the orbits gives *

$$\sin^2 \mathfrak{S} = \frac{1}{1 + \frac{p^2 V^4}{e^2 E^2} \left(\frac{mM}{M+m} \right)^2},$$

where $2\mathfrak{S}$ is the angle through which the direction of the relative motion is deflected by the collision. For the sake of brevity we shall in the following use the notation

$$\lambda = \frac{eE(M+m)}{V^2 m M}.$$

The velocity of the electron after the collision will make an angle equal to $\frac{\pi}{2} - \mathfrak{S}$ with the path of the particle before the collision, and its value will be given by

$$v = V \frac{M}{M+m} 2 \sin \mathfrak{S}.$$

The energy transferred to the electron by the collision is consequently equal to

$$Q_0 = \frac{2mM^2V^2}{(m+M)^2} \sin^2 \mathfrak{S}. \quad . \quad . \quad . \quad . \quad (1)$$

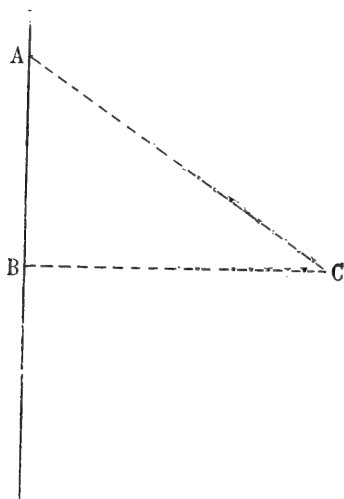
Further, we easily find that the displacement of the electron in a direction perpendicular to the path of the particle, at the moment in which the electrons and the particle are nearest each other, is equal to $\frac{eE}{mV^2} \cos \mathfrak{S}$. We see that \mathfrak{S} will be very small, and the velocity of the electron after the collision very nearly perpendicular to the path of the particle if p is great in comparison with λ ; in this case the displacement of the electron during the collision will further be very small in comparison with p .

Now proceeding to consider the effect of the forces on the electrons from the side of the atoms, we shall for the present assume that the frequency of the electrons is so small that the time of vibration is very long in comparison with the time of collision, for collisions in which p is of the same order of magnitude as λ ; this will, in fact, be satisfied for the lightest elements, as we shall see later. In this case we shall consequently only have to consider the influence

* Compare J. J. Thomson, 'Conduction of Electricity through Gases,' p. 376, and Phil. Mag. xxiii. p. 449 (1912); C. G. Darwin, *loc. cit.* p. 903.

of the forces in question for collisions in which p is great in comparison with λ . This simplifies the calculation very much, because then we can assume that the displacement during the collision is negligibly small in proportion to p . In the following calculation we shall consider separately the motion of the electrons perpendicular and parallel to the path of the particle; the total energy transferred to the electrons during the collisions will be the sum of the energy corresponding to these two motions.

In the figure the line AB represents the path of the particle, which in the collisions considered here (*i. e.*, p great



in proportion to λ) will be very nearly a straight line. Further, A is the position of the particle at the time t , and C is the mean position of the electron. BC is perpendicular to AB. According to the above notation, $\overline{BC} = p$; and assuming that the particle will be at B when the time is 0, we have $\overline{AB} = V \cdot t$.

For the force acting on the electron in the direction CB, we now get

$$F_1 = eE \frac{\overline{BC}}{\overline{AC}^3} = \frac{eE p}{(V^2 t^2 + p^2)^{\frac{3}{2}}} = m \cdot \phi(t).$$

For the equation of motion of the electron perpendicular to the path of the particle we get

$$\frac{d^2 x}{dt^2} + n^2 x = \phi(t),$$

in which n is the frequency corresponding to the forces in question.

The solution of this equation subject to the condition that

$$x=0 \quad \text{and} \quad \frac{dx}{dt}=0 \quad \text{for} \quad t=-\infty, \text{ is } *$$

$$x = \frac{1}{n} \int_{-\infty}^t \sin n(t-z) \cdot \phi(z) dz; \quad \frac{dx}{dt} = \int_{-\infty}^t \cos n(t-z) \cdot \phi(z) dz.$$

We have in the above expression assumed that the electron was at rest before the collision with the particle; if we assume that the electrons are in motion in the atoms before the collision (the dimension of their orbits must, however, for the justification of the above calculations be small in proportion to p ; for the fulfilment of this condition see later on p. 20), the effect will only be an introduction of some terms in the expressions for x and $\frac{dx}{dt}$ which will again disappear in the expression for the mean value of the energy transferred.

For the sum of the kinetic energy of the electron at the time t , and its potential energy due to its displacement relative to the rest of the atom, we have now

$$\begin{aligned} \frac{m}{2} \left(\frac{dx}{dt} \right)^2 + \frac{mn^2}{2} x^2 &= \frac{m}{2} \left[\int_{-\infty}^t \cos nz \cdot \phi(z) dz \right]^2 \\ &+ \frac{m}{2} \left[\int_{-\infty}^t \sin nz \cdot \phi(z) dz \right]^2. \end{aligned}$$

For the energy transferred to the electron by the collision, due to motion perpendicular to the path of the particle, we now get, observing that in this case $\phi(z)$ is an even function of z ,

$$Q_1 = \frac{m}{2} \left[\int_{-\infty}^{+\infty} \cos nz \cdot \phi(z) dz \right]^2,$$

and introducing for $\phi(z)$

$$Q_1 = \frac{1}{2} \frac{e^2}{m} E^2 p^2 \left[\int_{-\infty}^{+\infty} \frac{\cos nz}{(V^2 z^2 + p^2)^{\frac{3}{2}}} dz \right]^2,$$

$$Q_1 = \frac{2e^2 E^2}{m V^2 p^2} \cdot f^2 \left(\frac{np}{V} \right),$$

* See Lord Rayleigh, 'Theory of Sound,' i. p. 75. For the following analysis compare also J. H. Jeans, 'Kinetic Theory of Gases,' p. 198.

where
$$f(x) = \frac{1}{2} \int_{-\infty}^{+\infty} \frac{\cos xz}{(z^2 + 1)^{\frac{3}{2}}} dz$$

is represented for all values of x by the convergent series

$$\begin{aligned} f(x) = & 1 - \frac{1}{1.1.2} \frac{3}{1.2} \left(\frac{x}{2}\right)^4 - \frac{1}{1.2.1.2.3} \left(\frac{3}{1.2} + \frac{5}{2.3}\right) \left(\frac{x}{2}\right)^6 \dots \\ & - \frac{1}{(n-1)! n!} \left(\frac{3}{1.2} + \frac{5}{2.3} + \dots + \frac{2n-1}{(n-n)n}\right) \left(\frac{x}{2}\right)^{2n} \dots \\ & + \left(2\gamma + 2 \log \frac{x}{2} - 1\right) \left(\left(\frac{x}{2}\right)^2 + \frac{1}{1.1.2} \left(\frac{x}{2}\right)^4 + \frac{1}{1.2.1.2.3} \left(\frac{x}{2}\right)^6 \dots \right. \\ & \left. + \frac{1}{(n-1)! n!} \left(\frac{x}{2}\right)^{2n} \dots\right), \end{aligned}$$

where γ is Euler's constant, $\gamma = 0.5772$.

When x is large, $f(x)$ is represented by the asymptotic series

$$\begin{aligned} f(x) \sim & \sqrt{\frac{\pi}{2}} \cdot e^{-x} \sqrt{x} \left(1 + \frac{1.3}{8x} - \frac{1.3.5}{1.2} \left(\frac{1}{8x}\right)^2 + \frac{1.3.1.3.5}{1.2.3} \left(\frac{1}{8x}\right)^3 - \dots \right. \\ & \left. (-1)^{n+1} \frac{1.3.5 \dots (2n-3).1.3 \dots (2n-1) \dots}{n! (8x)^n} \dots\right). \end{aligned}$$

For the force acting on the electrons in the direction parallel to the path of the particles we have now (see figure, p. 15)

$$F_2 = eE \frac{\overline{AB}}{AC^3} = \frac{eEVt}{(V^2t^2 + p^2)^{\frac{3}{2}}} = m \cdot \psi(t).$$

For the energy transferred to the electron during the collision we get in the same manner as above ($\psi(t)$ an uneven function of t)

$$Q_2 = \frac{m}{2} \left[\int_{-\infty}^{+\infty} \sin nz \cdot \psi(z) dz \right]^2,$$

and introducing for $\psi(z)$

$$\begin{aligned} Q_2 &= \frac{1}{2} \frac{e^2}{m} E^2 V^2 \left[\int_{-\infty}^{+\infty} \frac{z \sin nz}{(V^2 z^2 + p^2)^{\frac{3}{2}}} dz \right]^2, \\ Q_2 &= \frac{2e^2 E^2}{m V^2 p^2} \cdot g^2 \left(\frac{np}{V} \right), \end{aligned}$$

where

$$g(x) = -\frac{1}{2} \int_{-\infty}^{+\infty} \frac{z \sin xz}{(z^2 + 1)^{\frac{3}{2}}} dz = \frac{x}{2} \int_{-\infty}^{+\infty} \frac{\cos xz}{(z^2 + 1)^{\frac{3}{2}}} dz = f'(x),$$

in which $f(x)$ is the same function as above.

While for the motion perpendicular to the direction of the particle the energy transferred is always smaller than the energy calculated by considering the electrons as free, this is not the case for the motion parallel to the path of the particle.

For the total energy transferred to the electron by the collision we have now

$$Q = Q_1 + Q_2 = \frac{2e^2 E^2}{mV^2 p^2} \cdot P\left(\frac{np}{V}\right), \quad . \quad . \quad . \quad (2)$$

where $P(x) = f^2(x) + g^2(x)$ is equal to 1 for $x=0$, and decreases very rapidly for increasing values of x , when x is great; for $x=0$ we notice that $P'(x)=0$.

Let us now consider a particle passing through matter. Let us assume that the numbers of atoms per unit volume is N , and that each atom contains r electrons of frequency n . Let further a be a constant, great in comparison with λ , but small in comparison with V/n (see p. 15), we then get for the total energy dT transferred to the electrons when the particle travels through a distance dx

$$dT = Nr \left[\int_0^a Q_0 2\pi p dp + \int_a^\infty Q_2 2\pi p dp \right] dx;$$

by help of (1) and (2) we get

$$dT = \frac{4\pi e^2 E^2 Nr}{mV^2} \left[\int_0^a \frac{p dp}{p^2 + \lambda^2} + \int_a^\infty \frac{1}{p} P\left(\frac{np}{V}\right) dp \right] dx.$$

Neglecting $(\lambda/a)^2$ (see above), we get

$$dT = \frac{4\pi e^2 E^2 Nr}{mV^2} \left[\log\left(\frac{a}{\lambda}\right) + \int_{\frac{an}{V}}^{\infty} \frac{1}{z} P(z) dz \right] dx,$$

$$dT = \frac{4\pi e^2 E^2 Nr}{mV^2} \left[\log\left(\frac{a}{\lambda}\right) - \log\left(\frac{an}{V}\right) \cdot P\left(\frac{an}{V}\right) - \int_{\frac{an}{V}}^{\infty} \log z \cdot P'(z) dz \right] dx.$$

According to our assumption, $\frac{an}{V}$ is very small, and we can

therefore put $P\left(\frac{an}{V}\right)=1$, and further take the limit for the integral to be 0 and ∞ , ($P'(0)=0$).

Putting

$$\int_0^{\infty} \log z P'(z) dz = -\log k,$$

we thus get

$$dT = \frac{4\pi e^2 E^2 N r}{m V^2} \log\left(\frac{V^3 k M m}{n_e E (M + m)}\right) dx.$$

I have calculated k by help of the above formulæ for $f(x)$ and found

$$k=1.123.$$

If we assume that the atoms contain electrons corresponding to different frequencies, and if we denote the frequencies of the r electrons in each atom by $n_1, n_2, \dots n_r$, we get

$$dT = \frac{4\pi e^2 E^2 N}{m V^2} dx \sum_{s=1}^{s=r} \log\left(\frac{V^3 k M m}{n_s e E (M + m)}\right). \quad (3)$$

Since dT is equal to the decrease in the kinetic energy of the particle, i. e., in $\frac{1}{2}MV^2$, we have

$$\frac{dV}{dx} = - \frac{4\pi e^2 E^2 N}{m M V^3} \sum_{s=1}^{s=r} \log\left(\frac{V^3 k M m}{n_s e E (M + m)}\right). \quad (4)$$

In establishing the formula (4) we have only considered the interaction between the particle and the electrons, and not the interaction between the particle and the central charge in the atoms; as Darwin* has shown, the effect of the latter interaction will, however, be negligibly small in comparison with the former: this conclusion will hold unaltered for the theory in the form it is given here.

The formula (4) expresses the rate of decrease of velocity of moving electrified particles as a function of the velocity of the particles and the number and frequencies of the electrons.

If V is very great we can neglect the variation in the logarithmic term, and get for the relation between V and the distance the particles have travelled through matter, denoting the velocity for $x=0$ by V_0 ,

$$V_0^4 - V_x^4 = ax, \quad (5)$$

where

$$a = \frac{16\pi e^2 E^2 N}{m M} \sum_{s=1}^{s=r} \log\left(\frac{V_0^3 k M m}{n_s e E (M + m)}\right).$$

* Darwin, *loc. cit.* p. 905.

This relation is of the same form as the one deduced by Sir J. J. Thomson, and shown by Whiddington to hold approximately for cathode-rays (see p. 10). For still greater velocities, corresponding to the fastest β -rays, the form of the relation between V and x will be altered on account of the rapid increase in the mass of the particles if their velocity is very near to the velocity of light (see later, p. 29).

For smaller values of the velocities of the particles the logarithmic term will be of material influence on the relation between V and x , the effect being of the sense as to diminish the power of V on the right side of the equation (5). This is in agreement with experiments on α -rays.

If we assume that the number of electrons in an atom is proportional to the atomic weight, and if we consider that the atoms of elements of increasing atomic weight contain electrons of increasing frequency, we see immediately that the formula (4) accounts for some of the principal features of the absorption of α -rays by different elements. It accounts for the fact that the absorption for equal weight of matter per square centimetre decreases for elements of increasing atomic weight*. It accounts further for the fact that the relative absorption for different elements varies with the velocity of the α -rays, the absorption for the heavier elements being comparatively greater for greater velocities of the rays†.

For a closer numerical comparison between the theory and the experiments we must, however, observe that in the deduction of the formula (4) we have made use of some assumptions about the magnitude of the frequency and velocity of the electrons which may not be satisfied with all the electrons in the atoms considered, for the velocities of the particles in question. These assumptions are:—

- (1) That the frequency n is small compared with V/λ ;
- (2) That the velocity τ of the electrons in their undisturbed orbits is small compared with the velocity of the particles;
- (3) That the linear dimensions ρ of the orbits in question are small compared with $\frac{V}{n}$ (see p. 16).

As regarding the order of magnitude τ and ρ are connected by the relation $\tau = n\rho$, we see that condition (2) is fulfilled at the same time as (3). The calculations involves still the assumption,

- (4) that the displacement of the electrons caused by the

* W. H. Bragg and R. Kleeman, *Phil. Mag.* x. p. 318 (1905).

† T. S. Taylor, *Phil. Mag.* xviii. p. 604 (1909).

forces from the particle is small compared with the dimensions of their undisturbed orbits, for such collisions for which we have to take the forces from the side of the atom into account; or in other words, that nothing of the same sort as ionization will occur for such collisions. As, however, the forces between the particles and the electrons for the same distance are of the same order of magnitude as the forces which act upon the electron from the central charge and the other electrons, we see that condition (4) is satisfied if condition (3) is.

It seems very difficult to account accurately for the alterations in the result, if the above assumptions are not satisfied; but it is easy to see that if the ratios $\frac{n\lambda}{V}$ and $\frac{n\rho}{V}$ are small quantities, then the corrections in the result will be proportional to the squares of these ratios*.

Comparison with Experiments.

I. α -rays.

We shall at first consider the absorption of α -rays, as the behaviour of these rays, on account of the small scattering, is much more accurately known than the corresponding facts for β - or cathode-rays.

Absolute measurements of the variation of the velocity of α -rays with the thickness of matter traversed have lately been made by Geiger † for air. This author found that the relation

$$V^3 = KR, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where V is the velocity of the α -rays and R the corresponding range of the rays in air, was satisfied with great accuracy for a very great part of the path of the rays. In determining K , we have that the range in air of α -rays from radium C is 7.06 cm. (at 76 cm. and 20° C.) ‡, and that the initial velocity of these rays is § $1.98 \cdot 10^9$ cm./sec.; this gives $K = 1.10 \cdot 10^{27}$.

Elaborate measurements of the relative absorption-coefficients of different elements for α -rays corresponding to different ranges in air have been made by Taylor ||. The

* Compare Darwin, *loc. cit.* p. 902.

† H. Geiger, *Proc. Roy. Soc. A.* lxxxiii. p. 505 (1910)

‡ Bragg and Kleeman, *loc. cit.* p. 318.

§ E. Rutherford, *Phil. Mag.* xii. p. 358 (1906). (The above value for V is Rutherford's value for $V \cdot M/E$, multiplied by $4.87 \cdot 10^3$, i. e. the value of E/M for helium.)

|| T. S. Taylor, *Phil. Mag.* xviii. p. 604 (1909).

ranges in air of the α -rays, when entering the absorbing sheets, varied in these experiments from about 5 to about 2 cm. The figures in the table below for the absorption relative to air are obtained by interpolation in Taylor's Tables II. and III. (*loc. cit.* pp. 608-610), the range quoted is the mean value of the ranges for the α -rays entering and leaving the absorption sheets, and the values for the absorption are the mean values calculated from the different series of experiments using same absorbing material.

Range in air	2.24.	4.87.
Hydrogen	0.267	0.224
Air	1.00	1.00
Aluminium	$1.69 \cdot 10^3$	$1.75 \cdot 10^3$
Tin	$2.33 \cdot 10^3$	$2.56 \cdot 10^3$
Gold	$4.71 \cdot 10^3$	$5.57 \cdot 10^3$
Lead	$3.06 \cdot 10^3$	$3.53 \cdot 10^3$

The ranges 2.24 and 4.87 are chosen as those corresponding to the velocities $1.35 \cdot 10^9$ and $1.75 \cdot 10^9$ according to the formula (5). According to the same formulæ we further get that for these velocities, $\frac{dV}{dx}$ in air is equal to respectively $-2.01 \cdot 10^8$ and $-1.20 \cdot 10^8$. From this we get by help of the above table the following values for $-\frac{dV}{dx}$:

Velocity	$1.35 \cdot 10^9$.	$1.75 \cdot 10^9$.
Hydrogen	$5.4 \cdot 10^7$	$2.7 \cdot 10^7$
Air	$2.01 \cdot 10^8$	$1.20 \cdot 10^8$
Aluminium	$3.4 \cdot 10^{11}$	$2.1 \cdot 10^{11}$
Tin	$4.7 \cdot 10^{11}$	$3.1 \cdot 10^{11}$
Gold	$9.5 \cdot 10^{11}$	$6.7 \cdot 10^{11}$
Lead	$6.1 \cdot 10^{11}$	$4.2 \cdot 10^{11}$

Hydrogen.

Comparing the above values with the theory, we shall start with hydrogen as the substance for which the assumptions mentioned on p. 20 are satisfied in the highest degree.

From the formula (4), p. 19, we get, putting

$$e = 4.65 \cdot 10^{-10}, \quad E = 2e, \quad e/m = 5.31 \cdot 10^{17}, \quad E/M = 1.46 \cdot 10^{14},$$

and $N = 2.59 \cdot 10^{19}$ (at 76 cm. and 20° C.),
for

$$\left. \begin{aligned} V &= 1.35 \cdot 10^9, & \frac{dV}{dx} &= 4.42 \cdot 10^6 \sum_{s=1}^{s=r} (\log(n_s \cdot 10^{-19}) + 0.59) \\ \text{and for} \\ V &= 1.75 \cdot 10^9, & \frac{dV}{dx} &= 2.03 \cdot 10^6 \sum_{s=1}^{s=r} (\log(n_s \cdot 10^{-19}) - 0.18) \end{aligned} \right\} \quad (7)$$

From experiments on the refraction and dispersion in hydrogen, and the discussion of these experiments according to Drude's theory, C. and M. Cuthbertson find that a hydrogen molecule in its normal state contains 2 electrons of frequency $n = 2.21 \cdot 10^{16}$ *.

Putting $r = 2$ and $n_1 = n_2 = 2.21 \cdot 10^{16}$ in the above formulæ, we get

$$\text{for} \quad V = 1.35 \cdot 10^9, \quad \frac{dV}{dx} = -4.9 \cdot 10^7,$$

and

$$\text{for} \quad V = 1.75 \cdot 10^9, \quad \frac{dV}{dx} = -2.6 \cdot 10^7.$$

These values are in close agreement with the values for $\frac{dV}{dx}$ in the table on p. 22, i. e. respectively

$$\frac{dV}{dx} = -5.4 \cdot 10^7 \quad \text{and} \quad \frac{dV}{dx} = -2.7 \cdot 10^7.$$

The small differences between the calculated and the observed values are not greater than was to be expected, as the values calculated, on account of possible experimental errors in the entering constants, are not certain within more than about 10 p.c. We shall further here examine to what

* C. and M. Cuthbertson, Proc. Roy. Soc. A. lxxxiii. p. 166 (1909); see also Drude, *Ann. d. Phys.* xiv. p. 714 (1904). (The agreement with Drude's theory is, however, not quite satisfactory, as the number of electrons works out somewhat less than 2. A probable explanation of this fact seems to be that the frequency of the electrons is not the same for displacements in all directions, a circumstance not to be expected in a system which has at most one axis of symmetry, i. e. the axis of the diatomic molecule. This question will be discussed in a later paper; for the present we shall use the above value for n , as the influence on the result of the correction in this value, which will follow from the discussion referred to, will not be greater than the inevitable errors due to the uncertainty in the other experimental constants entering into the calculations.)

degree the conditions on p. 20 are satisfied in the case in question. For $V=1.75 \cdot 10^9$, we get

$$\lambda = \frac{eE(M+m)}{V^2 M_m} = 1.6 \cdot 10^{-10} \quad \text{and} \quad V/n = 0.8 \cdot 10^{-7}.$$

We see that the first condition is amply satisfied. We have, further, that the maximum value to be assumed for the quantity ρ on p. 20 is about 10^{-8} , *i. e.* the "radius" of a hydrogen molecule; we thus get the maximum value to be

assumed for $\frac{\rho^n}{V}$ equal to about 0.1. As the corrections due to finite values for $\frac{\rho^n}{V}$, as mentioned on p. 20, are propor-

tional to the square of this quantity, we must, therefore, expect them very small in the considered case.

It may here be remarked that the above value for V/n shows that the effective limit, mentioned on p. 12, for the action of the electrons on the velocity of the particles, for hydrogen and for particles of the velocity considered is about 8 times the radius of the molecules; for β -rays of velocity near the velocity of light the limit in question would be more than 100 times the radius of the molecules.

We see that the absorption of α -rays in hydrogen can be satisfactorily accounted for by assuming the same number of electrons per molecule and the same frequencies, as those assumed in order to explain the refraction and dispersion in this gas. It may here be mentioned, that if we assumed that the hydrogen molecule contained more than two electrons, the theory shows that the frequencies of the other electrons must be extremely high, as the absorption due to them, after the above calculation, cannot amount to more than about 10 per cent. of the absorption due to the two electrons considered. Thus assuming that the molecule contains further two electrons, we get that n for them must be at least of the order of magnitude of 10^{18} ; a value for n which seems difficult to reconcile with experiments on characteristic Röntgen rays (comp. later, p. 26). If we adopt Rutherford's conception of the constitution of atoms, we see that the experiments on absorption of α -rays very strongly suggest, that a hydrogen atom contains only one electron outside the positively charged nucleus.

Helium.

For helium there is no measurement of the absorption coefficient for different velocities; the only experiment with this gas is a determination by Adams* of the range in

* E. P. Adams, *Physical Review*, xxiv. p. 113 (1907).

helium of α -rays from polonium. Adams finds the absorption in helium a little bigger than in hydrogen ; the ratio being 1.15.

According to Cuthbertson's experiments* and Drude's theory the dispersion in helium can be explained by assuming two electrons per atom (the calculated value is 2.3) of a frequency $n=3.72 \cdot 10^{16}$.

Introducing these values for r and n in the formula (4), p. 19, we get values for $\frac{dV}{dx}$ in helium which are a little smaller than those found above for hydrogen, the ratio being 0.92 for $V=1.75 \cdot 10^9$ and 0.90 for $V=1.35 \cdot 10^9$.

If this disagreement is real (Adams states (*loc. cit.* p. 111) that the purity of the gases used was not secured very effectively ; a little contamination of the helium with heavier gases will explain the disagreement in question) it suggests that even for helium the neglected corrections will be of sensible influence. As, however, the quantity $\frac{\rho n}{V}$ is to be assumed about twice as large for helium as for hydrogen, we see, on the other hand, that the corrections, being about 30 per cent. for helium, will not be more than about 10 per cent. for hydrogen. The following results for oxygen and aluminium seem, however, to indicate that the corrections considered are much smaller.

The value $r=2$ for the number of electrons in a helium atom, indicated by experiments on dispersion and on absorption of α -rays, is what we, adopting Rutherford's theory of atoms, necessarily must conclude from the behaviour of α -rays, according to which helium atoms formed from α -particles will only contain 2 electrons outside the central nucleus.

Oxygen.

For the ratio between the absorption in oxygen and in air, Adams (*loc. cit.* p. 113) found 1.03, and according to the table, p. 22, we therefore get for oxygen

$$\text{for } V=1.35 \cdot 10^9, \quad \frac{dV}{dx} = -2.07 \cdot 10^8,$$

and

$$\text{for } V=1.75 \cdot 10^9, \quad \frac{dV}{dx} = -1.24 \cdot 10^8.$$

* C. & M. Cuthbertson, Proc. Roy. Soc. A. lxxxiv. p. 13 (1910).

26 Dr. N. Bohr: *Theory of Decrease of Velocity of*
By comparison with the formulæ (7), p. 23, we now get

$$\sum_{s=1}^{s=r} (\log (n_s \cdot 10^{-19}) + 0.59) = -47,$$

$$\sum_{s=1}^{s=r} (\log (n_s \cdot 10^{-19}) - 0.18) = -61.$$

From this we get at first by subtraction

$$r \cdot 0.77 = 14 \quad \text{or} \quad r = 18.$$

According to Rutherford's theory of atoms we should expect 16 electrons in an oxygen molecule. The agreement between this value and the above value for r is very satisfactory.

From the above we get further

$$\sum_{s=1}^{s=r} \log (n_s \cdot 10^{-19}) = -58.$$

From experiments on dispersion* we have that an oxygen molecule contains 4 electrons of frequency $2.25 \cdot 10^{16}$; we get, therefore,

$$\sum_{s=5}^{s=r} \log (n_s \cdot 10^{-19}) = -58 + 4 \cdot 6.1 = -34.$$

If we for the present assume that the other 12 electrons supposed contained in an oxygen molecule have equal frequencies n' , we get

$$\log (n' \cdot 10^{-19}) = -2.8, \quad \text{and} \quad n' = 0.6 \cdot 10^{18}.$$

We know very little about the higher frequencies in oxygen, but we can get some estimation of what we should expect, from experiments on characteristic Röntgen rays. Whiddington† has found that the velocity of an electron just sufficient to excite the characteristic Röntgen rays in an element is equal to $A \cdot 10^8$ cm./sec., where A is the atomic weight of the element in question. The energy possessed by such

an electron is $\frac{m}{2} A^2 \cdot 10^{16}$. According to Planck's theory of radiation we further have that the smallest quantity of energy which can be radiated out from an atomic vibrator is equal to $v \cdot k$, where v is the number of vibrations per second and $k = 6.55 \cdot 10^{-27}$. This quantity must be expected to be equal

* C. & M. Cuthbertson, *loc. cit.* p. 166.

† R. Whiddington, *Proc. Roy. Soc. A.* lxxxv. p. 323 (1911).

to, or at least of the same order of magnitude as, the kinetic energy of an electron of velocity just sufficient to excite the radiation: putting them equal we get $vk = \frac{m}{2} A^2 \cdot 10^{16}$, and from this $v = A^2 \cdot 6 \cdot 7 \cdot 10^{14}$. No experiments on characteristic Röntgen rays are made for oxygen, but if we assume Whiddington's law to hold for this element, and put $A = 16$ in the above expression for v , we get $v = 1 \cdot 7 \cdot 10^{17}$, and accordingly for the frequency $n = 2\pi v = 1 \cdot 1 \cdot 10^{18}$. The agreement as to the order of magnitude between this value and the above value for n' , calculated from the absorption of α -rays, is remarkable.

An estimation of the magnitude of the corrections to be introduced in the formula (4) in case of oxygen, involves a discussion about the relation between the frequencies and the dimensions of the orbits of the electrons in the interior of the atoms; and must therefore be postponed till the later paper referred to in the note on p. 23.

For *aluminium, tin, gold, and lead*, we get in the same manner as for oxygen, by comparing the values in the table on p. 22 with the formula (4) on p. 19, the following values for r and $\sum \log (n_s \cdot 10^{-19})$.

Substance.	r .	$\sum_{s=1}^{s=r} (\log n_s \cdot 10^{-19})$.	Atomic weight.
Aluminium	14	41	27
Tin.....	38	94	119
Gold	61	126	197
Lead	65	132	207

According to Rutherford's theory we shall expect values for r equal to about the half of the atomic weight; we see that this is the case for aluminium, but that the values for r for the elements of higher atomic weight are considerably lower. The values found for $\sum \log n_s$ are of a magnitude to be expected if the atoms contained electrons of different frequencies varying from the order of magnitude of the frequencies observed by the dispersion in the transparent bodies to that of the characteristic Röntgen rays. It must, however, here be remarked that the magnitude of the corrections to be introduced in the formulæ (4) must be expected to increase with increasing atomic weight of the substance

considered, and that for the elements of higher atomic weight especially the values calculated for r are uncertain, as these values are determined by considering the difference in the absorption of α -rays of different velocities, and for these velocities the differences in the neglected corrections may be considerable.

II. Cathode rays and β -rays.

The most detailed measurements of the decrease of velocity of cathode rays in passing through matter have been made by Whiddington*. This author found, using cathode rays of velocity between about $5 \cdot 10^9$ and $9 \cdot 10^9$, that the variation in the velocity of the rays and the thickness of matter traversed was connected by a relation of the form given by the equation (5) on p. 19. The determination of the entering constant a gave

for Aluminium, $a = 7 \cdot 32 \cdot 10^{42}$; for Gold, $a = 2 \cdot 54 \cdot 10^{43}$:

and for Air at 760 mm. pressure of mercury and 15°C. ,
 $a = 2 \cdot 0 \cdot 10^{40}$.

From the expression for a on p. 19, we get, putting $v = 7 \cdot 10^9$ and introducing the values for r and $\sum \log n_s$ found above in considering the absorption of α -rays,

for Aluminium, $a = 1 \cdot 9 \cdot 10^{43}$; for Gold, $a = 7 \cdot 3 \cdot 10^{43}$;
and for Air, $a = 1 \cdot 1 \cdot 10^{40}$.

We see that the observed and calculated values agree as to the order of magnitude, but that the differences are very considerable, the values calculated for aluminium and gold being about three times greater than the values observed, and the value of air about half. It seems difficult to account for this disagreement, if it cannot in one way or other be referred to the extraordinary difficult experimental conditions. It may thus be remarked, that the ratio between the rates of decrease of velocity in aluminium and in air is found about five times smaller in Whiddington's experiments than in experiments with α -rays; a circumstance which seems difficult to reconcile with facts found as well by experiments with α -rays of different velocities as by comparing the results of experiments on β -rays with those for α -rays, *i. e.*, that the rate of decrease of velocity in different substances, calculated per number of atoms, is greater for substances of higher

* R. Whiddington, Proc. Roy. Soc. A. lxxxvi. p. 360 (1912).

atomic weight, and that the ratio between the rates of decrease increases with increasing velocity of the rays.

Measurements of the decrease of velocity of β -rays is made for very hard β -rays by W. Wilson*, and recently for slower rays by O. v. Baeyer†. The last author found by experiments with aluminium, and using β -rays, the velocity of which was between 1.10^{10} and 2.10^{10} cm./sec., that the variation in the velocity approximately satisfied a relation of the same form as that found by Whiddington. For a velocity of $1.5.10^{10}$ he found the constant a equal to about $1.1.10^{42}$.

From the expression for a on p. 19, we get for the velocity considered, introducing the values for r and $\Sigma \log n_s$, found for α -rays, and putting $M=1.54 m$, *i. e.* the longitudinal mass of an electron moving with a velocity equal to half the velocity of light (the influence of the alteration in the mass of the particles on the constant a is for this velocity already considerable, but the variation in the mass with the velocity is still too low to alter materially the form of the relation connecting V and x),

$$a=1.7 \cdot 10^{42}.$$

We see that the agreement for these faster rays is better than the one found above for cathode rays.

O. v. Baeyer has also made a few measurements of the decrease of velocity of β -rays in tin, copper, and platinum. The result of these experiments was that the rate of decrease for the same velocity varied approximately proportional to the density of the matter traversed; the elements of higher atomic weight seemed, however, to absorb a little less per same weight per cm.². These results are in conformity with what we should expect according to the theory.

Wilson found that the results of his experiments on the decrease of velocity of very hard β -rays in aluminium was in better conformity with an equation of the form $E_s - E_x = kx$, where E is the energy of the β -particle, than with the equation (4). This is, however, just what was to be expected according to the theory. For, on account of the very rapid increase of the β -particle with its velocity, when near to the velocity of light, the variation in V^2 is for such velocities small compared with the variation in the energy of the particle. By considering the equation (3) on p. 19, we consequently get that, the relation between the energy of the particle and the thickness of matter traversed for the velocities

* W. Wilson, Proc. Roy. Soc. A. lxxxiv. p. 141 (1910).

† O. v. Baeyer, *Physikalische Zeitschrift*, xiii. p. 485 (1912).

in question takes the same form as the one found by Wilson. From Wilson's Table II. (*loc. cit.* p. 147) we get

$$\text{for } V = 2.8 \cdot 10^{10}, \quad \frac{dE_x}{dx} = -8.0 \cdot 10^{-6}.$$

From the equation (3) on p. 19, we get for this velocity, and using the same values for r and $\Sigma \log n_s$ as above,

$$\frac{dE_x}{dx} = -8.8 \cdot 10^{-6},$$

a value which is in satisfactory agreement with Wilson's value. The better agreement between theory and experiments for fast β -rays than for slower ones and for cathode rays is probably connected with the simpler experimental conditions for the fast rays, for the latter keep their original uniformity in velocity to a much higher degree in passing through matter than is the case for the slower rays.

Conclusions.

In this paper the theory of the decrease of velocity of moving electrified particles in passing through matter is given in a form, such that the rate of the decrease in the velocity depends on the frequency of vibration of the electrons in the atoms of the absorbing material.

It is shown that the absorption of α -rays in the lightest elements can be calculated from the information about the number and frequencies of the electrons in the atoms which we get from the theory of dispersion, and that the values are in good agreement with experiment. For elements of higher atomic weight, it is shown that the number and frequencies of the electrons which we must assume, according to the theory, in order to explain the absorption of α -rays are of the order of magnitude to be expected.

It is further shown that the theory can account for the form of the relations between the velocity of the rays and the thickness of matter traversed, found by experiments with cathode- and β -rays. The absolute agreement as to the magnitude of the constants entering in the relations in question, is very good for the fastest β -rays, but not so good for slower β -rays and for cathode rays; a fact which may be due to the very difficult experimental conditions for these latter rays.

Adopting Prof. Rutherford's theory of the constitution of atoms, it seems that it can be concluded with great certainty,

from the absorption of α -rays, that a hydrogen atom contains only 1 electron outside the positively charged nucleus, and that a helium atom only contains 2 electrons outside the nucleus; the latter was necessarily to be expected from Rutherford's theory.

These questions and some further information about the constitution of atoms which may be got from experiments on the absorption of α -rays, will be discussed in more detail in a later paper.

I wish to express my sincere thanks to Prof. Rutherford for the kind interest he has taken in this work, and for the helpful advice he has given me.

Physical Laboratories,
The University, Manchester,
August 1912.

III. *On the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.* By S. A. SHORTER, B.Sc., Assistant Lecturer in Physics in the University of Leeds.—Part III. *The Action of Gravity on a Solution. The Solute Potential. Extension of the Theory**.

IN the parts of the present communication dealing with the action of gravity on a solution, and with the solute potential, the following new symbols will be used:—

G , the potential of gravity (defined so as to increase downwards);

$\psi_1(p, \theta)$, the chemical potential of the solid solute;

$S_0(s, p, \theta) \equiv \frac{\partial}{\partial s} f_0(s, p, \theta)$;

$S_1(s, p, \theta) \equiv \frac{\partial}{\partial s} f_1(s, p, \theta)$;

$P_1(s, p, \theta) \equiv \frac{\partial}{\partial p} f_1(s, p, \theta)$;

$\Delta_1(s, p, \theta) \equiv \psi_1(p, \theta) - f_1(s, p, \theta)$;

$l_1(s, p, \theta)$ the heat of solution.

The new symbols used in the last section will be defined as they occur in the text.

* Communicated by the Author.

The Action of Gravity on a Solution.

In his well-known work "On the Equilibrium of Heterogeneous Substances," Gibbs* deals with the problem of the effect of gravity on a system containing any number of components, and establishes the following general theorem:—

"When a fluid mass is in equilibrium under the influence of gravity, and has the same independently variable components throughout, the intrinsic potentials† for the several components are constant in any given level, and diminish uniformly as the height increases, the difference of the values of the intrinsic potentials for any component at two different levels being equal to the work done by the force of gravity when a unit of matter falls from the higher to the lower level."

We will first deduce by means of this theorem an expression for the concentration gradient in a binary fluid mixture. Afterwards we will give an elementary proof of the theorem in the case of a system containing two components. Suppose that at a certain point in a solution the gravitational potential is G , and the concentration, pressure, and temperature are s , p , and θ respectively. Suppose that at another point where the gravitational potential is $G + dG$, the concentration and pressure are $s + ds$ and $p + dp$ respectively. Then, according to the above theorem, we have

$$f_0(s + ds, p + dp, \theta) - f_0(s, p, \theta) = dG, \quad . \quad . \quad (1)$$

and

$$f_1(s + ds, p + dp, \theta) - f_1(s, p, \theta) = dG. \quad . \quad . \quad (2)$$

We will call these equations, which express Gibbs's theorem mathematically, the "Gibbs equations." They may be written in the form

$$S_0(s, p, \theta)ds + P_0(s, p, \theta)dp = dG, \quad . \quad . \quad . \quad (3)$$

$$S_1(s, p, \theta)ds + P_1(s, p, \theta)dp = dG. \quad . \quad . \quad . \quad (4)$$

Now

$$S_0 + sS_1 = 0,$$

$$P_0 + sP_1 = (1 + s)v(s, p, \theta),$$

so that we have

$$v(s, p, \theta)dp = dG, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is the ordinary equation of hydrostatic equilibrium.

* Collected Works, vol. i. p. 144.

† *I. e.* chemical potentials.

Eliminating dp between equations (3) and (5) we obtain the equation

$$\frac{ds}{dG} = \frac{\frac{s(1+s)}{v(s, p, \theta)} \frac{\partial}{\partial s} v(s, p, \theta)}{S_0(s, p, \theta)}. \quad (6)$$

This equation is due to Duhem *, who deduced it from first principles. It has also been established as an approximate result by Vegard †. It may be regarded as the fundamental equation for the effect of gravity on a binary mixture.

This equation may be established in the following elementary manner in the case of a solution of an involatile solute. Suppose that the solution is separated from the solvent vapour by a vertical partition pierced by a number of horizontal capillary channels whose walls are not wetted by the liquid. Suppose that one of the channels is at a level where the gravitational potential, concentration, pressure in the solution, and vapour-pressure are G , s , p , and \mathbf{P} respectively. The equilibrium equation is

$$f_0(s, p, \theta) = F_0(\mathbf{P}, \theta).$$

Suppose that there is another channel at a level where the above quantities are respectively $G + dG$, $s + ds$, $p + dp$, and $\mathbf{P} + d\mathbf{P}$. The equilibrium equation is

$$f_0(s + ds, p + dp, \theta) = F_0(\mathbf{P} + d\mathbf{P}, \theta).$$

Hence we have

$$S_0(s, p, \theta)ds + P_0(s, p, \theta)dp = V(\mathbf{P}, \theta)d\mathbf{P}.$$

Now the equation of hydrostatic equilibrium of the vapour is

$$V(\mathbf{P}, \theta)d\mathbf{P} = dG,$$

so that we have

$$S_0(s, p, \theta)ds + P_0(s, p, \theta)dp = dG.$$

This is one of the Gibbs equations. The remaining Gibbs equation and equation (6) may readily be deduced from this equation and the equation of hydrostatic equilibrium of the solution.

Devices similar to the above have been extensively used for establishing in an elementary manner various relations.

* *Journal de Physique*, 2^e série, vii. 1888, p. 391. This paper contains, in a note at the end, a proof of equation (9) of Part I. of the present work (connecting the vapour pressures of two solutions with the pressures under which they coexist in osmotic equilibrium). This important result seems to have been overlooked by subsequent writers. The method of proof adopted in the present work is rather simpler than that adopted by Duhem.

† *Phil. Mag.* vol. xiii. p. 589, May 1907.

It is interesting to note the connexion between such methods of proof and the more general method of Gibbs. In the case of a system containing only one component, Gibbs's general theorem gives a single equation which is the ordinary equation of hydrostatic equilibrium. By the above device we are able to deduce immediately the Gibbs equation for the solvent in the solution by means of the coexisting column of solvent vapour. The remaining Gibbs equation is deducible in the manner stated above. We could have obtained the same result by supposing the solution to be separated from the pure liquid solvent by a membrane permeable to the solvent only*.

In order to obtain formulæ for the practical calculation of the concentration gradient we must express the quantity $S_0(s, p, \theta)$ in terms of quantities which may be measured experimentally. This may be done in three ways—in terms of experimental data relating to (1) equilibrium between the solution and solvent vapour, (2) osmotic equilibrium between the solution and the liquid solvent, (3) equilibrium between the solution and the solid solvent. The three expressions thus obtained are of considerable importance in the general theory of solutions. In the next section we will merely obtain these expressions without actually performing the substitution in equation (6). The expressions for the concentration gradient are hardly of such importance as to justify writing them out in full.

*Expressions for the Practical Calculation of the
Concentration Derivative of the Solvent Potential.*

In Part II. of the present work three expressions were deduced for the solvent potential lowering. Since

$$S_0(s, p, \theta) = - \frac{\partial}{\partial s} \Delta_0(s, p, \theta),$$

the three expressions for the concentration derivative of the solvent potential may be obtained from the corresponding expressions for the solvent potential lowering by differentiation with respect to the concentration †.

* This method is open to the objection that if the pressure in the solution is low, equilibrium may not be possible unless the pure solvent is capable of existing in a state of tension.

† It will be noticed that none of the three expressions for the solvent potential lowering is of the most general nature possible. Equations (15) and (16) of Part II. give the value of Δ_0 corresponding to the temperature at which the experimental measurements are made, and any pressure, while equation (17) gives the value corresponding to the experimental pressure and any temperature. Expressions for the value of Δ_0 at any temperature and any pressure are easily obtained by means of equations (12) and (14) of Part II.

Equation (16) of Part II., which gives the value of the solvent potential lowering in terms of vapour-pressure data, may be written in the form *

$$\Delta_0(s, p, \theta) = \int_{\Pi}^{\Pi_0} V(x, \theta) dx - \int_{\Pi}^p P_0(s, x, \theta) dx + \int_{\Pi_0}^p v(0, x, \theta) dx. \quad (7)$$

Hence we have

$$S_0(s, p, \theta) = \{V(\Pi, \theta) - P_0(s, \Pi, \theta)\} \frac{\partial \Pi}{\partial s} + \int_{\Pi}^p \frac{\partial}{\partial s} P_0(s, x, \theta) dx. \quad (8)$$

If we substitute this value in equation (6) we obtain Duhem's † expression for the concentration gradient.

Equation (15) of Part II., which gives the value of the solvent potential lowering in terms of osmotic pressure data, may be written in the form

$$\Delta_0(s, p, \theta) = \int_p^{p_0 + \Omega(s, p_0, \theta)} P_0(s, x, \theta) dx + \int_{p_0}^p v(0, x, \theta) dx. \quad (9)$$

Hence we have ‡

$$S_0(s, p, \theta) = -P_0(s, p_0 + \Omega, \theta) \frac{\partial}{\partial s} \Omega(s, p_0, \theta) - \int_p^{p_0 + \Omega} \frac{\partial}{\partial s} P_0(s, x, \theta) dx. \quad (10)$$

If we substitute this value in equation (6) we obtain an expression for the concentration gradient in terms of osmotic pressure data. If in this expression we make $p = p_0 + \Omega$, we obtain the expression given by Berkeley and Burton §. As these writers point out, a differential coefficient of the osmotic pressure with respect to the concentration may be measured experimentally even when the pressure on the solution is so low that equilibrium with the pure solvent is experimentally

* This equation applies only to a solution of an involatile solute. The more complicated problem of expressing the solvent potential lowering in terms of experimental data relating to the equilibrium between a solution of a volatile solute and the vapour phase, will be considered in a later communication.

† *Loc. cit.*

‡ This expression and the preceding one may readily be obtained by differentiating the respective equilibrium equations with respect to the concentration. The values of S_0 thus obtained will not correspond to the pressure p . It will be readily seen that the first terms in the above two expressions are the values derived from the equilibrium equations, and the second terms the pressure corrections.

§ Phil. Mag. vol. xvii. p. 598, April 1909.

impossible. From the point of view of the present method of treatment of the subject, this may be explained in the following way. Suppose that a solution of concentration s under a pressure p is found to be in osmotic equilibrium with a solution of concentration $s + \delta s$ under a pressure $p + \delta p$. By taking various values of the increment δs , it is possible to estimate the value of

$$\lim_{\delta s \rightarrow 0} \frac{\delta p}{\delta s},$$

and since

$$f_0(s, p, \theta) = f_0(s + \delta s, p + \delta p, \theta),$$

we have

$$S_0(s, p, \theta) = -P_0(s, p, \theta) \lim_{\delta s \rightarrow 0} \frac{\delta p}{\delta s}.$$

If p is a sufficiently large pressure, then it will be possible to find a pressure p_0 such that

$$f_0(s, p, \theta) = f_0(0, p_0, \theta),$$

in which case

$$\lim_{\delta s \rightarrow 0} \frac{\delta p}{\delta s} = \frac{\partial}{\partial s} \Omega(s, p_0, \theta).$$

If we differentiate equation (17) of Part II. with respect to the concentration, we obtain the following expression for $S_0(s, p, \theta)$ in terms of freezing-point data :

$$\begin{aligned} S_0(s, p, \theta) = & \frac{\theta}{T^2} \frac{\partial T}{\partial s} \left[L_0 - l_0(s, p, \theta_0) - \int_T^{T_0} \gamma_a(p, \tau) d\tau + \int_T^{\theta_0} l'_0(s, p, \tau) d\tau \right] \\ & + \frac{\theta - T}{T} \frac{\partial}{\partial s} l_0(s, p, \theta_0) - \frac{\theta}{T} \int_T^{\theta_0} \frac{\partial}{\partial s} l'_0(s, p, \tau) d\tau + \int_\theta^{\theta_0} \frac{\partial}{\partial s} l'_0(s, p, \tau) d\tau \\ & + \theta \int_T^\theta \frac{1}{\tau} \frac{\partial}{\partial s} l'_0(s, p, \tau) d\tau. \quad \dots \quad (11) \end{aligned}$$

If we suppose the specific heats involved in the above expression to be independent of the temperature, the equation reduces to the simpler form

$$\begin{aligned} S_0(s, p, \theta) = & \frac{\theta}{T^2} \frac{\partial T}{\partial s} [L_0 - l_0(s, p, \theta_0) - (T_0 - T)\gamma_a + (\theta_0 - T)l'_0] \\ & + \frac{\theta - T}{T} \frac{\partial}{\partial s} l_0(s, p, \theta_0) - \frac{\partial l'_0}{\partial s} \left[\frac{\theta_0(\theta - T)}{T} - \theta \log \frac{\theta}{T} \right]. \quad (12) \end{aligned}$$

The Chemical Potential of the Solute.

Hitherto we have considered the variation of the chemical potential of the solvent only. The chemical potential of the solute is connected with that of the solvent by the equation

$$\frac{\partial}{\partial s} f_0(s, p, \theta) + s \frac{\partial}{\partial s} f_1(s, p, \theta) = 0.$$

Hence if s_1 and s_2 are two values of the concentration we have

$$\begin{aligned} f_1(s_2, p, \theta) - f_1(s_1, p, \theta) &= - \int_{s_1}^{s_2} \frac{1}{s} \frac{\partial}{\partial s} f_0(s, p, \theta) ds \\ &= \int_{f_0(s_2, p, \theta)}^{f_0(s_1, p, \theta)} \frac{df_0(s, p, \theta)}{s} \dots \quad (13) \end{aligned}$$

Hence if the value of $f_0(s, p, \theta)$, to an undetermined constant, be calculated from experimental data, the value of $f_1(s, p, \theta)$, to an undetermined constant, may be calculated by a simple quadrature.

The solute potential is involved directly in the equilibrium between the solution and the solid solvent. The saturation concentration \bar{s} is determined as a function of the temperature and pressure by the equation

$$f_0(\bar{s}, p, \theta) = \psi_1(p, \theta).$$

Hence we have

$$\Delta_1(s, p, \theta) = f_1(\bar{s}, p, \theta) - f_1(s, p, \theta).$$

If the experimental data giving the value, to an arbitrary constant, of the solvent potential, extend to the saturation concentration, the value of the solute potential lowering may be calculated by means of the equation

$$\Delta_1(s_1, p, \theta) = \int_{f_0(\bar{s}, p, \theta)}^{f_0(s_1, p, \theta)} \frac{df_0(s, p, \theta)}{s} \dots \quad (14)$$

The heat of solution is connected with the solute potential lowering by the equation *

$$\frac{\partial}{\partial \theta} \left\{ \frac{\Delta_1(s, p, \theta)}{\theta} \right\} = - \frac{l_1(s, p, \theta)}{\theta^2}.$$

* Duhem, *La Mécanique Chimique*, vol. iii. p. 133.

Extension of the Theory to Solutions containing any number of Involatile Solutes.*

Most of the formulæ established in the previous parts of the present work may readily be generalized so as to apply to solutions containing any number of involatile solutes. Consider a solution containing a mass M_0 of a solvent S_0 , and masses M_1, M_2, \dots, M_n of the involatile solutes S_1, S_2, \dots, S_n respectively. The total thermodynamical potential of the solution may be written in the form

$$\Phi = f_0(s_1, s_2, \dots, s_n, p, \theta)M_0 + \sum_{i=1}^{i=n} f_i(s_1, s_2, \dots, s_n, p, \theta)M_i,$$

where
$$s_i = \frac{M_i}{M_0}.$$

The quantities f_0, f_1, \dots, f_n are, of course, the chemical potentials of the components of the solution.

Now

$$\frac{\partial \Phi}{\partial p} = (M_0 + M_1 + \dots + M_n)v(s_1, s_2, \dots, s_n, p, \theta),$$

where $v(s_1, s_2, \dots, s_n, p, \theta)$ is the specific volume of the solution. From this equation we can readily deduce the relation

$$P_0(s_1, s_2, \dots, s_n, p, \theta) = v(s_1, s_2, \dots, s_n, p, \theta) - (1 + s_1 + \dots + s_n) \sum_{i=1}^{i=n} s_i \frac{\partial v}{\partial s_i}, \quad \dots \quad (15)$$

where

$$P_0(s_1, s_2, \dots, s_n, p, \theta) \equiv \frac{\partial f_0}{\partial p}.$$

If we use a notation for the mean value of P_0 between two values of the pressure similar to that adopted previously, we have, in the case of a slightly compressible liquid,

$$P_0(s_1, s_2, \dots, s_n, p_1 \rightarrow p_2, \theta) = P_0(s_1, s_2, \dots, s_n, \varpi, \theta) \left\{ 1 - \lambda \left(\frac{p_1 + p_2}{2} - \varpi \right) \right\}$$

where λ is related to the compressibility β by the equation

$$\lambda = \beta - (1 + s_1 + \dots + s_n) \frac{v(s_1, s_2, \dots, s_n, \varpi, \theta)}{P_0(s_1, s_2, \dots, s_n, \varpi, \theta)} \sum_{i=1}^{i=n} s_i \frac{\partial v}{\partial s_i}. \quad (16)$$

* The formulæ relating simply to osmotic equilibrium and to equilibrium between the solution and the solid solvent also apply, of course, to solutions of volatile solutes.

If the pure solvent under a pressure p_0 is in osmotic equilibrium with the solution under a pressure p , we have

$$\psi_0(p_0, \theta) = f_0(s_1, s_2, \dots, s_n, p, \theta),$$

where ψ_0 is the chemical potential of the pure solvent*. If we write

$$p - p_0 = \Omega(s_1, s_2, \dots, s_n, p_0, \theta),$$

we have

$$\psi_0(p_0, \theta) = f_0(s_1, s_2, \dots, s_n, p_0 + \Omega, \theta).$$

The effect of variation of the pure solvent pressure on the osmotic pressure is given by the equation

$$\frac{\partial}{\partial p_0} \Omega(s_1, s_2, \dots, s_n, p_0, \theta) = \frac{v_0(p_0, \theta)}{P_0(s_1, s_2, \dots, s_n, p, \theta)} - 1, \quad (17)$$

where $v_0(p_0, \theta)$ is the specific volume of the pure solvent.

If we write

$$\Delta_0(s_1, s_2, \dots, s_n, x, \theta) = \psi_0(x, \theta) - f_0(s_1, s_2, \dots, s_n, x, \theta),$$

we have

$$\Delta_0(s_1, s_2, \dots, s_n, p_0, \theta) = \Omega(s_1, s_2, \dots, s_n, p_0, \theta) P_0(s_1, s_2, \dots, s_n, p_0 \rightarrow p, \theta). \quad \dots (18)$$

If the pure solvent is in equilibrium with the solvent vapour under a pressure Π_0 we have

$$\psi_0(\Pi_0, \theta) = F_0(\Pi_0, \theta).$$

If the solution is in equilibrium with the solvent vapour under a pressure Π we have

$$f_0(s_1, s_2, \dots, s_n, \Pi, \theta) = F_0(\Pi, \theta).$$

Hence we have

$$\begin{aligned} \Delta_0(s_1, s_2, \dots, s_n, \Pi_0, \theta) &= \int_{\Pi}^{\Pi_0} V(x, \theta) dx \\ &= (\Pi_0 - \Pi) P_0(s_1, s_2, \dots, s_n, \Pi \rightarrow \Pi_0, \theta). \end{aligned} \quad (19)$$

If the pure solvent is in equilibrium with the solid solvent at a temperature T_0 , we have

$$\psi_0(p, T_0) = \phi_0(p, T_0).$$

* The symbol $f_0(0, 0, \dots, 0, p_0, \theta)$ is rather unwieldy.

If the solution is in equilibrium with the solid solvent at a temperature T , we have

$$f_0(s_1, s_2, \dots, s_n, p, T) = \phi_0(p, T).$$

Hence we have

$$\Delta_0(s_1, s_2, \dots, s_n, p, T) = \int_T^{T_0} \Gamma_0(p, \theta) d\theta.$$

The value of the integral in terms of experimental data has been found in Part II. Substituting this value in the above equation we obtain the result

$$\Delta_0(s_1, s_2, \dots, s_n, p, T) = \frac{I_0(T_0 - T)}{T_0} - \int_T^{T_0} \gamma_d(p, \tau) d\tau + T \int_T^{T_0} \frac{\gamma_d(p, \tau)}{\tau} d\tau. \quad (20)$$

Duhem's expression for the heat of dilution $l_0(s_1, s_2, \dots, s_n, p, \theta)$ may be written in the form*

$$\frac{\partial}{\partial \theta} \left\{ \frac{\Delta_0(s_1, s_2, \dots, s_n, p, \theta)}{\theta} \right\} = - \frac{l_0(s_1, s_2, \dots, s_n, p, \theta)}{\theta^2}. \quad (21)$$

Hence if θ_1 and θ_2 are any two temperatures, we have

$$\frac{\Delta_0(s_1, s_2, \dots, s_n, p, \theta_2)}{\theta_2} - \frac{\Delta_0(s_1, s_2, \dots, s_n, p, \theta_1)}{\theta_1} = - \int_{\theta_1}^{\theta_2} \frac{l_0(s_1, s_2, \dots, s_n, p, \theta)}{\theta^2} d\theta. \quad (22)$$

We can obtain a formula involving the value of the heat of dilution at one temperature only, by making use of the relation†

$$l_0'(s_1, s_2, \dots, s_n, p, \theta) = \gamma_0(p, \theta) - \gamma(s_1, s_2, \dots, s_n, p, \theta) + (1 + s_1 + \dots + s_n) \sum_{i=1}^{i=n} s_i \frac{\partial \gamma}{\partial s_i}. \quad (23)$$

We will not write this formula out, as the necessary alterations in equations (12) of Part II. are obvious, as are also the alterations in equations (15), (16), and (17) of Part II. necessary to make them applicable to a solution containing any number of solutes.

* *La Mécanique Chimique*, vol. iii. p. 49. Duhem establishes the formula by the aid of a general theorem relating to the heat evolved in any change of a system, but the formula is easily proved from first principles.

† This relation may be proved by equating the total heat evolved when an infinitesimal mass of the solvent is added to the solution, and the solution then heated from θ to $\theta + \delta\theta$, to the heat evolved when the solution and solvent are heated separately from θ to $\theta + \delta\theta$, and then mixed.

The pressures under which two solutions of different concentrations coexist in osmotic equilibrium are connected with the vapour pressures of the two solutions by the equation

$$\int_{\Pi}^{\Pi'} V(x, \theta) dx = (p - \Pi) P_0(s_1, s_2, \dots, s_n, \Pi \rightarrow p, \theta) - (p' - \Pi') P_0(s_1', s_2', \dots, s_n', \Pi' \rightarrow p', \theta), \quad (24)$$

where, as in equation (9) of Part I., quantities relating to one of the solutions are distinguished by accents from the corresponding quantities relating to the other solution. Since any of the concentrations may have the value zero, this equation is applicable to two solutions in the same solvent of two totally distinct sets of solutes.

The theory of the coexistence of solution and solvent vapour under different pressures is easily generalized. The necessary alterations in equations (2) and (4) of Part II., and in the theorem following this latter equation, are obvious.

It will be seen that the extension of the theory to solutions containing any number of involatile solutes is very simple. The extension may be made more simply still, however, by means of an important principle in the theory of chemical potential. This principle is that the choice of the components of a system may be made quite arbitrarily so long as every possible variation in the composition of any part of the system may be specified by variations of the masses of the components chosen *. Thus in the case of a solution containing two actual substances S_0 and S_1 , we may choose any imaginary compound of S_0 and S_1 in sufficient amount to use up the whole of S_0 (or S_1) as one of the components, and the additional amount (positive or negative) of S_1 (or S_0) as the other component. If we choose a compound containing a mass r of S_1 per unit mass of S_0 , then a solution containing masses M_0 of S_0 and M_1 of S_1 may be regarded as containing either masses $M_0(1+r)$ of the compound and $M_1 - rM_0$ of S_1 , or masses $M_1\left(1 + \frac{1}{r}\right)$ of the compound and $M_0 - \frac{1}{r}M_1$ of S_0 .

In the case of a solution of n solutes S_1, S_2, \dots, S_n we can choose an imaginary compound \mathbf{S} consisting of all the solutes in a certain proportion, making the amount of the compound sufficient to use up the whole of any one solute. The composition of any solution may be specified by the masses, per unit mass of solvent, of this compound and of the remaining $(n-1)$ solutes. The masses of the solutes may, of course,

* Gibbs, Collected Works, vol. i. p. 63.

be negative. In general this choice of an imaginary compound as one of the components of the system does not result in any simplification. In the case of the three two-phase systems we have been considering, however, we can make a great simplification in this way. This is due to the fact that in these systems, the only possible virtual modification is the passage of a certain mass of the solvent from one part of the system to the other. Now this modification does not change the relative proportions of the various solutes, so that if we choose for the compound \mathbf{S} a mixture of S_1, S_2, \dots, S_n in the proportions in which they exist in one particular state of the system, so as to make the concentrations of the remaining $(n-1)$ solutes zero in that state, these concentrations will remain zero throughout all modifications of the system. Hence the formulæ we have obtained for a binary system will apply to a solution containing any number of involatile solutes.

Many of these formulæ involve differentiation with respect to the concentration. We must, therefore, find out what is meant by differentiation with respect to the concentration of the imaginary compound. The concentration \mathbf{s} of the compound is related to the concentrations of the separate solutes by the equation

$$\mathbf{s} = s_1 + s_2 + \dots + s_n.$$

In order to obtain a solution of concentration $\mathbf{s} + \delta\mathbf{s}$ it is necessary to increase the concentrations of s_1, s_2, \dots, s_n by the respective amounts

$$\delta s_i = s_i \frac{\delta \mathbf{s}}{\mathbf{s}} \quad (i = 1, 2, \dots, n).$$

Hence if V be any function of the composition of the solution we have

$$\delta V = \sum_{i=1}^{i=n} \frac{\partial V}{\partial s_i} \delta s_i = \frac{\delta \mathbf{s}}{\mathbf{s}} \sum_{i=1}^{i=n} s_i \frac{\partial V}{\partial s_i},$$

so that

$$\mathbf{s}(1 + \mathbf{s}) \frac{\partial V}{\partial \mathbf{s}} = (1 + s_1 + \dots + s_n) \sum_{i=1}^{i=n} s_i \frac{\partial V}{\partial s_i}.$$

If we compare the equations giving the value of P_0 , λ , and l_0' for a binary solution with the corresponding equations in the present section, we see that this simple method of generalizing the equations leads to results in agreement with those obtained previously.

The University, Leeds,
Sept. 3, 1912.

IV. *The Theory of Radiation.* By S. B. McLAREN, M.A.,
Assistant Lecturer in Mathematics in the University of
Birmingham*.

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§ 1. INTRODUCTION.

THE unrest of our time has invaded even the world of Physics, where scarcely one of the principles long accepted as fundamental passes unchallenged by all. The spirit of revolution is seen at its boldest in the theory of radiation. It is not only that Einstein's idea of the quantum is destructive of the continuous medium and all that was built upon it in the nineteenth century. His form of atomism excludes what has been fundamental in Physical science, the ideal of mechanical explanation. Mechanism tries to resolve into motion every form of change; matter is to be simply what moves and the laws of its motion are the whole of Physics. But the behaviour of Einstein's quanta is strictly analogous to a chemical process. It is governed by laws of change which are not laws of motion. We have always been used to think of the past and the present states of the material universe as joined with no gap between. Einstein, on the contrary, requires us to allow a sudden break from one to the other. The changes of which he speaks are not motions, they need no longer be even continuous.

This paper is an attempt to save the classical view of radiation as a continuous wave motion. If that can be done, it seems to me a small thing to sacrifice the ordinary mechanical notions of matter. Indeed, I am convinced that some such idea as that of Einstein's quantum is necessary to explain its most elementary properties. It need be no obscure inference from the laws of radiation. The various forms of matter are in no continuous series; the gaps between may be crossed perhaps in a radioactive transformation, but they are not occupied. Matter is stamped in a few definite moulds, and always retains their impress. It is hard to imagine how continuous laws of motion can lead to such results. And the theory of relativity increases the difficulty,

* Communicated by the Author.

for it denies the possibility of rigid bodies anywhere. I am prepared, therefore, to accept Einstein's atomism for matter but not for radiation. The hypothesis that radiation is a continuous wave motion appears to me indispensable. It penetrates and simplifies the complexity of observed fact so profoundly that a rival version seems almost impossible.

The methods of this paper are at once more simple and more general than those given in *Phil. Mag.* July 1911 and April 1912. I assume the ordinary undulatory theory of light, but I do not assume the formulæ of classical dynamics. The laws of motion of matter are not deduced from the principle of least action, they need not even be laws of continuous motion at all. A mathematical theory of emission and absorption complete radiation and refraction, in fact of the whole process of interaction between radiation and material systems, can be reached without these restrictions. But some at least of the variables specifying the state of matter must have a continuous range; that is required by conservation of energy and the continuous theory of radiation.

§ 2. STATISTICAL THEORY.

The material system is exposed to radiation in a space bounded by walls which prevent its escape. For any wavelength $2\pi\kappa_m^{-1}$ I suppose that there exists a differential equation of the form

$$\frac{1}{c^2} \frac{d^2 \alpha_m}{dt^2} + \kappa_m^2 \alpha_m = \phi_m. \quad . \quad . \quad . \quad . \quad (1)$$

$$(m=1, 2, \dots \infty)$$

Here c is the velocity of light, and ϕ_m is defined by the material state at the time t . The variables α_m , &c., fix the state of the field of radiation. By increasing the space enclosed α_m can be made simple harmonic for as many periods as we please.

$$\alpha_m = (\alpha_m)_0 \cos (c\kappa_m t - c\kappa_m t_0) + \left(\frac{d\alpha_m}{dt} \right)_0 (c\kappa_m)^{-1} \sin (c\kappa_m t - c\kappa_m t_0). \quad . \quad . \quad . \quad . \quad (2)$$

$(\alpha_m)_0$ and $\left(\frac{d\alpha_m}{dt} \right)_0$ denote values at time t_0 . (2) holds so

long as $t - t_0$ is sufficiently small.

Where Lorentz's electromagnetic theory is assumed I have shown (*Phil. Mag.* April 1912) how α_m and ϕ_m are to be determined. The variables defining the state of the material system I denote by x_1, x_2 , &c., x_n . These have all

a continuous though not necessarily an unrestricted range of variation. If discontinuous changes are admitted we must suppose them to involve a transformation in the nature of these variables. The values of the new and the old must be connected by equations sufficient to determine the one when the others are given.

I write dN for the probability of a material state in which $x_1 x_2 \dots x_n$ have values lying within the infinitesimal intervals $dx_1, dx_2 \dots dx_n$.

$$\left. \begin{aligned} dN &= \rho' dV. \\ dV &= dx_1 dx_2 \dots dx_n. \end{aligned} \right\} \dots \dots \dots (3)$$

Let a material system change from the time t_1 to the time t_2 , whether continuously or not.

$$(dN)_2 = (dN)_1, \dots \dots \dots (4)$$

where the suffixes denote the values of dN at t_2 and at t_1 . Then the most general solution of (3) and (4) is given by (5)

$$\rho' = e^{-hH} \times \rho, \dots \dots \dots (5)$$

where ρ is any particular solution and h is an arbitrary constant. The statistical method leads to (5) even for laws of change so general as those here assumed. H is the total energy, and it is taken for granted that the only quantities invariant throughout all change are functions of H .

Since ρ' and ρ are both solutions of (3) and (4),

$$(\rho'/\rho)_2 = (\rho'/\rho)_1,$$

ρ'/ρ is therefore an invariant, and

$$\rho' = \rho \times f(H). \dots \dots \dots (6)$$

The essential postulate of the statistical method is that for the purposes of the theory of heat any finite body can be divided into finite physically independent parts. Call these parts A and B,

$$dN = (dN)_A \times (dN)_B.$$

$$\begin{aligned} \text{By (6)} \quad dN_A &= f(H_A) \rho_A dV_A, \quad dN_B = f(H_B) \rho_B dV_B, \\ dN &= f(H_A) f(H_B) \rho_A \rho_B dV_A dV_B. \dots \dots \dots (7) \end{aligned}$$

$$\begin{aligned} \text{Now} \quad (\rho_A dV_A)_2 &= (\rho_A dV_A)_1, \\ (\rho_B dV_B)_2 &= (\rho_B dV_B)_1. \end{aligned}$$

$$\text{Hence} \quad (\rho_A \rho_B dV_A dV_B)_2 = (\rho_A \rho_B dV_A dV_B)_1.$$

It follows that $\rho_A \rho_B dV_A dV_B$ is a particular value of dN in (3) and (4), and since (7) gives the general solution

$$f(H_A) \times f(H_B)$$

is by (6) a function of $H_A + H_B$, the total energy.

Hence $f(H)$ varies as e^{-hH} , and we have the result (5).

§ 3. INTERACTION OF MATTER AND RADIATION.

The motion of the material system and the distribution represented by (5) are disturbed by the presence of radiation. At any instant the actual values $x_1 + \delta x_1$, &c. of the co-ordinates differ slightly from $x_1, x_2 \dots x_n$, the coordinates in what I shall call the undisturbed motion. The increments δx , &c., are due to the radiation, and are small quantities (see Phil. Mag. July 1911, p. 69). Their average values are calculated directly by allowing material systems distributed according to (5) to move for a sufficient time in the presence of radiation. The full effect of that radiation will be reached after a period described in kinetic theory as the time of a free path. Only the deviation arising within this very short interval is correlated with the disturbing forces at any instant. It is the source of absorption and refraction.

Let ϕ be any function of $x_1 x_2 \dots x_n$, and $\delta\phi$ the increment in ϕ due to the increments $\delta x_1, \delta x_2$, &c., in the values of $x_1, x_2 \dots x_n$. Then the average value of $\delta\phi$ is

$$\int^N \delta\phi dN. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For start at time t_0 with a distribution such that the frequency dN_0 of systems lying in the n 'ple volume element dV_0 is given by

$$dN_0 = \rho_0 e^{-hH_0} dV_0.$$

Let these systems move disturbed by radiation till time t . Then the average value of $\delta\phi$ at this time is

$$\int^N \delta\phi dN_0.$$

But in the undisturbed motion

$$dN_0 = dN. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(8) follows, and it is to be remembered that the integrations

involved in dN are extended over the range of the variables x_1, x_2 , &c. in the undisturbed motion.

$$\delta\phi = \sum_{r=1}^{r=n} \frac{d\phi}{dx_r} \delta x_r, \quad (r=1, 2 \dots n),$$

and δx_r , &c. are functions of $(x_1)_0$, &c. and of the time which appears explicitly in the expressions of the disturbing forces given in (2).

$\delta x_1, \delta x_2$, &c. can therefore also be expressed as functions of $x_1, x_2 \dots x_n$, &c. and t . It is evident that

$$\int \delta\phi dN = \delta \int \phi dN - \int \phi \delta(dN). \quad . \quad . \quad . \quad (10)$$

(10) is true whether or no the motion is continuous.

The disturbing radiation may precipitate a transformation of the variables. Then $\delta(dN)$ involves a finite change in x_1, x_2 , &c., but only an infinitesimal change in dN itself.

In the ordinary mechanical systems

$$\delta \int \phi dN = 0. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The variables are here coordinates of position and momenta. The presence of radiation does not affect the range of values they can assume. Hence (11), since ϕ is a definite function of the variables and the limits of integration are not disturbed. I shall throughout use the result (11). It is thus assumed that if there are discontinuous changes they are governed by conditions not directly dependent on the presence of radiation. For example, they may take place when the velocities or coordinates reach certain given values.

(10) now becomes

$$\int \delta\phi dN = - \int \phi \delta(dN), \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and this result is in the present state of our knowledge no less general than (10) itself. For dN still contains the arbitrary function ρ , which reduces to a constant only in the classical dynamics.

An important consequence follows at once from (12). The average value of $\delta\phi$ is zero if $\delta(dN) = 0$.

If the disturbing forces leave unaltered the canonical distribution in phase, to use Willard Gibbs's term, they produce no observable effects at all. It is so with magnetic force in the ordinary theory. Niels Bohr has pointed out* that $\delta(dN) = 0$ when the only disturbing force is due to a steady

* *Studier over Metallernes Elektrontheori*, p. 106.

magnetic field *. There can, therefore, be no kinetic theory of induced magnetization. This is one more argument against the ultimate validity of ordinary mechanics.

$$\delta(dN) = (dN)_t - (dN)_0. \quad . \quad . \quad . \quad (13)$$

The suffixes denote the actual values of dN at times t and 0 in the motion as disturbed. Remembering (9) the right-hand side of (13) is seen to be the difference in value of dN due to the disturbance. From (13)

$$\delta(dN) = \int_{t_0}^t \frac{d}{dt} (dN) dt. \quad . \quad . \quad . \quad (14)$$

The quantity

$$\frac{d}{dt} (dN)$$

is zero in the undisturbed motion

$$\frac{d}{dt} (dN) = \sum_{r=1}^{r=n} \frac{d}{dx_r} \left(\rho' \frac{dx_r}{dt} \right) dN,$$

or

$$\frac{d}{dt} (dN) = \sum \frac{1}{\rho} \frac{d}{dx_r} \left(\rho \frac{dx_r}{dt} \right) dN - h \frac{dH}{dt} dN. \quad . \quad (15)$$

In (15) the right-hand side is zero when the motion is not affected by radiation, but if the equations of motion are given it can be expressed as a linear function of $\alpha_m, \frac{d\alpha_m}{dt}$, &c., which are functions of the time, and of x_1, x_2 , &c. These equations of motion are taken to be

$$\frac{dx_r}{dt} = f_r(x_1, x_2, \dots x_n) + \sum_{m=1}^{m=\infty} \left(\frac{d\alpha_m}{dt} \chi'_{rm} + \alpha_m \chi_{rm} \right). \quad (16)$$

The terms in α_m and $\frac{d\alpha_m}{dt}$ must of necessity be linear if the absorption is to be proportional as in fact it is to the intensity of radiation. $\chi'_{(rm)}$ and $\chi_{(r,m)}$ are functions of $x_1, x_2, \dots x_n$.

The rate of increase of the material energy $\frac{dH}{dt}$ is given by

$$\frac{dH}{dt} = \sum_{r=1}^{r=n} \frac{dH}{dx_r} \frac{dx_r}{dt}.$$

* See also W. Voigt, *Ann. d. Phys.* ix. p. 115 (1902).

When α_m is for all values of m zero, H is constant, so that

$$\sum_{r=1}^{r=n} \frac{dH}{dx_r} f_r = 0,$$

and

$$\begin{aligned} \frac{dH}{dt} = & \sum_{m=1}^{m=\infty} \frac{d\alpha_m}{dt} \left(\sum_{r=1}^{r=n} \frac{dH}{dx_r} \chi'_{rm} \right) \\ & + \sum_{m=1}^{m=\infty} \alpha_m \left(\sum_{r=1}^{r=n} \frac{dH}{dx_r} \chi_{r,m} \right). \quad . \quad . \quad . \quad (17) \end{aligned}$$

The æthereal energy is

$$\sum_{m=1}^{m=\infty} \frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)^2 + \frac{1}{2} \kappa_m^2 \alpha_m^2.$$

The rate of increase of the æthereal energy is by (1)

$$\sum_{m=1}^{m=\infty} \phi_m \frac{d\alpha_m}{dt} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By adding (17) and (18) we have the total rate of increase of the purely material and the purely æthereal energy. The total energy, since there is conservation, must be expressible in the form

$$H + \sum_{m=1}^{m=\infty} \left\{ \frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)^2 + \frac{1}{2} \kappa_m^2 \alpha_m^2 + \psi_m \alpha_m \right\}. \quad . \quad (19)$$

And on making the total rate of change vanish,

$$\sum_{r=1}^{r=n} \frac{dH}{dx_r} \chi'_{(r,m)} + \phi_m + \psi_m = 0. \quad . \quad . \quad . \quad (20)$$

$$\sum_{r=1}^{r=n} \frac{dH}{dx_r} \chi_{(r,m)} + \frac{d\psi_m}{dt} = 0, \quad . \quad . \quad . \quad . \quad (21)$$

or

$$\sum_{r=1}^{r=n} \frac{dH}{dx_r} \chi_{(r,m)} + \sum_{r=1}^{r=n} \frac{d\psi_m}{dx_r} f_r = 0. \quad . \quad . \quad . \quad (22)$$

In passing from (21) to (22) I write

$$\frac{d\psi_m}{dt} = \sum_{r=1}^{r=n} \frac{d\psi_m}{dx_r} f_r,$$

neglecting terms involving the α 's which are here small quantities compared with those retained. (20) and (22) are conditions necessary for the conservation of energy.

§ 4. EMISSION AND ABSORPTION.

The rate of increase of the æthereal energy of wave-length

$$2\pi\kappa_m^{-1} \text{ is } \phi_m \frac{d\alpha_m}{dt}. \quad . \quad . \quad . \quad . \quad (23)$$

In a steady state this vanishes on the average, the emission balances the absorption. I calculate each directly, and by equating the results arrive at a formula for complete radiation.

In calculating the absorption $\frac{d\alpha_m}{dt}$ is treated as a simple-harmonic function of period $2\pi(c\kappa_m)^{-1}$. The absorption is due to the disturbance produced by the presence in (16) of the terms involving α_m and $\frac{d\alpha_m}{dt}$. The rate of absorption is the average value of

$$\begin{aligned} & -\delta\phi_m \frac{d\alpha_m}{dt}, \\ \text{or} & -\frac{d\alpha_m}{dt} \int \delta\phi_m dN, \\ \text{or} & \frac{d\alpha_m}{dt} \int_N \phi_m \int_{t_0}^t \frac{d}{dt} (dN) dt. \quad . \quad . \quad . \quad (24) \end{aligned}$$

The rate of emission is found by treating ϕ_m in (23) as a given function of the time and of the initial values of $x_1, x_2, \&c.$ (1) may then be regarded as the equation of motion of a simple pendulum slightly disturbed. I have already shown that the average rate of emission is

$$c^2 \int_N \phi_m \int_0^\epsilon \phi_m \cos(c\kappa_m \epsilon) d\epsilon dN, \quad . \quad . \quad (25)$$

ϵ is a time taken large enough to ensure that in (23) $\phi_m(t-\epsilon)$ is included so long as it is correlated with $\phi_m(t)$ (Phil. Mag. April 1912, p. 532, equation (72)).

To calculate (24) use (15), (5), (16), retaining in the last only the terms which involve α_m and $\frac{d\alpha_m}{dt}$, since only these are correlated in value with $\frac{d\alpha_m}{dt}$.

Then (24) becomes

$$\begin{aligned} & -h \frac{d\alpha_m}{dt} \int_N \phi_m \int_{t-\epsilon}^t \frac{dH}{dt} dt dN, \\ & + \frac{d\alpha_m}{dt} \int_N \phi_m \int_{t-\epsilon}^t \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} \left(\rho \frac{dx_r}{dt} \right) dt dN. \quad . \quad . \quad (26) \end{aligned}$$

Now $\frac{dH}{dt} + \sum_{m=1}^{m=\infty} \phi_m \frac{d\alpha_m}{dt} + \frac{d}{dt} \left(\sum_{m=1}^{m=\infty} \psi_m \alpha_m \right) = 0$, . (27)

since (19) is the expression for the total energy. In the value of $\frac{dH}{dt}$ given by (27) only the terms involving α_m need be retained to be substituted in (26), and the rate of absorption reduces to

$$\begin{aligned} & h \frac{d\alpha_m}{dt} \int_{\mathbf{N}} \phi_m \int_{t-\epsilon}^t \phi_m \frac{d\alpha_m}{dt} dt d\mathbf{N}, \\ & + h \frac{d\alpha_m}{dt} \int_{\mathbf{N}} \phi_m \int_{t-\epsilon}^t \frac{d}{dt} (\psi_m \alpha_m) dt d\mathbf{N}, \\ & + \frac{d\alpha_m}{dt} \int_{\mathbf{N}} \phi_m \int_{t-\epsilon}^t \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi'_{r_m}) \frac{d\alpha_m}{dt} dt d\mathbf{N}, \\ & + \frac{d\alpha_m}{dt} \int_{\mathbf{N}} \phi_m \int_{t-\epsilon}^t \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi_{r,m}) \alpha_m dt d\mathbf{N}. \quad (28) \end{aligned}$$

The second term of (28) disappears since

$$\int_{t-\epsilon}^t \frac{d}{dt} (\psi_m \alpha_m) dt dN = [\psi_m \alpha_m]_{t-\epsilon}^t dN,$$

and the average value of $\frac{d\alpha_m}{dt} \times \alpha_m$ is zero.

Substitute in other terms the values of α_m and $\frac{d\alpha_m}{dt}$ given by (2). (28) reduces to

$$\begin{aligned} & h \left(\frac{d\alpha_m}{dt} \right)^2 \int_{\mathbf{N}} \phi_m \int_{(t-\epsilon)}^{\epsilon} \phi_m \cos c\kappa_m \epsilon \, d\epsilon \, d\mathbf{N}, \\ & + \left(\frac{d\alpha_m}{dt} \right)^2 \int \phi_m \int_0^{\epsilon} \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi'_{r,m})_{t-\epsilon} \cos c\kappa_m \epsilon \, d\epsilon \, d\mathbf{N}, \\ & + (c\kappa_m)^{-1} \left(\frac{d\alpha_m}{dt} \right)^2 \int_{\mathbf{N}} \phi_m \int_0^{\epsilon} \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi_{r,m}) \sin c\kappa_m \epsilon \, d\epsilon \, d\mathbf{N}. \end{aligned} \quad (29)$$

The formula for complete radiation results by equating (29) to (25). The second and third terms in (29) vanish in the form of electromagnetic theory due to Lorentz. Here (16) become

$$\frac{dp_r}{dt} + \frac{dH}{dq_r} = \frac{d\Phi}{dq_r} - \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right), \quad \frac{dq_r}{dt} - \frac{dH}{dp_r} = 0. \quad (30)$$

$$r=1, 2 \dots K.$$

The variables $x_1 \dots x_n$ become the momenta $p_1 \dots p_\kappa$ and the coordinates $q_1 q_2 \dots q_\kappa$. The number n is here even being 2κ . In (30)

$$u_r = \frac{dq_r}{dt} = \frac{dH}{dp_r},$$

and

$$\Phi = \sum_{m=1}^{m=\infty} \alpha_m \sum_{s=1}^{s=\kappa} u_s \omega_s.$$

Φ is a linear function of the velocities, so that ω_{sm} is here a function of $q_1 q_2 \dots q_\kappa$ only (see Phil. Mag. April 1912).

Arranging the 2κ variables with all the momenta first, it follows by comparing (16) and (30) that for values of r from 1 to κ ,

$$\chi_{(r,m)} = \sum_{s=1}^{s=\kappa} u_s \frac{d\omega_{sm}}{dq_r} - \sum_{s=1}^{s=\kappa} \frac{d\omega_{rm}}{dq_s} u_s = \sum_{s=1}^{s=\kappa} \frac{dH}{dp_s} \left(\frac{d\omega_{sm}}{dq_r} - \frac{d\omega_{rm}}{dq_s} \right)$$

$$\chi'_{(r,m)} = -\omega_{(r,m)}.$$

And for values of r from $\kappa+1$ to n ,

$$\chi_{(r,m)} = \chi'_{(r,m)} = 0.$$

Hence

$$\sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi'_{rm}) = - \sum_{r=1}^{r=\kappa} \frac{d}{dp_r} (\omega_{rm}) = 0,$$

$\rho=1$ and ω_{rm} is not a function of the momenta.

$$\sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} (\rho \chi_{r,m}) = \sum_{s=1}^{s=\kappa} \frac{d^2 H}{dp_r dp_s} \left(\frac{d\omega_{sm}}{dq_r} - \frac{d\omega_{rm}}{dq_s} \right) = 0.$$

(29) reduces to the first term only.

§ 5. COMPLETE RADIATION.

In this case the formula for complete radiation becomes by equating (29) and (25)

$$\frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)^2 = \frac{1}{2h} \cdot \dots \dots \dots (31)$$

This represents equipartition of the radiant energy. (31) is equivalent to Rayleigh's formula

$$E_\lambda = 8\pi R \theta \lambda^{-4} \cdot \dots \dots \dots (32)$$

If ρ is not unity, that is if the laws of radiation are not deduced from the principle of least action, the second and

third terms in (29) are not zero. There is no longer equipartition of the radiation, but the further question now arises whether the distribution can be such as is at least empirically represented in Planck's formula. Instead of (32), (29) leads to the formula

$$E_{\lambda} = 8\pi R\theta\lambda^{-4}\Phi_m(\Phi_m + \Psi_m)^{-1} \quad (33)$$

$$\Phi_m = \int_N \phi_m \int_0^{\epsilon} \phi_{m(t-\epsilon)} \cos(c\kappa_m\epsilon) d\epsilon dN,$$

or
$$\Phi_m = \int_0^{\infty} f(\lambda, H) e^{-H/R\theta} dH, \quad (34)$$

$$\Psi_m = \frac{1}{h} \int_N \phi_m \int_0^{\epsilon} \sum_{r=1}^{r=n} \frac{1}{\rho} \frac{d}{dx_r} \{ \rho \chi'_{rm} \cos c\kappa_m\epsilon + \rho \chi_{rm} (c\kappa_m)^{-1} \sin c\kappa_m\epsilon \} d\epsilon dN,$$

or
$$\Psi_m = \theta \int_0^{\infty} g(\lambda, H) e^{-H/R\theta} dH. \quad (35)$$

(33) suggests a formula of the same type as Planck's.

Let
$$f(\lambda, H) = f(\lambda H) \quad (36)$$

$$g(\lambda, H) = \lambda F(\lambda H). \quad (37)$$

So that $f(\lambda H)$ and $F(\lambda H)$ are functions only of the product of wave-length and energy. The ordinary mechanical theories in which radiation is explained as due to the accelerated motion of electrons, make $f(\lambda H)$ contain some such factor as $e^{-a\lambda H}$, so that the function has an essential singularity and vanishes when H diminishes to zero.

I assume that $f(\lambda H)$ and $F(\lambda H)$ both behave in this way for the zero value of λH , and further that a series for $F(\lambda H)$ exists such that

$$F(\lambda H) = \sum_{n=0}^{n=\infty} a_n \frac{d^n}{d(\lambda H)^n} f(\lambda H). \quad (38)$$

Note that $f(\lambda H)$ and all its differential coefficients vanish when λH vanishes.

$$\begin{aligned} \Psi_m &= \lambda\theta \int_0^{\infty} F(\lambda H) e^{-H/R\theta} dH, \\ &= \lambda\theta \left\{ \sum_{n=0}^{n=\infty} (-1)^n \frac{a_n}{(R\lambda\theta)^n} \right\} \int_0^{\infty} f(\lambda H) e^{-H/R\theta} dH. \end{aligned}$$

$$E_{\lambda} = 8\pi R\theta\lambda^{-4} \left\{ 1 + \lambda\theta \sum_{n=0}^{n=\infty} (-1)^n a_n \frac{a_n}{(R\lambda\theta)^n} \right\}^{-1} \quad (39)$$

A result similar to Planck's can be obtained by putting

$$\alpha_0 = 0,$$

$$\alpha_n = \kappa_1 \frac{(-\kappa R)^n}{n}, \quad n = 1, 2 \dots \infty,$$

$$E_\lambda = 8\pi R \theta \lambda^{-4} \{1 + \kappa_1 \lambda \theta (e^{\kappa/\lambda \theta} - 1)\}^{-1}. \quad (40)$$

For large values of $\lambda \theta$ this gives

$$E_\lambda = 8\pi R \theta \lambda^{-4} (1 + \kappa \kappa_1)^{-1}. \quad (41)$$

For small values of $\lambda \theta$ it gives

$$E_\lambda = 8\pi R \lambda^{-5} e^{-\kappa/\lambda \theta} (\kappa_1)^{-1}. \quad (42)$$

Thus if we abandon the principle of least action a wave theory of radiation is at least a formal possibility. But nothing has been done to show what laws of motion lead to the results (36), (37), (38), or, indeed, that they are consistent with any continuous laws of motion whatever.

Rayleigh's formula for the complete radiation is independent of all particular properties of matter. It is enough if the laws of motion are deduced from the principle of least action. Once abandon that and various results can be reached inconsistent with each other and with the truth. But because an object can be imagined without logical contradiction it does not therefore exist. The distribution of energy depends only upon such properties of matter as are common to all forms which actually exist. It does not follow that these are found in matter as it is by us imagined. This seems the only answer to the difficulties raised by Poincaré. The mechanical interchange of energy leads to equipartition. But it is not shown that any such process exists, or at least that it alone exists in any actual species of matter.

§ 6. THEORY OF A SIMPLE WAVE-TRAIN.

The main object of this paper is to show that the effect of radiation on matter is calculable although the laws of motion may differ widely from those known to ordinary dynamics. The behaviour of a simple harmonic wave-train advancing through any material system is easily determined.

The vector potential F_1 satisfies the equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 + 4\pi c^{-1} \rho u = 0, \quad (43)$$

$$F_1 = (F_1, G'_1, 0) e^{ipt - inz - kz}.$$

As explained in my previous paper F_1 excludes all the irregular interatomic field. (43) gives

$$(p^2/c^2 + \kappa^2 - n^2 + 2ink)F_1 + 4\pi\rho u/c = 0. \quad (44)$$

Let dS represent an element of area parallel to the wave front, dz an element of length perpendicular to it. dz though not infinitesimal is very small compared with the wavelength

$$(p^2/c^2 + k^2 - n^2 + 2ink)F_1 dS dz + 4\pi c^{-1} \int \rho u dS dz = 0.$$

Or since we are concerned only with the disturbance due to the passage of the wave

$$(p^2/c^2 + k^2 - n^2 + 2ink)F_1 dS dz + 4\pi c^{-1} \delta \int \rho u dS dz = 0. \quad (45)$$

Evidently the average value of $\delta \int \rho u dS dz$ is proportional to $dS dz$.

It may be shown by the methods of this article that (45) is equivalent to two equations of the form

$$\left. \begin{aligned} (p^2/c^2 + k^2 - n^2 + 2ink)F_1 + \Phi_{11}F_1 + \Phi_{12}G_1 &= 0 \\ (p^2/c^2 + k^2 - n^2 + 2ink)G_1 + \Phi_{21}F_1 + \Phi_{22}G_1 &= 0 \end{aligned} \right\}. \quad (46)$$

I do not here consider further these results.

§ 7. THEORY OF INDUCED MAGNETIZATION.

I end by demonstrating the inadequacy of the classical dynamics to explain magnetic phenomena. Suppose the only disturbing force a steady magnetic field. Then

$$\frac{d\alpha_m}{dt} = 0, \quad m = 1, 2 \dots \infty, \quad (47)$$

$$\delta dN = \int_{t_0}^t \frac{d}{dt} (dN) dt, \quad (48)$$

It follows that $\frac{d}{dt} (dN) = -h \frac{dH}{dt} dN$, by (30).. (49)

$$\begin{aligned} \frac{dH}{dt} &= + \sum_{r=1}^{r=\kappa} \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right) u_r - \sum_{r=1}^{r=\kappa} \frac{d\Phi}{dq_r} \frac{dq_r}{dt}, \\ &= \frac{d}{dt} \left(\sum u_r \frac{d\Phi}{du_r} \right) - \sum_{r=1}^{r=\kappa} \left(\frac{d\phi}{dq_r} \frac{dq_r}{dt} + \frac{d\phi}{du_r} \frac{du_r}{dt} \right), \\ \frac{dH}{dt} &= \frac{d}{dt} \left(\sum u_r \frac{d\Phi}{du_r} - \Phi \right) - \left(\frac{d\phi}{dt} \right)_{\text{exp.}} \quad (50) \end{aligned}$$

$\left(\frac{d\phi}{dt} \right)_{\text{exp.}}$ denotes the differential of ϕ with respect to the time, in so far as that occurs explicitly.

$$\Phi = \sum_{m=1}^{m=\infty} \alpha_m \phi_m.$$

By (47) $\left(\frac{d\Phi}{dt}\right)_{\text{exp.}} = 0.$

Since Φ is a linear function of the velocities

$$\sum_{r=1}^{r=k} u_r \frac{d\Phi}{du_r} - \Phi = 0.$$

Hence $\frac{dH}{dt} = 0,$ and $\frac{d}{dt}(dN) = 0$ by (49) and (50).

Therefore as I have already argued, a steady magnetic field has no effect. The same argument does not hold for a steady electric field. For in arriving at the equations (30) electrostatic energy is supposed included in H . Its presence already determines the canonical distribution from which the motion starts.

§ 8. CONCLUSIONS.

To save the "æther" it is necessary to give up the classical mechanics. This paper shows that the theory of radiation can proceed without using the principle of minimum action. A formula for the complete radiation naturally suggested is

$$E_{\lambda} = 8\pi R\theta\lambda^{-4} \{1 + \kappa_1\lambda\theta(e^{\frac{\kappa}{\lambda\theta}} - 1)\}^{-1},$$

κ_1 and κ are arbitrary constants. This gives a result similar to Rayleigh's for large values of $\lambda\theta$, a result similar to Wien's for small values.

June 10, 1912.

V. *Note on the Energetics of the Induction Balance.* By JOHN P. DALTON, M.A., B.Sc., Department of Physics, University College, Dundee*.

- § 1. **I**N the generalized induction balance in which each arm contains resistance, inductance, and capacity:
- (i.) steady balance is conditioned by the usual Wheatstone relationship between the resistances;
 - (ii.) an approximate impulsive balance is given by zero integral extra-current in the galvanometer; while
 - (iii.) true impulsive balance necessitates zero extra-current in the galvanometer at any time.

Heaviside† used his operational method to solve the case

* Communicated by Professor Wm. Peddie, D.Sc., F.R.S.E.

† O. Heaviside, 'Electrical Papers,' ii. p. 280.

in which each arm consists of a coil and condenser in parallel. Slightly greater generality is obtained, however, and more practical methods are embraced in the general solution, if the condenser is shunted across part of the coil only. In that case, if R and L denote the resistance and inductance respectively of the whole coil, and r and l the corresponding values for that part shunting the condenser, then the voltage across the coil terminals is determined by

$$v = L \frac{di}{dt} + Ri - r\dot{q} - l\ddot{q}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where i is the total current and q is the condenser charge at that particular moment. Elimination of q from (1) at once gives Z , the resistance operator (generalized resistance), for this case:

$$Z = R - r + (L - l)D + \{CD + (r + lD)^{-1}\}^{-1}, \quad . \quad . \quad (2)$$

where C is the capacity of the condenser, and D is the time operator $\frac{d}{dt}$. From the expansion of $Z_1 Z_4 = Z_2 Z_3$, the condition to be fulfilled for a first order balance is found to be

$$R_4(L_1 - r_1^2 C_1) - R_3(L_2 - r_2^2 C_2) = R_2(L_3 - r_3^2 C_3) - R_1(L_4 - r_4^2 C_4). \quad . \quad . \quad . \quad . \quad (3)$$

All practical methods of measurement are so chosen that no second order effects occur; and hence, in such methods, true balance is uniquely determined by satisfying condition (ii.), that is, the appropriate modification of equation (3). But Heaviside's method of functional operators, though rigorous and elegant, is not, as a rule, appreciated by the ordinary student; and it is therefore desirable to have an alternative method of the same general applicability. The object of the present note is to show that simple energy considerations lead to an equation equivalent to (3), and that the result summarizes in a simple and convenient way the relationships existing between the circuit constants in the state of balance in all bridge methods of comparing inductances and capacities.

§ 2. If, in equation (1), v is initially zero and eventually reaches a steady value V , then integration with respect to the time yields

$$\int_0^\infty (v - Ri) dt = LI - rQ, \quad . \quad . \quad . \quad . \quad (4)$$

where Q and l are the final steady values of q and i

respectively. This equation is equivalent to

$$I \int_0^\infty (v - Ri) dt = 2(T - U), \quad . \quad . \quad . \quad (5)$$

or

$$IP = 2(T - U), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where U and T are the energies in the steady state, electric and magnetic respectively, and P is the total impulse, or generalized momentum generated in the circuit in the steady state. This result is here obtained for a specific circuit, but is much more generally applicable.

Putting $v = \text{const.} = E$, we obtain

$$\int_0^\infty E(i - I) dt = 2(U - T), \quad . \quad . \quad . \quad . \quad (7)$$

a theorem, enunciated and proved by Heaviside* in most general terms, connecting the amounts of work performed by a cell of constant e.m.f. in establishing a given final distribution of current with, or without, the storing of energy in the field.

§ 3. Now arrange a balance containing in each arm a coil in part shunting a condenser. Since no current traverses the galvanometer in the state of balance, its resistance may be taken to be zero without any loss of generality. The extra current in one direction through the galvanometer is $\frac{e_1 - e_2}{R_1 + R_2}$, while that in the opposite direction is $\frac{e_3 - e_4}{R_3 + R_4}$, where e is the impulsive e.m.f. generated in an arm; for the parts of the balance separated by the galvanometer are, in effect, independent of each other as far as internal actions are concerned. For balance these extra currents must be equal, or, on integration, the condition for zero integral extra-current becomes

$$\frac{P_1 - P_2}{R_1 + R_2} = \frac{P_3 - P_4}{R_3 + R_4}; \quad . \quad . \quad . \quad . \quad (8)$$

whence, in conjunction with (6),

$$\frac{T_1 - U_1}{R_2} - \frac{T_2 - U_2}{R_1} = \frac{T_3 - U_3}{R_4} - \frac{T_4 - U_4}{R_3}. \quad . \quad . \quad (9)$$

This energy equation also follows at once on applying equation (5) to each arm of the bridge in succession subject

* O. Heaviside, 'Electrical Papers,' i. p. 464; ii. p. 361.

to the balancing conditions,

$$i_1 = i_3; \quad i_2 = i_4. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$v_1 = v_2; \quad v_3 = v_4. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In the generalized bridge it conditions a first order balance, while in practical cases it uniquely determines a true balance, and, as the following examples show, the appropriate formula to be applied to any bridge method of comparison can be derived from inspection.

§ 4. I. *Comparison of Inductances.*

Maxwell's method * :—

$$(1) \quad U_1 = U_2 = U_3 = U_4 = 0; \quad T_1 = T_3 = 0.$$

$$\frac{T_2}{R_1} = \frac{T_4}{R_3}, \quad \therefore \frac{L_2}{L_4} = \frac{R_2}{R_4}.$$

$$(2) \quad U_1 = U_2 = U_3 = U_4 = 0; \quad T_3 = T_4 = 0.$$

$$\frac{T_1}{R_2} = \frac{T_2}{R_1}, \quad \therefore \frac{L_1}{L_2} = \frac{R_1}{R_2}.$$

II. *Comparison of Capacities.*

Bridge method :—

(1) Condensers open :

$$T_1 = T_2 = T_3 = T_4 = 0; \quad U_1 = U_3 = 0.$$

$$\frac{U_2}{R_1} = \frac{U_4}{R_3}, \quad \therefore \frac{C_2}{C_4} = \frac{R_3}{R_1}.$$

(2) Condensers in parallel with two adjacent arms of balanced bridge ; same conditions as (1).

(3) Condensers across parts (r_2 and r_4) only of the arms:

$$T_1 = T_2 = T_3 = T_4 = 0; \quad U_1 = U_3 = 0.$$

$$\frac{U_2}{R_1} = \frac{U_4}{R_3}, \quad \therefore \frac{C_2}{C_4} = \frac{R_1 r_4^2}{R_3 r_2^2}.$$

* Clerk Maxwell, 'Electricity and Magnetism' (3rd ed.) ii. § 757, p. 398.

III. Comparison of an Inductance with a Capacity.

Maxwell's method *:—

$$U_1 = U_2 = U_4 = 0; \quad T_1 = T_3 = T_4 = 0.$$

$$\frac{T_2}{R_1} = \frac{U_3}{R_4}, \quad \therefore \frac{L_2}{C_3} = R_2 R_3.$$

Rimington's modification †:—

$$\text{As before, } \frac{T_2}{R_1} = \frac{U_3}{R_4}, \quad \therefore \frac{L_2}{C_3} = \frac{R_2 r_3^2}{R_3}.$$

Pirani's method ‡:—

$$U_1 = U_2 = U_3 = 0; \quad T_1 = T_2 = T_3 = 0.$$

$$T_4 - U_4 = 0, \quad \therefore \frac{L_4}{C_4} = r_4^2.$$

This is a very interesting case. Three of the arms are non-inductive resistances, hence, for a balance, the impulsive effect of the fourth arm must vanish. By Heaviside's theorem (7) this happens when the energies are equal.

§ 5. Equation (9) is, as is to be expected, of the same form as the ordinary condition for steady balance with non-inductive resistances; for, if H represents the heat developed in any given time, we may put the condition $R_1 R_4 = R_2 R_3$ in the form

$$\frac{H_1}{R_2} - \frac{H_3}{R_4} = \frac{H_2}{R_1} - \frac{H_4}{R_3}, \quad \dots \dots \dots (12)$$

where, instead of energies stored, we now have energies dissipated.

The form is so simple that one naturally suspects the possibility of a more direct method of deducing it. It is, perhaps, suggestive that it represents dimensionally the equalization of mechanical momenta, thereby determining the distribution of energy in the field conditioned by the mechanical equilibrium of the current indicator; but, until more is known regarding the nature of the processes of storing and dissipating energy in electrical phenomena, its true dynamical interpretation must necessarily remain obscure.

* Clerk Maxwell, 'Electricity and Magnetism' (3rd. ed.) ii. § 778, p. 425.

† E. C. Rimington, Phil. Mag. July 1887.

‡ Cf. C. H. Lees, Phil. Mag. [6] xviii. p. 432 (1909). J. P. Kuenen, Phil. Mag. [6] xix. p. 439 (March 1910).

VI. *Internal Pressure and Latent Heat of Liquids.* By WM. C. McC. LEWIS, M.A., D.Sc., *Chemical Laboratory, University College, London* *.

IN the *Phil. Mag.* (xxiii. p. 955, 1912) Mr. Sukhodski has criticised an expression given by the writer for the internal pressure of a liquid. The expression referred to is

$$K - l = T \frac{\partial K}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K is the internal pressure and l was taken to mean the latent heat of vaporization of 1 c.c. of the liquid (Dupré).

I was aware that the further assumption, viz.

$$\frac{1}{K} \frac{\partial K}{\partial T} = \frac{1}{l} \frac{\partial l}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

could not hold over a wide range of temperature, being evidently incorrect at the critical temperature, at which point l is zero while K is still positive (and probably fairly large) as Mr. Sukhodski points out.

It may be mentioned that if l is taken to be the latent heat of expansion of the homogeneous phase (entirely liquid for example), that is, the heat which has to be added to the system while it expands isothermally by 1 c.c., such a quantity will not become zero at the critical temperature, but will have a positive value. By attaching this meaning to l , the physical significance of equation (1) would be of course considerably modified. Equation (2) might, under these circumstances, be fairly correct, but as there is no direct means of testing this, it may be dropped.

Whether we regard l as referring to the latent heat of vaporization of 1 c.c. or to the latent heat of expansion of the liquid itself, equation (1) would still be of little use for experimental purposes, owing to the presence of the term $\frac{\partial K}{\partial T}$. Recently, however, it has become possible to obtain a fairly accurate estimate of this quantity by a new method.*

In the *Phil. Mag.* (April and September 1912) Mr. H. Davies has put forward several very interesting applications of the Cailletet-Mathias law of the rectilinear diameter. One of these is an expression for the temperature coefficient of the internal pressure of a liquid which is found to be simply identical with the coefficient of expansion, viz.

$$\frac{1}{K} \frac{\partial K}{\partial t} = -\alpha.$$

* Communicated by the Author.

It has also been shown that K itself can be calculated, but as the basis of the method consists in applying an equation of the van der Waals' type, I do not think that it presents much advantage over the method of setting $K = \frac{a}{v^2}$ in van der Waals' equation itself. The temperature coefficient being, however, a much smaller quantity, is no doubt given by Davies' expression with a considerable degree of accuracy, the simplicity of the expression rendering it particularly useful.

Thus starting with equation (1)

$$K - l = T \frac{\partial K}{\partial T},$$

and substituting Davies' expression for $\frac{\partial K}{\partial T}$, one obtains finally

$$K = \frac{l}{1 + T\alpha},$$

this being identical with Davies' equation (24) (*l. c.*).

Davies himself has calculated the value of K in a few cases employing the above expression, in which l is taken as the latent heat of *vaporization* of unit volume of the liquid. The results obtained are given in the second column of the following table, the third column containing the values obtained by Davies' alternative method without introducing equation (1). The last column is the van der Waals' value*.

Substance.	K atmos.	K atmos.	$K = \frac{a}{v^2}$
Benzene	912	1102	1380
Toluene	1042	1188	1180.
Aniline	1315	1176	—
Cymene	686	661	—

The agreement between columns 2 and 3 is fairly good.

In the above l is taken to be the latent heat of vaporization of 1 c.c. of the liquid. It seems of interest to see what sort

* Calculated by Traube, *Zeitsch. Phys. Chem.* lxxviii. p. 293 (1909).

of values are obtained if one considers l to be the latent heat of expansion of the liquid itself. A simple expression for l having this signification may be obtained as follows.

For the heterogeneous as well as homogeneous system we have, on purely thermodynamic grounds,

$$l = T \frac{\partial p}{\partial T},$$

and on introducing the further expression

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T = -1,$$

which holds only for a homogeneous system (say the liquid form), one obtains

$$l = T \frac{\partial p}{\partial T} = \frac{-\frac{T}{v} \left(\frac{\partial v}{\partial T}\right)_p}{\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T} = -T \frac{\alpha}{\beta},$$

where α is the coefficient of thermal expansion and β the compressibility of the liquid.

In the following table are given some values of l thus calculated; the α and β data being taken from Landolt and Börnstein's tables.

Latent Heat of Expansion of non-associated
Liquids at 0° C.

Substance.	l atmos./cm. ² .	l cals./c.c.
Ethyl ether	2730	65
Chloroform	3700	88
Carbon tetrachloride	3332	79
Carbon disulphide	3822	91
Acetone	4336	103
Mercury.....	13280	316
Cymene	3370	80
Xylene	3547	84
Toluene	3644	86
Benzene	3430	82
Ethyl acetate.....	3305	78

It will be observed that in general the latent heat of expansion of the liquid is of quite the same order of magnitude as its latent heat of vaporization. In the case of associated

liquids, the differences are greater owing to the work involved in breaking down the complexes almost completely on vaporization. The following table allows of a rough comparison.

Substance.	l atmos./cm. ² .	Temperature 0° C.	
		l cal./c.c.	Lvaporization of 1 gram.
Methyl alcohol	4095	97	290
Ethyl alcohol	3453	82	225
<i>n</i> Propyl alcohol	2348	55	165
Isopropyl alcohol.....	3000	71	161

It is rather remarkable that the values of the heat of vaporization and of expansion should be as alike as they are in the case of normal liquids. One would have expected, I think, that the numerical values would have been of a different order of magnitude. In the process of vaporization the molecules are pulled so far apart that they must be nearly independent of one another compared with their relation in the liquid. In expanding a liquid at constant temperature—a process the results of which are realized in experiments in which a completely filled and closed vessel is cooled without corresponding contraction of the liquid—the relative separation of the molecules from one another, even in the expanded state, must be small compared with that of the vapour molecules. The fact that both heat effects are nearly the same suggests that the range of attraction must be extremely small, of the same order as the mean distance apart of the molecules of the liquid in its normal state (about 10^{-8} cm.).

With the values thus obtained for l (latent heat of expansion) we can calculate the values of K by means of the expression

$$K = \frac{l}{1 + \alpha T},$$

the results being as follows :—

Internal Pressure of Liquids at 0° C.

Substance.	K in atmos.
Ether	1932
Chloroform	2780
Carbon tetrachloride	2518
Carbon disulphide	2917
Acetone	3188
Mercury.....	12645
Cymene	2718
Xylene	2815
Toluene	2847
Benzene.....	2639
Ethyl acetate	2466

It will be seen that the values of K obtained by this method are approximately double of those previously given. This in itself is not sufficient to discriminate between the two possible meanings to be attached to l . In an associated liquid l —in either of its significations—may be no measure of K at all.

It is still an open question, therefore, whether in calculating internal pressures from latent heats, one should employ the latent heat of vaporization of 1 c.c. of the liquid or the latent heat of expansion of the liquid itself.

VII. *The Recombination of Ions produced by Röntgen Rays.*
By S. J. PLIMPTON, *Ph.D.*, Yale University*.

WHEN a gas is exposed to the continued action of Röntgen rays the number of ions contained in a unit volume of the gas does not go on increasing indefinitely because of the electrostatic field associated with the ions. A continuous diffusion takes place from the region of maximum ionization, and in addition oppositely charged ions recombine under their attractive forces. The process of diffusion is a relatively slow one, and with properly designed apparatus may be disregarded in measuring the changes in ionization due to recombination.

According to the accepted theory of ionization in gases, the rate of change of the number of ions of either sign per unit volume is proportional to the square of this number; that is,

$$\frac{dn}{dt} = -\alpha n^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α is a constant known as the coefficient of recombination and is independent of n .

* Communicated by the Author.

This law of recombination has been shown by several experimenters to hold good to a high degree of approximation.

In the early experiments of Rutherford* and of McClung† the gas was confined in a closed metal chamber provided with an aluminium window for admitting the rays. Inside the vessel were two parallel metal plates, one of which was connected with a source of potential and the other with an electrometer.

Under the action of the rays the gas between the electrodes was ionized until a steady state was attained, when the ionization was balanced by diffusion and recombination; the rays were then switched off, and the charge remaining in the gas at definite times after the cessation of the rays was then determined. A pendulum interrupter was provided, so that this time-interval could be varied at will. In this manner corresponding values of n and t were obtained, and were found to agree satisfactorily with the relation

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is obtained immediately by integrating equation (1), n_0 being the number of ions per cubic centimetre present in the gas when the steady state has been established, and n being the corresponding number after the ions have been allowed to recombine for a time t .

Another method was also employed by McClung‡ to demonstrate the validity of the law of recombination, and was used by him to determine an absolute value of the coefficient α . The saturation current was measured while the rays were acting, a strong electric field being maintained between the electrodes. From this observation the number of ions (q) produced per cubic centimetre per second in the gas was determined in arbitrary units. The electric field was then withdrawn, and the rays were allowed to act until a steady state of ionization was produced; this is expressed by the equation

$$q = \alpha n^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n denotes the number of ions of either sign present per cubic centimetre in the gas when the steady state has been reached. The rays were then cut off and a strong

* Rutherford, Phil. Mag. xliv. p. 422 (1897).

† McClung, Phil. Mag. xiii. p. 283 (1902).

‡ *Loc. cit.*

electric field immediately applied sufficient to drive over to the electrodes all the ions remaining in the gas.

By measuring the charge given to the electrode, n was determined. The determination of both q and n sufficed to afford an absolute estimation of α .

Rutherford* and Townsend† made use of another method for verifying the law of recombination. The saturation currents were measured at different parts of a tube through which ionized air was streaming. These currents give the values of n at the place of observation; and if the rate of flow of the air is determined, and the distance from the region where the ions are formed is known, the series of values of n corresponding to different time-intervals can be plotted. This method can be employed only when the gas used is available in large quantities.

Langevin‡ has shown that the coefficient of recombination α is capable of being expressed in the following form:

$$\frac{\alpha}{e} = 4\pi(k_1 + k_2)\epsilon,$$

where e denotes the charge on the ions, k_1 and k_2 the ionic mobilities, *i. e.* the velocities with which the positive and negative ions respectively move under unit electrostatic field, and ϵ is a number which is less than unity. According to the theory of Langevin, ϵ represents the ratio of the number of collisions between oppositely charged ions which result in recombination to the total number of collisions: in this theory it is assumed that the ions move under their mutual attractions, following the same law and with the same mobilities as if they moved under the influence of an externally impressed field. The following method was devised by Langevin for the experimental determination of ϵ . The gas between the two parallel plate electrodes was ionized by a single flash of very short duration from a Röntgen-ray bulb; the ions are regarded as being formed uniformly in layers parallel to the electrodes, although the density of ionization may vary from one layer to another. The charge communicated to the electrodes for electric fields of different intensity is measured by an electrometer; the electric field between the plates is in general chosen very small, so that appreciable recombination may take place during the passage of the ions through the gas. The

* *Loc. cit.*

† Townsend, *Phil. Trans.* 1899, A, p. 157.

‡ Langevin, *Ann. de Chim. et de Phys.* xxviii. p. 289 (1903).

charge Q brought over by a field X is given by the formula

$$Q = \frac{X}{4\pi\epsilon} \log \left(1 + \frac{4\pi Q_0 \epsilon}{X} \right),$$

where Q_0 is the charge corresponding to a field of sufficient intensity to prevent appreciable recombination.

Applying this method, and making use of the previously determined values of k_1 and k_2 , Langevin found that the values of α showed a considerable falling off when the air-pressure was reduced below one atmosphere; whereas the experimental results obtained by McClung*, who used the method described above, had assigned a value to α which was practically independent of the pressure below one atmosphere. This discrepancy was almost certainly due to the abnormally large corpuscular radiation which proceeded from the electrodes in McClung's experiment when the Röntgen rays were acting.

It is convenient to indicate here briefly three main sources of error which are liable to occur in the course of experimental work on this subject :

- (1) Diffusion of the ions.
- (2) Presence of corpuscular radiation proceeding from the electrodes.

This gives an abnormally high density of ionization near the plates, making the value of α greater than for a uniform distribution. The error becomes greater as the pressure is reduced.

- (3) Variations in the intensity and penetration of the Röntgen rays due to continued working of the bulb.

The method adopted in the present series of experiments reduces these sources of error to a minimum. It consists essentially in ionizing the gas between two parallel plate electrodes as uniformly as possible by means of a single flash from a Röntgen-ray bulb, allowing the ions thus produced to recombine in the absence of any external field for small intervals of time which can be regulated and determined mechanically, and by the sudden application of a strong electric field driving over to the electrodes those ions which remain in the gas. In this way we obtain a series of values of n corresponding to different values of t , and values

* *Loc. cit.*

of α are then determined for different conditions of gas-pressure by means of a variation of equation (2) which is indicated below.

This method is believed to have the following advantages :

- (1) By using radiation of smaller intensity and by shortening the time-intervals, the effect of diffusion is greatly reduced.
- (2) By restricting the beam of rays between the electrodes diffusion is further reduced and corpuscular radiation practically removed.
- (3) By the use of single flashes of X-rays the difficulty of maintaining uniformity in the rays is greatly lessened.
- (4) Since the duration of the flash is very brief, it is possible to study the initial stages of recombination.

In connexion with (4) it is worthy of mention that in previous investigations no information has been afforded with regard to the initial stages of recombination. In a steady state of ionization, ions of practically all ages are present, diffusion has become very appreciable except in the case of the ions of recent formation, and the ionization is necessarily very intense, so that, on the whole, a practically uniform distribution of the ions prevails at the instant when the rays are cut off.

With single flashes of Röntgen rays the case is different. At the instant when the flash has ceased the ions are approximately all of the same age, and diffusion has been practically inoperative ; so that any peculiarity in the initial distribution of the ions is capable of being detected by experimental observation. Such an initial effect has made itself manifest in the present series of experiments, and will be described later.

Preparation of Gases and Vapours.

The carbon dioxide gas used in these experiments was obtained in the usual way by the action of hydrochloric acid on marble in a Kipp generator. The sulphur dioxide was taken from a cylinder of the compressed gas. The vapours were evaporated in each case from the liquid as supplied by the chemist. In all cases, before admitting the gas or vapour, the apparatus was pumped out to a few millimetres of mercury. The substance to be tested was then let in until the greatest allowable pressure was reached, and then

pumped out as before. This process was repeated at least three times.

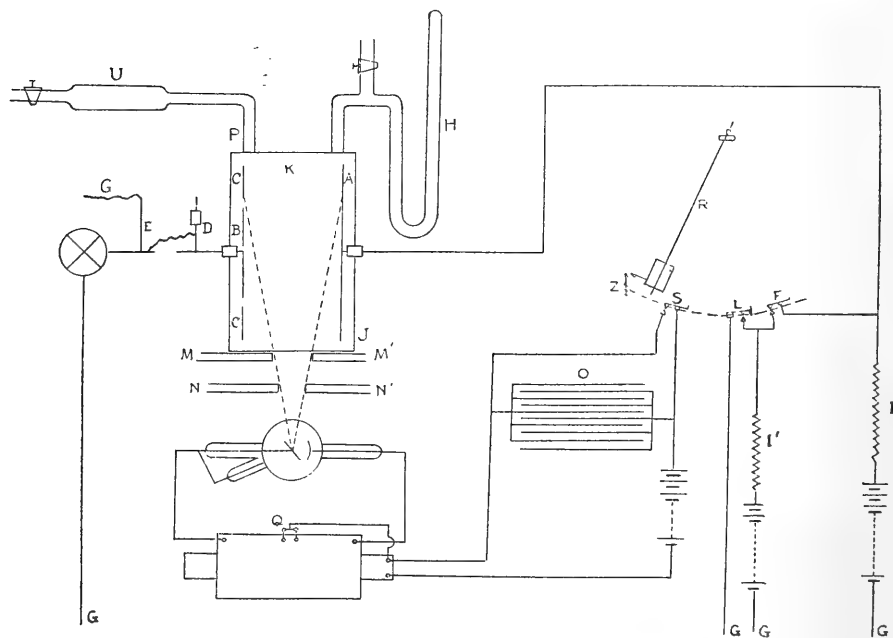
Great care was taken in every case to make the gas or vapour dust-free, by passing it through several inches of glass-wool and then allowing it to settle for several hours.

The gases were dried by passing slowly through a tube containing phosphorus pentoxide, and the vapours were bubbled through sulphuric acid when necessary and were always passed through a calcium-chloride drying-tube.

Description of Apparatus.

The general arrangement of apparatus is shown in fig. 1. The ionization chamber K is lined with aluminium and provided with two parallel plate electrodes A and B of aluminium, the latter being surrounded by a guard-ring C

Fig. 1.



which is connected with the walls of the chamber. The insulated electrode B may be connected with an electrometer by means of a key D. The beam of X-rays is restricted by adjustable lead screens, MM' and NN', so that it does not fall on the electrodes. A pendulum R is used for automatically giving the flash of X-rays by opening the key S and after a definite interval of time, applying a potential to the electrode A by opening the switch F, which may be placed at any position along the path of the pendulum.

In order to obtain X-ray flashes of sufficient intensity it

was sometimes necessary to interrupt a current of 25 amperes at the key S. Although a large adjustable condenser was used for suppressing the spark, considerable difficulty was experienced at first in getting uniform conditions in the induction-coil at the instant when the break occurred in the primary circuit. This difficulty was overcome by the use of a specially constructed key for breaking the large primary current.

In designing keys for purposes of this sort, attention has usually been centered on getting a rapid motion at the instant of break. It was found possible to use very moderate motion provided a firm uniform pressure was maintained between the contacts up to the instant of breaking and separation of the contacts then effected without vibration or chattering. The most successful break was constructed as follows :—

A rigid bar armature of T section was mounted in conical bearings at one end and carried a platinum contact at the other. The complementary platinum contact was mounted rigidly on the same heavy case with the bearing. The key was closed firmly by a permanent horse-shoe magnet. The bearings were kept in such adjustment that the magnet could just overcome the friction at a particular position. The bearing screws were locked in place by another pair of set screws. A looseness in these bearings which was not sensible to the touch, would vary the electrometer readings from five to ten per cent.

When this key was used with a current strong enough to properly excite the bulb, the flashes of X-rays produced almost perfectly uniform readings of the electrometer.

The apparatus as a whole is operated in the following manner :—

The pendulum R (referring again to fig. 1) is fastened by a catch, Z, at a position of maximum displacement from the vertical. The keys are then all closed, bringing the electrodes A and B to potential zero and closing the primary of the induction-coil which operates the X-rays tube. The key D is then opened and the pendulum quickly released from the catch Z. The pendulum automatically opens the key S, giving rise to a flash of rays which ionizes the gas between the electrodes in the chamber K. Since both electrodes are at zero potential, the ions continue to recombine until the pendulum has opened the key F, when a potential is applied to the electrode A, which drives over the ions of one sign remaining between the electrodes to the plate B. The earthing key is now opened and the key D

closed, so that the charge received on B may be measured by the electrometer.

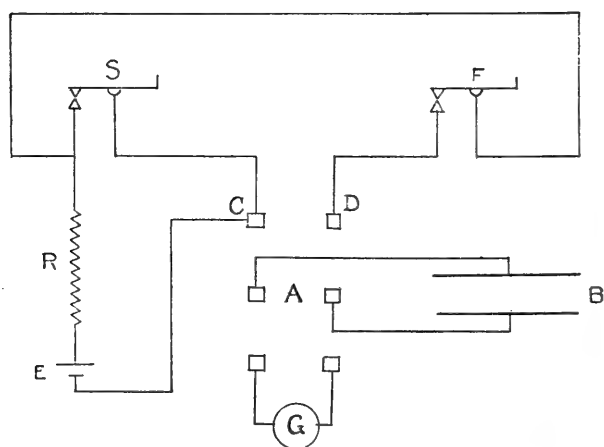
By taking a series of readings in this way with the key at different positions along the path of the pendulum, the relative numbers of ions remaining in the gas after definite intervals of time was obtained directly. Throughout the experiment, readings were frequently repeated with the key F in such a position that the field was applied before the flash occurred in order to detect any lack of uniformity in the action of the apparatus.

Calibration of Pendulum.

In order to ascertain the time intervals during which the ions were allowed to re-combine when the switch which applied the field to the gas was placed at various positions along the path of the pendulum, the following method was used:—

The switches S and F which applied the X-ray flash and the field respectively, were connected as shown in fig. 2.

Fig. 2.



Both switches were initially closed and the double pole-switch *A* was closed at *CD*, putting a standard condenser *B* in series with the switches *S* and *F*. The pendulum was then released, opening the switch *S*, and thus permitting a storage-cell *E* to charge the condenser through a known high resistance, *R*. The charging continued until the pendulum opened the switch *F* which breaks the charging circuit. The condenser was then allowed to discharge through a galvanometer by closing the double throw-switch *A* in the opposite direction.

The time required by the pendulum to swing from the

switch S to the switch F was then computed by means of the formula

$$t = - \frac{CR \log \left(1 - \frac{q}{CE} \right)}{\log e}$$

where

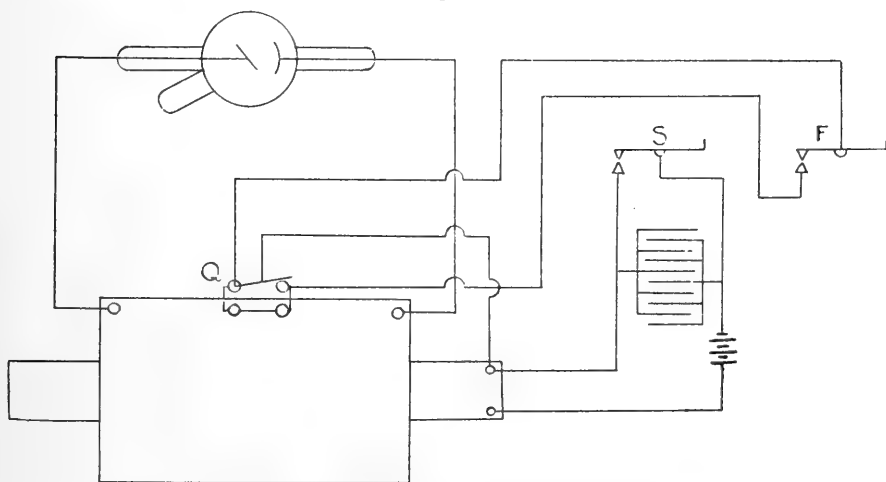
- C=capacity of condenser ;
- q=charge received by condenser as measured by a ballistic galvanometer ;
- E=potential of battery ;
- e=base of Naperian logarithms ;
- R=resistance in charging circuit.

The values of t obtained in this way were also checked by means of a chronograph.

The duration of the flash was obtained as follows :—

In fig. 3 is shown the induction-coil, X-ray tube, and keys S and F, as in fig. 1, except that the key F is disconnected

Fig. 3.



entirely from the potential battery system and put in parallel with a spark-gap Q, which is in series with the secondary of the induction-coil and X-rays tube. Q is a brass connector between the two halves of the secondary coil and connected also to the primary coil for protection to insulation. This brass connector was removed from one binding screw to a distance of 0.5 millimetre.

Since the connector Q is in series with the X-ray tube, a spark will occur at Q simultaneously with the flash in the tube unless the contacts of the key F are closed or so nearly closed that the discharge takes place at F instead of at Q.

If when the discharge occurs the key F is closed or opened to a greater distance, no spark will be seen at F. A spark is seen at F only when the key F is so situated in the path of the pendulum with regard to the key S that the contacts of the key F are separated by a distance less than 0.5 millimetre and greater than 0 millimetre during the flash of X-rays. If it opens near the beginning of the flash, only a small spark will appear since the discharge potential has not then attained its maximum, so that when the key has opened only a short distance, the resistance becomes too great and the spark ceases. On the other hand, if the key F begins to open so near the end of the duration of the discharge that when its contacts have separated only a very small distance, the discharge has ceased, then again only a small spark will be observed. By placing the key F at different positions relative to S, it was found that the discharge in the X-ray tube began practically simultaneously with the opening of the key S, increased to maximum and then fell to zero, the total duration of the flash being 0.0035 second. The limiting position of the key F at which the discharge ceased could be determined within a distance corresponding to 0.0001 second.

The calibration of the pendulum, as determined by the condenser method described above, was corrected for the time occupied by the flash by subtracting 0.0015 second from each value. It was necessary to know the total duration of the flash accurately also for a special experiment to be described.

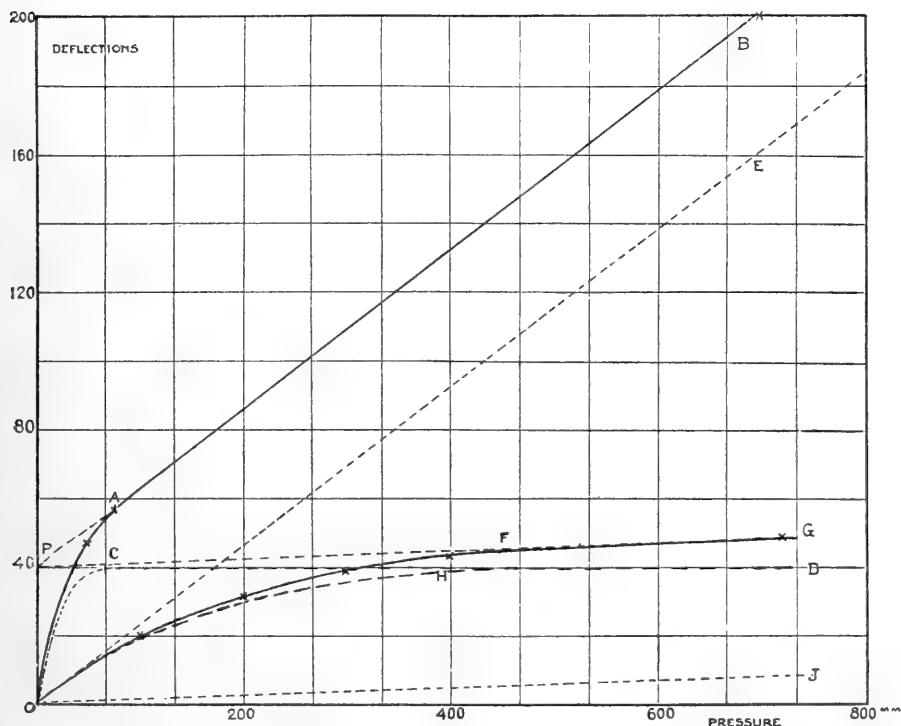
Preliminary Experiment.

In order to ascertain the effect of secondary and corpuscular radiation from the electrodes A and B of fig. 1, the lead screens MM' and NN' were removed, allowing the Röntgen rays to fall on A and B as well as in the space between them. The plate A was charged continuously to 160 volts. Air was introduced into the chamber K and a series of deflexions noted for different pressures using single flashes of X-rays of constant intensity. The air was then pumped out and similar readings taken for hydrogen. The results are plotted in fig. 4, where the abscissæ represent pressure in millimetres of mercury, and the ordinates electrometer readings in scale-divisions. It will be seen that each curve beginning at the left has a marked curvature but eventually becomes a straight line, and that these two

straight lines if produced will intersect the vertical axis in a common point.

From this it is concluded that the air curve OAB is the sum of two curves OCD and OE, where OE is parallel to PB and OCD approaches a line through PD parallel to the pressure axis. In a similar way the curve OFG is the

Fig. 4.



sum of the curves OJ parallel to PG and OHD, which also approaches PD. Curves OE and OJ are due to ionization produced by the Röntgen rays in the gas, and the curves OCD and OHD are due mainly to corpuscular radiation from the plates which is completely absorbed at a definite pressure. After replacing the lead screens MM' and NN' so as to confine the X-rays between the electrodes A and B, the series of readings was repeated and found to give the straight lines OE and OJ. Throughout the rest of the investigation the rays were restricted between the electrodes so as to avoid corpuscular radiation.

Experimental Results.

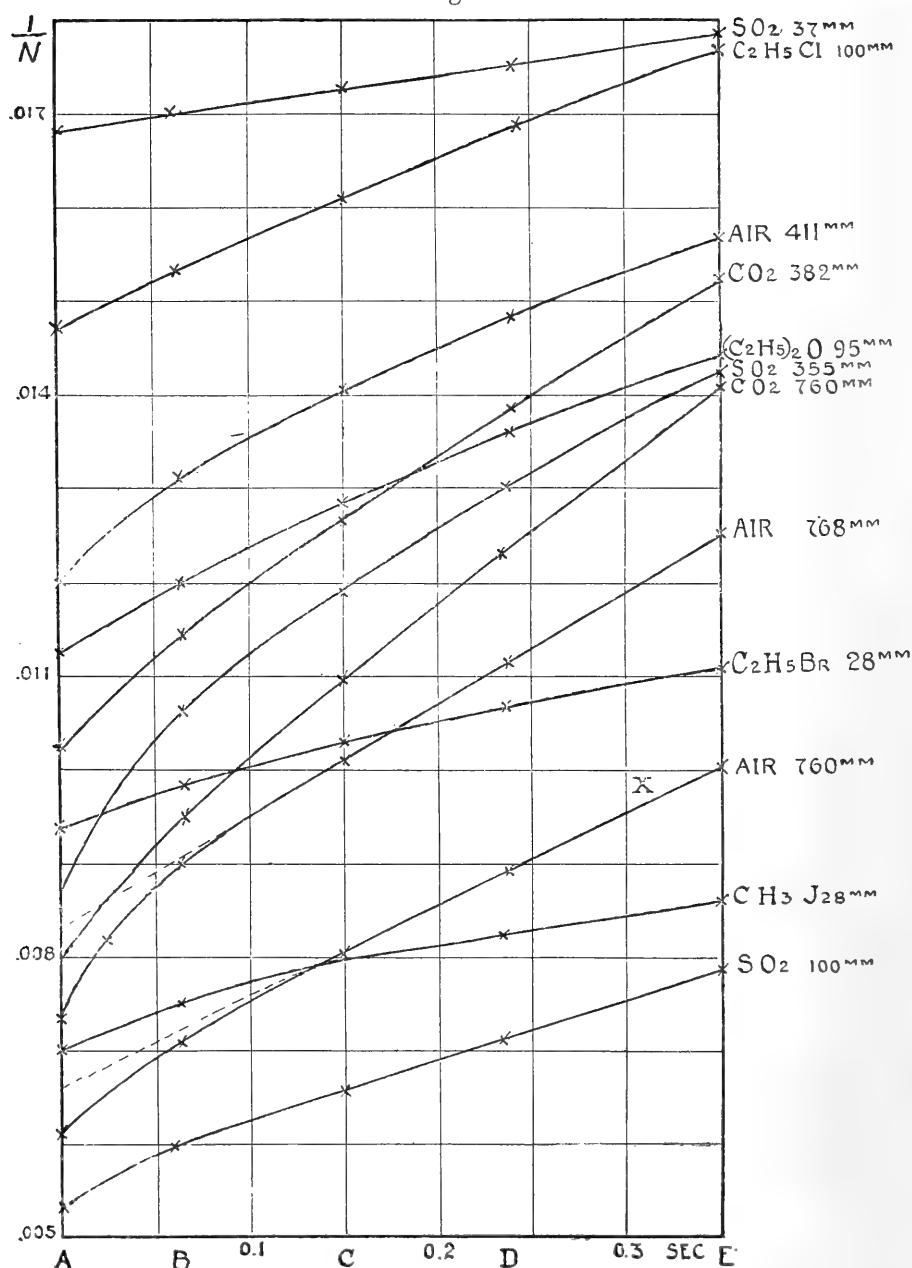
There is reason to believe that certain peculiar conditions are present in the initial stages of recombination. On this account it was thought advisable not to use formula (2),

which involves the number of ions initially present, but to modify the formula in the following manner :—

$$\alpha = \frac{d\left(\frac{1}{n}\right)}{dt}.$$

In this way the determinations of α are rendered independent of the initial conditions.

Fig. 5.



In fig. 5 the reciprocals of the deflexions are plotted for the various time intervals. The slope of these curves should be proportional to α .

For short intervals of time, however, there is a marked curvature indicating that α is relatively large for the initial stages of recombination, but diminishes, becoming in most cases nearly constant for t greater than about one-third of a second. The curve for air is nearly straight at the end. In the case of carbon dioxide the curve is surprisingly steep at the end, indicating a very large value of α as compared with air, and one would suppose that it must ultimately become more nearly horizontal. It was therefore desirable to further extend the curve for air and carbon dioxide. In order to do this the pendulum was arranged to operate the keys on the return stroke. A key operated by hand was put in parallel with the key which applied the field and held down by hand until the pendulum was approaching the latter on the return stroke. The pendulum key was then quickly closed and the hand key released.

In this way it was possible to extend the air and carbon-dioxide curves to $t=1.06$ seconds. The air curve was found to bend very little more, but the carbon-dioxide curve became finally only a little steeper than the air curve.

Discussion of Results.

The high initial values of α and the subsequent falling off of its value, first rapidly and then more slowly, may be explained as follows:—

If we suppose the action of Röntgen rays is the liberation of rapidly moving electrons from the gas molecules, which in turn liberate slow moving electrons from molecules in their path, thus ionizing them, one would expect the ions to be segregated in the path of the rapidly moving electrons as shown by C. T. R. Wilson's cloud experiment. This would make the value of α greater than for a uniform distribution of ionization and as a result of diffusion the value of α would slowly diminish. This would probably not account for the very high initial values of α . It has been found* that the β particle produces on the average only about 67 ions per centimetre of path. As a rule, therefore, there must be a very large number of molecules between them, and the distance between the two ions constituting an initial pair would be in general less than the average distance between the ions strewn along the path of the β particle.

If a similar condition exists in the case of ionization by the electrons expelled under the action of X-rays, there would be a relatively great probability of collision between the positive

* Geiger and Kovarik, *Phil. Mag.* (6) xxii. p. 604 (1911).

and negative ions which are close together giving the large initial values of α .

Comparing the curves of fig 5 for air and carbon dioxide at 760 millimetres, it will be seen that for both gases the high initial values of α are indicated by the steepness of the curves for short intervals of time, but that the air curve becomes linear at about one-third of a second, while for carbon dioxide the curve is very steep at this point, suggesting that it has probably not reached its final value. When the two curves were extended further, it was found, as stated above, that the air curve remained almost linear but that the carbon-dioxide curve became almost parallel with the air curve after about two-thirds of a second. This result is in accord with the supposition that the variations in α are due to a non-uniform distribution of the ions produced by Röntgen rays. Since carbon-dioxide ions diffuse only about one-half as quickly as the ions of air, the final effectively uniform distribution in which α becomes constant would be reached in carbon dioxide after about twice the time required in the case of air.

The Absolute Value of α .

In order to ascertain the absolute value of α at any time, it is necessary to know the number of ions present in the gas per unit volume. If the ions are distributed non-uniformly as indicated by these experiments, the rate of recombination at any instant would not be uniform throughout the volume but would vary according to the density of the ions. If the distribution of the ions were known so that an average density for the total volume of the gas ionized could be computed by integration, it might be proved that α does not vary with the time. Since this datum is not available, the true absolute value of α cannot be computed. In the following table, the effect of a non-uniform distribution of the ions is disregarded and α is computed as if the ions were distributed uniformly by using the equation,

$$\frac{1}{n_2} - \frac{1}{n_1} = \alpha(t_2 - t_1).$$

It is obvious that the values of n_2 and n_1 obtained in this way will be too small, since when the ions are segregated they do not properly occupy the entire volume between the electrodes, but only a small part of that volume. The absolute values of

α given in this way are therefore much too large, but diminish with the time during which the ions are allowed to recombine and diffuse, since the tendency of diffusion is toward a uniform distribution.

The values given were obtained as follows :—

If

q = the charge which causes electrometer deflexion of 1 mm.;

e = the charge carried by the electron;

D = the electrometer deflexions;

n = the number of ions per unit volume;

V = the total volume of the gas ionized;

then

$$qD = nVe \quad \text{or} \quad \frac{1}{n} = \frac{Ve}{qD},$$

therefore by equation (2)

$$\alpha = \frac{\frac{1}{n_2} - \frac{1}{n_1}}{t_2 - t_1} = \frac{Ve}{q(t_2 - t_1)} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) = \frac{4.07 \times 10^5}{(t_2 - t_1)} \left(\frac{1}{D_2} - \frac{1}{D_1} \right).$$

In computing the volume V a correction was made for the distortion of the field between the electrodes due to the charge induced by the field on the insulated electrodes. This was obtained by first applying the usual field while the electrometer electrode was earthed. The earthing key was then opened and a flash of X-rays applied giving a reading of the electrometer D' .

The process was then repeated in the same way except that the electrometer electrode was insulated before the field was applied, thus receiving an induced charge which distorts the field. In this instance, therefore, a smaller reading D'' was obtained owing to the distortion of the field. The corrected value of V was obtained by measuring the volume subtended between the electrodes and multiplying this by the ratio $\frac{D''}{D'}$.

The following table gives the average values of $\frac{\alpha}{e}$ (where e is the charge carried by the electron) between the successive pairs of points A, B, C, D, E of fig. 5.

In the case of the gases air and carbon dioxide, the curves were extended to a point F where $t = 1.06$ seconds.

Absolute Values of $\frac{\alpha}{e}$.

Gas or Vapour.	Pressure.	A - B.	B - C.	C - D.	D - E.	E - F.
Air	768	11540	6100	4680	4600	3960
„	411	7150	4580	3280	2820	
CO ₂	760	10000	7100	6700	6500	4880
„	382	7500	6100	5610	5310	
SO ₂	355	12500	7640	5150	4600	
„	100	4400	3560	2900	2830	
„	37	1560	1270	1160	1060	
C ₂ H ₅ I	28	3440	2540	1240	1170	
C ₂ H ₅ Cl ...	100	4100	4070	2870	2830	
C ₂ H ₅ Br ...	28	2380	2200	1850	1440	
(C ₂ H ₅) ₂ O...	95	4400	4070	3700	3180	

Effect of a Field on the Ionization.

In order to ascertain the effect of an impressed field upon the ionization, a potential of sixteen volts was applied to the gas during the flash of X-rays and removed immediately after the cessation of the flash, the recombination then being measured in the usual way.

The result is shown in curve X of fig. 5 for the case of air at 760 millimetres pressure. Comparing this with the corresponding curve for air without the application of this field during the flash, it will be seen that the final slope is not changed noticeably but that the initial slope is lessened. This result is in accord with the explanation of initial recombination given above. The positive and negative ions in the initial pairs would be separated more widely by the field and the probabilities of collisions between them would be reduced, giving a lower value of α .

Conclusions.

(1) The recombination of ions takes place approximately in accordance with the law

$$\frac{dn}{dt} = -\alpha n^2,$$

provided that sufficient time has elapsed to enable an effectively uniform distribution of the ions to be established in the gas.

(2) When α is determined by considering a certain volume of ionized gas as a whole without regard to the distribution of the ions, α as given in the above expression is not a constant but has an initial maximum value, and approaches its final constant value at first rapidly and then more slowly.

(3) An explanation of this effect is suggested, based on the assumption of a non-uniform distribution of the ionization produced by Röntgen rays, the final values of α corresponding to an effectively uniform distribution.

(4) The value of α is shown to fall off as the pressure of the gas is reduced.

I wish to express my gratitude to Prof. E. M. Wellisch for suggesting these experiments, and for his very helpful interest throughout the work.

Sloane Laboratory,
Yale University.
August, 1912.

VIII. *The Stability of Flow of an Incompressible Viscous Fluid.* By Professor A. H. GIBSON, D.Sc., University College, Dundee *.

AS a result of experiment Osborne Reynolds † concluded that the conditions tending to stability of flow, *i. e.* to stream-line as opposed to sinuous flow, of an incompressible viscous fluid are :—

- (1) Free (exposed to air) surfaces.
- (2) Converging boundaries.
- (3) Curvilinear motion with the velocity greatest at the outside of the curve.
- (4) An increase in viscosity.
- (5) A diminution in density.

From an examination of the equations of motion he also showed ‡ that conditions (4) and (5) might be predicted from theoretical considerations.

As regards conclusion (3), recent experiments by the author § indicate that for increased stability in curvilinear motion the greatest velocity should be at the inside, not at the outside of the curve, and the object of the present paper is to point out that this, as well as the truth of conclusions (1) and (2), might also be inferred from the general equations of motion.

* Communicated by the Author.

† Proc. Royal Institution of Great Britain, 1884.

‡ Phil. Trans. 1883.

§ Memoirs Manchester Lit. and Phil. Soc. vol. lv. (1910-11), ii.

For such a fluid, subject to no external forces, these equations may be written

$$\left. \begin{aligned} \rho \frac{du}{dt} &= - \left\{ \frac{d}{dx} (p_{xx} + \rho uu) + \frac{d}{dy} (p_{yx} + \rho uv) + \frac{d}{dz} (p_{zx} + \rho uw) \right\} \\ \rho \frac{dv}{dt} &= - \left\{ \frac{d}{dx} (p_{xy} + \rho vu) + \frac{d}{dy} (p_{yy} + \rho vv) + \frac{d}{dz} (p_{zy} + \rho vw) \right\} \\ \rho \frac{dw}{dt} &= - \left\{ \frac{d}{dx} (p_{xz} + \rho wu) + \frac{d}{dy} (p_{yz} + \rho wv) + \frac{d}{dz} (p_{zz} + \rho ww) \right\} \end{aligned} \right\} (1)$$

and
$$\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} = 0. \quad . \quad . \quad . \quad . \quad (2)$$

Multiplying respectively by u , v , w , integrating, adding, and writing

$$E = \frac{\rho}{2} (u^2 + v^2 + w^2)$$

the rate of increase of kinetic energy per unit volume is given by

$$\begin{aligned} \left(\frac{d}{dt} + u \frac{d}{dx} + v \frac{d}{dy} + w \frac{d}{dz} \right) E = & \\ & - \left\{ \begin{aligned} & \frac{d}{dx} (up_{xx}) + \frac{d}{dy} (up_{yx}) + \frac{d}{dz} (up_{zx}) \\ & + \frac{d}{dx} (vp_{xy}) + \frac{d}{dy} (vp_{yy}) + \frac{d}{dz} (vp_{zy}) \\ & + \frac{d}{dx} (wp_{xz}) + \frac{d}{dy} (wp_{yz}) + \frac{d}{dz} (wp_{zz}) \end{aligned} \right\} \\ & + \left\{ \begin{aligned} & p_{xx} \frac{du}{dx} + p_{yx} \frac{du}{dy} + p_{zx} \frac{du}{dz} \\ & + p_{xy} \frac{dv}{dx} + p_{yy} \frac{dv}{dy} + p_{zy} \frac{dv}{dz} \\ & + p_{xz} \frac{dw}{dx} + p_{yz} \frac{dw}{dy} + p_{zz} \frac{dw}{dz} \end{aligned} \right\} . \quad . \quad (3) \end{aligned}$$

The first term on the right of this equation represents the rate at which work is being done by the surrounding fluid per unit of volume, so that, for conservation of energy, as pointed out by Stokes * the second term on the right must

* Cambridge Phil. Trans. vol. ix. p. 57.

equal the rate of conversion of energy of motion into heat energy, or *vice versâ*.

If u, v, w in these equations denote the component velocities at a given point in the fluid, and if $\bar{u}, \bar{v}, \bar{w}$ represent the velocities of the instantaneous centre of gravity of the element of fluid surrounding this point, while u', v', w' represent the velocities relative to this centre of gravity, Reynolds has pointed out* that two equations of energy may be obtained, one dealing with the mean motions $\bar{u}, \bar{v}, \bar{w}$, and the other with the relative motions u', v', w' , and from a consideration of these equations has shown that the limit of stability of motion is attained when

$$\begin{aligned}
 & -\rho \iiint \left\{ \begin{aligned} & u'u' \frac{d\bar{u}}{dx} + u'v' \frac{d\bar{u}}{dy} + u'w' \frac{d\bar{u}}{dz} \\ & + v'u' \frac{d\bar{v}}{dx} + v'v' \frac{d\bar{v}}{dy} + v'w' \frac{d\bar{v}}{dz} \\ & + w'u' \frac{d\bar{w}}{dx} + w'v' \frac{d\bar{w}}{dy} + w'w' \frac{d\bar{w}}{dz} \end{aligned} \right\} dx \cdot dy \cdot dz, \\
 & = \mu \iiint \left\{ \begin{aligned} & 2 \left\{ \left(\frac{du'}{dx} \right)^2 + \left(\frac{dv'}{dy} \right)^2 + \left(\frac{dw'}{dz} \right)^2 \right\} \\ & + \left(\frac{dw'}{dy} + \frac{dv'}{dx} \right)^2 + \left(\frac{du'}{dz} + \frac{dw'}{dx} \right)^2 \\ & + \left(\frac{dv'}{dx} + \frac{du'}{dy} \right)^2 \end{aligned} \right\} dx \cdot dy \cdot dz. \quad (4)
 \end{aligned}$$

The left-hand side of this equation represents the conversion of energy of mean motion into energy of relative motion, while the right-hand side represents the conversion of the energy of relative motion into heat. So long as the first of these terms is less than the second, the motion as a whole is steady, while if the second is the smaller, the motion is essentially unstable, and eddies are formed.

By integrating equation (4) it may be shown † that in the case of flow through a uniform circular tube, the condition for stability is $\frac{VL\rho}{\mu} < \kappa$ where κ is a definite numerical constant.

An examination of the equation, however, enables further general conclusions to be drawn as to the effect of any variation from a state of rectilinear motion, on the stability

* Phil. Trans. 1895.

† Scientific Papers, "Reynolds," vol. ii. p. 561. Also Phil. Trans. *ibid*.

of flow. Evidently any factor which tends to diminish the relative magnitude of the left-hand side of the equation tends to reduce the tendency to eddy formation and to increase the stability of flow and *vice versa*. Thus, as is well known, an increase in μ or a diminution in ρ tends to increased stability.

Effect of Free Boundaries.—With “free” as opposed to “solid” boundaries, the boundary velocities are increased and, assuming flow to take place in the direction of increasing x , the magnitudes of $\frac{d\bar{u}}{dy}$ and of $\frac{d\bar{u}}{dz}$ are diminished. Since these are negative and since the quantity in brackets on the left-hand side of equation (4) is essentially negative, this tends to diminish this term and hence to increase the stability of flow.

Effect of Converging Boundaries.—The same effect may be seen to follow the introduction of converging as opposed to parallel boundaries, or indeed any convergence of stream lines accompanying a change from pressure to kinetic energy. In such a case $\frac{d\bar{u}}{dx}$, $\frac{d\bar{v}}{dy}$, and $\frac{d\bar{w}}{dz}$ instead of being zero become positive and thus diminish the absolute (negative) value of the term in brackets. Conversely, a retardation in the direction of flow, such as is produced by diverging boundaries, diminishes the stability of flow.

Effect of Curvature of the Path.—If, in curvilinear motion, the direction of x be taken as tangential to the path at a given point and if $\frac{dx}{dt}$ and $\frac{dy}{dt}$ are positive, the value of $\frac{d\bar{u}}{dy}$ is greater if the velocity is greatest at the outside of the curve, than it is with rectilinear motion. Since, under these conditions, $\frac{d\bar{u}}{dy}$ is essentially negative, the absolute value of the first term of (4) is greater than with rectilinear motion, and the stability of motion is consequently diminished. Conversely, with the velocity greatest at the inside of the curve the stability is increased.

IX. *The Transverse Vibrations of a Rod of Varying Cross-Section.* By P. F. WARD, M.Sc. (Manch.).*

1. **T**HE following paper contains an extension of some results given by Kirchhoff in his memoir on the vibrations of a bar of variable section †. It is assumed that the cross-sections are small, their centres of gravity in a straight line, and their principal axes in the same directions. Such a rod can execute small vibrations parallel to either of these two directions. The rod is further supposed to be of rectangular section.

After the differential equation has been formed, it is simplified by making a special assumption as to the law of variation of the cross-section. It is then solved in terms of Bessel's functions, by an extension of the artifice used by Kirchhoff in the case where the rod has the form of a very acute-angled wedge or cone. The thin end of the rod is supposed to be free, and the solution is investigated for the cases where the other end is clamped, free, or supported, respectively. The lower modes of vibration are then investigated in the case of the wedge and cone. As Kirchhoff found, the amplitude of vibration can become relatively very large near the thin end of the rod. It is also shown that there is an approximate relation between the positions of the nodes, points of maximum excursion, and points of inflexion, and the roots of certain Bessel's functions, the approximation being closer the higher the mode, and the nearer the points in question to the thin end of the rod.

A discussion is appended of some cases of wave-motion in a canal of variable cross-section, which are easily solved by means of Bessel's functions.

2. Take the line of centres of the cross-sections in the equilibrium position as the z -axis of a rectangular system, the axis of x being in the direction of vibration. Then, if E denotes Young's modulus, ω the area of the cross-section, κ the radius of gyration of a section about an axis through its centre parallel to y , ξ the transverse displacement of the centre of a section, and ρ the volume-density, the equation of motion is

$$\rho\omega\frac{\partial^2\xi}{\partial t^2} = -\frac{\partial^2}{\partial z^2}\left(E\omega\kappa^2\frac{\partial^2\xi}{\partial z^2}\right). \quad . \quad . \quad (1)$$

* Communicated by Prof. H. Lamb, F.R.S.

† *Gesammelte Abhandlungen*, p. 339.

Assuming $\xi = u \cos \lambda t$, this becomes

$$\frac{\rho \omega \lambda^2}{E} u = \frac{d^2}{dz^2} \left(\omega \kappa^2 \frac{d^2 u}{dz^2} \right). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now let the dimensions parallel to x and y vary as z^m and z^n respectively. Then, the section being rectangular, we have

$$\omega = \omega' z^{m+n}, \quad \kappa^2 = \kappa'^2 z^{2n},$$

where ω' and κ' are the values of ω and κ at $z=1$. Substituting these values in (2), we have

$$\frac{\rho \lambda^2}{E \kappa'^2} z^{m+n} u = \frac{d^2}{dz^2} \left(z^{3m+n} \frac{d^2 u}{dz^2} \right). \quad . \quad . \quad . \quad (3)$$

The solution of this equation in terms of infinite series is given by Kirchhoff. We need only notice that if $m \geq 2$ the analysis breaks down at the point $z=0$, the solution becoming infinite at this point.

The most interesting cases arise when $m=1$. The equation (3) now reduces to

$$\frac{\rho \lambda^2}{E \kappa'^2} z^{n+1} u = \frac{d^2}{dz^2} \left(z^{n+3} \frac{d^2 u}{dz^2} \right), \quad . \quad . \quad . \quad . \quad (4)$$

which may be written

$$\frac{\rho \lambda^2}{E \kappa'^2} u = \left(\frac{1}{z^{n+1}} \frac{d}{dz} z^{n+2} \frac{d}{dz} \right)^2 u. \quad . \quad . \quad . \quad . \quad (5)^*$$

Hence we have to solve the two equations

$$\frac{1}{z^{n+1}} \frac{d}{dz} z^{n+2} \frac{du}{dz} = \pm \sqrt{\frac{\rho \lambda^2}{E \kappa'^2}} u. \quad . \quad . \quad . \quad (6)$$

Writing $z \sqrt{\left(\frac{\rho \lambda^2}{E \kappa'^2} \right)} = x$, these reduce to

$$x \frac{d^2 u}{dx^2} + (n+2) \frac{du}{dx} = \pm u. \quad . \quad . \quad . \quad . \quad (7)$$

If we now put $4x = \eta^2$, we have

$$\frac{d^2 u}{d\eta^2} + \frac{(2n+3)}{\eta} \frac{du}{d\eta} = \pm u, \quad . \quad . \quad . \quad . \quad (8)$$

* The substitution here used is a special case of the more general one,

$$\frac{1}{z^s} \frac{dr}{dz^r} \left(z^{r+s} \frac{dr}{dz^r} \right) = \left(\frac{1}{z^s} \frac{d}{dz} + 1 \right) \left(\frac{d}{dz} \right)^r.$$

and on writing $u=t/\eta^{n+1}$, this becomes

$$\frac{d^2 t}{d\eta^2} + \frac{1}{\eta} \frac{dt}{d\eta} + t - \frac{(n+1)^2}{\eta^2} t = 0, \quad . \quad . \quad . \quad (9)$$

which is the Bessel's equation of order $n+1$.

If we take one end of the bar to be at $z=0$, and consider that end to be free, then, since the displacement there must be finite, we only need the Bessel's functions of the first kind in the solution of (9). Hence

$$t = AI_{n+1}(\eta) + BJ_{n+1}(\eta), \quad . \quad . \quad . \quad (10)$$

$$\text{or} \quad u = A\phi_n(x) + B\psi_n(x), \quad . \quad . \quad . \quad (11)$$

where

$$\phi_n(x) = \frac{1}{x^{\frac{n+1}{2}}} I_{n+1}(2\sqrt{x}), \quad \psi_n(x) = \frac{1}{x^{\frac{n+1}{2}}} J_{n+1}(2\sqrt{x}). \quad (12)$$

3. Clamped-Free Bar.

Suppose the rod to be clamped at $z=l$. The conditions to be fulfilled at a clamped end are $\xi=0$ and $\partial\xi/\partial z=0$, which in our case reduce to $u=0$ and $du/dx=0$. From (12) we then have

$$A\phi_n(x_1) + B\psi_n(x_1) = 0, \quad . \quad . \quad . \quad (13)$$

$$A \frac{d\phi_n(x_1)}{dx} + B \frac{d\psi_n(x_1)}{dx} = 0, \quad . \quad . \quad . \quad (14)$$

where x_1 is the value of x corresponding to $z=l$. Now according to our notation ϕ_{n-1} , ψ_{n-1} are certain integrals of the equations

$$\left. \begin{aligned} x \frac{d^2 \phi_{n-1}}{dx^2} + (n+1) \frac{d\phi_{n-1}}{dx} &= \phi_{n-1}, \\ x \frac{d^2 \psi_{n-1}}{dx^2} + (n+1) \frac{d\psi_{n-1}}{dx} &= -\psi_{n-1}. \end{aligned} \right\} . \quad . \quad . \quad (15)$$

$$\text{Also} \quad \phi_n = \frac{d\phi_{n-1}}{dx} \quad \text{and} \quad \psi_n = -\frac{d\psi_{n-1}}{dx}. \quad . \quad . \quad . \quad (16)$$

Hence (13) and (14) give

$$\left. \begin{aligned} A \frac{d\phi_{n-1}}{dx} - B \frac{d\psi_{n-1}}{dx} &= 0, \\ A \frac{d^2 \phi_{n-1}}{dx^2} - B \frac{d^2 \psi_{n-1}}{dx^2} &= 0. \end{aligned} \right\} . \quad . \quad . \quad (17)$$

Taking (17) in connexion with (15) we obtain

$$A\phi_{n-1} + B\psi_{n-1} = 0; \quad . \quad . \quad . \quad (18)$$

and finally by eliminating A and B we obtain as the equation to determine x_1 , and therefore the values of λ ,

$$\frac{d}{dx}(\phi_{n-1}\psi_{n-1}) = 0. \quad . \quad . \quad . \quad (19)$$

To solve (19) we proceed as follows, the method being an extension of that employed by Kirchhoff in the cases of $n=0$, $n=1$. If we multiply the two equations (15) respectively and successively by

$$\psi_{n-1}, -\phi_{n-1}; \quad \frac{d\psi_{n-1}}{dx}, \frac{d\phi_{n-1}}{dx}; \quad \psi_{n-1}, \phi_{n-1};$$

and add, we obtain

$$\begin{aligned} 2\phi_{n-1}\psi_{n-1} &= \frac{1}{x^n} \frac{d}{dx} \left\{ x^{n+1} \left(\frac{d\phi_{n-1}}{dx} \psi_{n-1} - \frac{d\psi_{n-1}}{dx} \phi_{n-1} \right) \right\}, \\ \frac{d\phi_{n-1}}{dx} \psi_{n-1} - \frac{d\psi_{n-1}}{dx} \phi_{n-1} &= -\frac{1}{x^{2n+1}} \frac{d}{dx} \left\{ x^{2n+2} \frac{d\phi_{n-1}}{dx} \frac{d\psi_{n-1}}{dx} \right\}, \\ x \left(\frac{d^2\phi_{n-1}}{dx^2} \psi_{n-1} + \frac{d^2\psi_{n-1}}{dx^2} \phi_{n-1} \right) &+ (n+1) \frac{d}{dx} (\phi_{n-1}\psi_{n-1}) = 0, \end{aligned}$$

which with the identity

$$\frac{d^2}{dx^2}(\phi_{n-1}\psi_{n-1}) = \phi_{n-1} \frac{d^2\psi_{n-1}}{dx^2} + 2 \frac{d\phi_{n-1}}{dx} \frac{d\psi_{n-1}}{dx} + \psi_{n-1} \frac{d^2\phi_{n-1}}{dx^2},$$

yield the differential equation

$$4\phi_{n-1}\psi_{n-1} = -\frac{1}{x^n} \frac{d}{dx} \frac{1}{x^n} \frac{d}{dx} x^{n+1} \frac{d}{dx} x^{n+1} \frac{d}{dx} (\phi_{n-1}\psi_{n-1}). \quad (20)$$

From (20) it is found that the required series for $\phi_{n-1}\psi_{n-1}$ is

$$1 - \frac{x^2}{(n+1)^2(n+2)} + \frac{x^4}{2! (n+1)^2(n+2)^2(n+3)(n+4)} - \dots \quad (21)$$

Therefore from (19) the equation to find λ is

$$0 = \frac{1}{(n+1)^2(n+2)} - \frac{x^2}{1! (n+1)^2(n+2)^2(n+3)(n+4)} + \dots, \quad (22)$$

which if n is integral may be written

$$0 = \frac{1}{(n+1)! (n+2)!} - \frac{x^2}{1! (n+2)! (n+4)!} + \frac{x^4}{2! (n+3)! (n+6)!} - \dots \quad (23)$$

4. If we put $n=0$ we obtain the case of a wedge-shaped rod free at the thin end and clamped at the other: the direction of vibration being parallel to the planes of triangular section*.

From (11) we have

$$u = A\phi_0(x) + B\psi_0(x), \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\text{or} \quad u = \frac{A}{\sqrt{x}} I_1(2\sqrt{x}) + \frac{B}{\sqrt{x}} J_1(2\sqrt{x}).$$

The equation to determine x_1 , and therefore λ , is by (23)

$$0 = \frac{1}{1!2!} - \frac{x^2}{1!2!4!} + \frac{x^4}{2!3!6!} - \frac{x^6}{3!4!8!} + \dots \quad (25)$$

I find that the first four roots of this equation are

$$5.3151, \quad 15.207, \quad 30.020, \quad 49.763.$$

Since x_1 is the value of x corresponding to $z=l$, we have

$$l \sqrt{\left(\frac{\rho\lambda^2}{E\kappa'^2}\right)} = x_1, \quad \text{or} \quad \lambda = \frac{x_1}{l} \sqrt{\left(\frac{E\kappa'^2}{\rho}\right)},$$

giving the frequency corresponding to any root x_1 of (25).
Also since

$$z \sqrt{\left(\frac{\rho\lambda^2}{E\kappa'^2}\right)} = x,$$

we have

$$z = \frac{l}{x_1} x. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

From (18) the ratio of the constants A and B is found to be

$$A/\phi_{-1}(x_1) = -B/\psi_{-1}(x_1) = C \text{ (say),}$$

$$\text{whence} \quad u = C\{\psi_{-1}(x_1)\phi_0(x) - \phi_{-1}(x_1)\psi_0(x)\}. \quad . \quad (27)$$

We notice that

$$\phi_{-1} = I_0(2\sqrt{x}) \quad \text{and} \quad \psi_{-1} = J_0(2\sqrt{x}).$$

In the first mode we have $x_1=5.3151$, and therefore

$$u = -C\{19.2773\psi_0(x) + .293327\phi_0(x)\}.$$

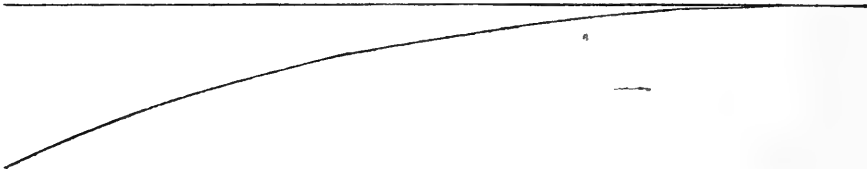
* The case of a vibration perpendicular to the planes of triangular section is treated by F. Meyer zur Capellen in Wiedemann, *Annalen der Physik*, vol. xxxiii. 1888, p. 661.

To find the form assumed by the rod we construct the following table :—

$x.$	$\phi_0(x).$	$\psi_0(x).$	$-u/C.$	$z/l.$
0	1·000000	1·000000	19·5707	·000000
1	1·590636	·576724	11·5842	·188143
2	2·394833	·282992	6·15779	·376287
3	3·468650	·0880035	2·71392	·564430
4	4·879732	−·0330216	·79478	·752574
5	6·70929	−·0999263	·04169	·940717

The curve is shown in fig. 1.

Fig. 1.



In the second mode $x=15\cdot207$, and

$$u = C\{ \cdot215563\phi_0(x) - 354\cdot429\psi_0(x) \}.$$

The corresponding table is

$2\sqrt{x}.$	$x.$	$\phi_0(x).$	$\psi_0(x).$	$u/C.$	$z/l.$
{ 3·8 3·82	0			−354·214	·000000
	1			−204·065	·065759
	2			− 99·784	·131518
	3			− 30·4433	·197277
	3·61	4·28443	+·00674789	− 1·46809	
	3·6481	4·33994	+·00247215	+ ·059329	
	4			+ 12·7557	·263037
	5			+ 36·8631	·328796
	6	9·05436	−·128413	+ 47·4651	·394555
	7	12·03039	−·130723	+ 48·9251	·460314
	8	15·77410	−·116292	+ 44·6177	·526073
	9	20·47731	−·0922279	+ 37·1025	·591833
	10	26·23987	−·0637983	+ 28·2683	·657592
	11	33·3748	−·0347379	+ 19·4980	·723351
	12	42·1129	−·0076087	+ 11·7747	·789110
	15	81·2433	−·0106065	+ ·05391	·986388

By interpolation the node is found to be at the point

$$x = 3.64662, \quad z/l = .239799.$$

The point of maximum excursion is given by

$$\frac{du}{dx} / C = .215563 \frac{d\phi_0}{dx} - 354.429 \frac{d\psi_0}{dx} = 0.$$

We may notice that

$$\frac{d\phi_0}{dx} = \phi_1 = \frac{1}{x} I_2(2\sqrt{x}) \quad \text{and} \quad \frac{d\psi_0}{dx} = -\psi_1 = -\frac{1}{x} J_2(2\sqrt{x}).$$

I find as corresponding values :

$2\sqrt{x}.$	$x.$	$\frac{d\phi_0}{dx}.$	$\frac{d\psi_0}{dx}.$	$\frac{du}{dx} / C.$
$\left\{ \begin{array}{l} 5.16 \\ 5.18 \end{array} \right.$	$\left\{ \begin{array}{l} 6.6564 \\ 6.7081 \end{array} \right.$	$\left\{ \begin{array}{l} 3.08065 \\ 3.11787 \end{array} \right.$	$\left\{ \begin{array}{l} .00124091 \\ .00223670 \end{array} \right.$	$\left\{ \begin{array}{l} +.224260 \\ -.120653 \end{array} \right.$

Hence the point of maximum excursion is found to be at

$$x = 6.69001, \quad z/l = .439930.$$

At the point of inflexion

$$\frac{d^2u}{dx^2} / C = .215563 \frac{d^2\phi_0}{dx^2} - 354.429 \frac{d^2\psi_0}{dx^2} = 0.$$

We note that

$$\frac{d^2\phi_0}{dx^2} = \frac{d\phi_1}{dx} = \phi_2 = \frac{1}{x^{3/2}} I_3(2\sqrt{x}),$$

and

$$\frac{d^2\psi_0}{dx^2} = -\frac{d\psi_1}{dx} = \psi_2 = \frac{1}{x^{3/2}} J_3(2\sqrt{x}).$$

The following are corresponding values :

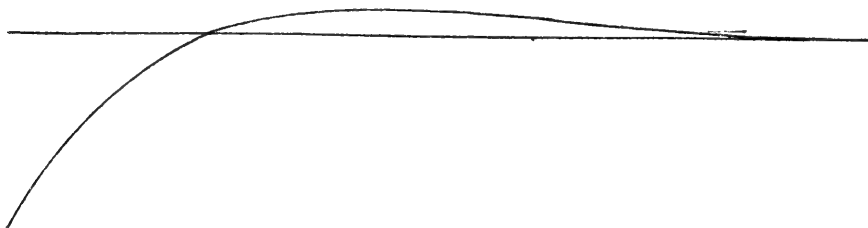
$2\sqrt{x}.$	$x.$	$\frac{d^2\phi_0}{dx^2}.$	$\frac{d^2\psi_0}{dx^2}.$	$\frac{d^2u}{dx^2} / C.$
$\left\{ \begin{array}{l} 6.28 \\ 6.30 \end{array} \right.$	$\left\{ \begin{array}{l} 9.8596 \\ 9.9225 \end{array} \right.$	$\left\{ \begin{array}{l} 1.305855 \\ 1.320731 \end{array} \right.$	$\left\{ \begin{array}{l} .000971393 \\ .000769200 \end{array} \right.$	$\left\{ \begin{array}{l} -.062796 \\ +.012074 \end{array} \right.$

Therefore the point of inflexion is at

$$x = 9.91236, \quad z/l = .651829.$$

The form of the rod is shown in fig. 2.

Fig. 2.



In the third mode $x_1 = 30.020$, and therefore

$$u = -C\{7003.06\psi_0(x) + .178460\phi_0(x)\}.$$

To find the nodes we have

$\sqrt{x.}$	$x.$	$\phi_0(x).$	$\psi_0(x).$	$u/C.$
$\begin{cases} 3.82 \\ 3.84 \end{cases}$	$\begin{matrix} 3.6481 \\ 3.6864 \end{matrix}$	$\begin{matrix} \dots\dots\dots \\ 4.39630 \end{matrix}$	$\begin{matrix} \dots\dots\dots \\ -.00173794 \end{matrix}$	$\begin{matrix} -18.0871 \\ +11.3863 \end{matrix}$
$\begin{cases} 7.00 \\ 7.02 \end{cases}$	$\begin{matrix} 12.25 \\ 12.3201 \end{matrix}$	$\begin{matrix} 44.5826 \\ 45.2971 \end{matrix}$	$\begin{matrix} -.00133795 \\ +.000377234 \end{matrix}$	$\begin{matrix} +1.41354 \\ -10.72551 \end{matrix}$

Hence the nodes are given by

$$\begin{aligned} x &= 3.67160, & 12.25816, \\ z/l &= .122305, & .408334. \end{aligned}$$

To find the points of maximum excursion we have

$2\sqrt{x.}$	$x.$	$\frac{d\phi_0}{dx}.$	$\frac{d\psi_0}{dx}$	$-\frac{du}{dx}/C.$
$\begin{cases} 5.12 \\ 5.14 \end{cases}$	$\begin{matrix} 6.5536 \\ 6.6049 \end{matrix}$	$\begin{matrix} 3.00776 \\ 3.94395 \end{matrix}$	$\begin{matrix} -.000810898 \\ +.000225034 \end{matrix}$	$\begin{matrix} +5.14201 \\ -2.11915 \end{matrix}$
$\begin{cases} 8.46 \\ 8.48 \end{cases}$	$\begin{matrix} 17.8929 \\ 17.9776 \end{matrix}$	$\begin{matrix} 28.6109 \\ 29.0341 \end{matrix}$	$\begin{matrix} -.000646653 \\ -.000943240 \end{matrix}$	$\begin{matrix} -.57735 \\ +1.42413 \end{matrix}$

The required points together with the actual displacement are then as given below :

$2\sqrt{x.}$	$x.$	$\phi_0(x).$	$\psi_0(x).$	$u/C.$	$z/l.$
5.13417	6.58993	10.72545	-.132279	+924.445	.219523
8.46577	17.91733	146.746	+.0644071	-477.235	.596845

To find the points of inflexion we have

$2\sqrt{x}$	x	$\frac{d^2\phi_0}{dx^2}$	$\frac{d^2\psi_0}{dx^2}$	$-\frac{d^2u}{dx^2}/C$
$\begin{cases} 6.38 \\ 6.40 \end{cases}$	$\begin{cases} 10.1761 \\ 10.24 \end{cases}$	$\begin{cases} 1.38222 \\ 1.389101 \end{cases}$	$\begin{cases} +.00000147866 \\ -.000180292 \end{cases}$	$\begin{cases} -.257026 \\ +1.01470 \end{cases}$
$\begin{cases} 9.62 \\ 9.64 \end{cases}$	$\begin{cases} 23.1361 \\ 23.2324 \end{cases}$	$\begin{cases} 10.8118 \\ 10.9617 \end{cases}$	$\begin{cases} -.000317421 \\ -.000270646 \end{cases}$	$\begin{cases} +.29345 \\ -.06087 \end{cases}$

The required points are then given by

$$x=10.18901, \quad 23.21586,$$

$$z/l = .339407, \quad .773348.$$

The form of the rod is shown in fig. 3.

Fig. 3.



In the fourth mode $x_1=49.763$,

$$u=C\{.155668\phi_0(x)-143695\psi_0(x)\}$$

The positions of the nodes, loops, and points of inflexion are then as follows:

	x	z/l
Nodes	3.67055	.073762
	12.30668	.247306
	25.80624	.518582
Loops	6.59392	.132506
	17.70437	.355774
	34.07126	.684669
Inflexions	10.17609	.204491
	23.84908	.479254
	41.37971	.831536

5. By putting $n=1$ we obtain the case of a very sharply pointed pyramid on a square base. It can be readily shown that the same analysis applies to the case of a circular cone.

From (12)

$$u = A\phi_1(x) + B\psi_1(x), \quad . \quad . \quad . \quad . \quad . \quad (28)$$

or

$$u = \frac{A}{x} I_2(2\sqrt{x}) + \frac{B}{x} J_2(2\sqrt{x}).$$

From (23) the equation to determine x_1 and therefore λ is

$$0 = \frac{1}{2! 3!} - \frac{x^2}{1! 3! 5!} + \frac{x^4}{2! 4! 7!} - \dots, \quad . \quad . \quad (29)$$

the lower roots of which are found to be

$$8.7192, \quad 21.146, \quad 38.453.$$

The ratio of the constants A and B is from (18) found to be

$$-A/\psi_0(x_1) = B/\phi_0(x_1) = C \text{ (say),}$$

whence

$$u = C\{\phi_0(x_1)\psi_1(x) - \psi_0(x_1)\phi_1(x)\}.$$

In the first mode $x_1 = 8.7192$,

$$u = C\{.0996438 \phi_1(x) + 19.0308 \psi_1(x)\}.$$

In the second mode $x_1 = 21.146$,

$$u = C\{270.325 \psi_1(x) - .0473844 \phi_1(x)\}.$$

We then find as corresponding values:

$2\sqrt{x}.$	$x.$	$\phi_1(x).$	$\psi_1(x).$	$u/C.$
$\left\{ \begin{array}{l} 5.12 \\ 5.14 \end{array} \right.$	$\begin{array}{l} 6.5536 \\ 6.6049 \end{array}$	$\begin{array}{l} \dots\dots \\ \dots\dots \end{array}$	$\begin{array}{l} \dots\dots \\ \dots\dots \end{array}$	$\begin{array}{l} +.076685 \\ -.205068 \end{array}$

Hence the node is at the point

$$x = 6.56756, \text{ or } z/l = .310582.$$

Again we find :

$2\sqrt{x}.$	$x.$	$\frac{d\phi_1}{dx}.$	$\frac{d\psi_1}{dx}.$	$\frac{du}{dx} \bigg C.$
$\left\{ \begin{array}{l} 6.40 \\ 6.42 \end{array} \right.$	$\begin{array}{l} 10.24 \\ 10.3041 \end{array}$	$\begin{array}{l} \dots\dots \\ 1.414192 \end{array}$	$\begin{array}{l} \dots\dots \\ +.000358052 \end{array}$	$\begin{array}{l} -.0175107 \\ +.0297799 \end{array}$

The point of maximum excursion is then given by

$$x = 10.26373 \text{ or } z/l = .485373.$$

In the third mode $x_1=38.453$,

$$u = C\{4306.80 \psi_1(x) + .0290930 \phi_1(x)\}.$$

We then have as corresponding values :

$2\sqrt{x}.$	$x.$	$\phi_1(x).$	$\psi_1(x).$	$u/C.$
$\begin{cases} 5.12 \\ 5.14 \end{cases}$	$\begin{matrix} 6.5536 \\ 6.6049 \end{matrix}$	$\begin{matrix} \dots\dots \\ \dots\dots \end{matrix}$	$\begin{matrix} \dots\dots \\ \dots\dots \end{matrix}$	$\begin{matrix} +3.57988 \\ - .880662 \end{matrix}$
$\begin{cases} 8.40 \\ 8.42 \end{cases}$	$\begin{matrix} 17.64 \\ 17.7241 \end{matrix}$	$\begin{matrix} 27.3792 \\ 27.7838 \end{matrix}$	$\begin{matrix} -.000265556 \\ +.000042188 \end{matrix}$	$\begin{matrix} - .347188 \\ + .989993 \end{matrix}$

The nodes are therefore given by

$$\begin{aligned} x &= 6.59477, & 17.66184, \\ z/l &= .171502, & .459298. \end{aligned}$$

Again :

$2\sqrt{x}.$	$x.$	$\frac{d\phi_1}{dx}.$	$\frac{d\psi_1}{dx}.$	$\frac{du}{dx}/C.$
$\begin{cases} 6.36 \\ 6.38 \end{cases}$	$\begin{matrix} 10.1124 \\ 10.1761 \end{matrix}$	$\begin{matrix} 1.366545 \\ - \end{matrix}$	$\begin{matrix} -.000187291 \\ - \end{matrix}$	$\begin{matrix} -.766870 \\ +.0338437 \end{matrix}$
$\begin{cases} 9.80 \\ 9.82 \end{cases}$	$\begin{matrix} 24.01 \\ 24.1081 \end{matrix}$	$\begin{matrix} 12.2416 \\ 12.4124 \end{matrix}$	$\begin{matrix} -.0000824478 \\ -.000123829 \end{matrix}$	$\begin{matrix} +.001051 \\ -.172201 \end{matrix}$

Hence the points of maximum excursion are given by

$$\begin{aligned} x &= 10.17341, & 24.01059, \\ z/l &= .264567, & .624414. \end{aligned}$$

Returning to the equation (27)

$$u = C\{\psi_{-1}(x_1)\phi_0(x) - \phi_{-1}(x_1)\psi_0(x)\},$$

we notice that when x is small and x_1 relatively great, the chief term in the expression is the second. Thus the positions of the nodes, loops, and points of inflexion are given approximately by the roots of the equations

$$\psi_0(x)=0, \quad \frac{d\psi_0}{dx}=0, \quad \frac{d^2\psi_0}{dx^2}=0,$$

that is by

$$J_1(2\sqrt{x})=0, \quad J_2(2\sqrt{x})=0, \quad J_3(2\sqrt{x})=0,$$

respectively ; the approximation being closer the higher the mode and the nearer the points in question to the thin end.

The degree of approximation is illustrated by the following tables.

Nodes of wedge-shaped bar.

First mode.....	—	—	—	—
Second mode.....	3·64662	—	—	—
Third mode	3·67160	12·25816	—	—
Fourth mode	3·67055	12·30668	25·80624	—
Roots of $J_1(2\sqrt{x})=0$.	3·67049	12·30461	25·87487	44·38026

Points of Maximum Amplitude.

First mode.....	—	—	—	—
Second mode	6·69001	—	—	—
Third mode	6·58993	17·91733	—	—
Fourth mode	6·59392	17·70437	34·07126	—
Roots of $J_2(2\sqrt{x})=0$.	6·59366	17·71249	33·75520	54·73142

Points of Inflexion.

First mode.....	—	—	—
Second mode	9·91236	—	—
Third mode	10·18901	23·21586	—
Fourth mode	10·17609	23·84908	41·37971
Roots of $J_3(2\sqrt{x})=0$.	10·17661	23·81939	42·34886

6. *Free-Free Bar.*

Since both ends of the rod are now free the conditions to be fulfilled at $z=0$ and $z=l$ are

$$\omega\kappa^2 \frac{\partial^2 \xi}{\partial z^2} = 0, \text{ and } \frac{\partial}{\partial z} \left(\omega\kappa^2 \frac{\partial^2 \xi}{\partial z^2} \right) = 0,$$

which in our case reduce to

$$x^{n+3} \frac{d^2 u}{dx^2} = 0, \text{ and } \frac{d}{dx} \left(x^{n+3} \frac{d^2 u}{dx^2} \right) = 0.$$

Applying these to (11), we have

$$A \frac{d^2 \phi_n}{dx^2} + B \frac{d^2 \psi_n}{dx^2} = 0, \quad . \quad . \quad . \quad . \quad (30)$$

and

$$A \frac{d^3 \phi_n}{dx^3} + B \frac{d^3 \psi_n}{dx^3} = 0. \quad . \quad . \quad . \quad . \quad (31)$$

By differentiation of (7) and the use of (30) and (31) we obtain

$$A \frac{d\phi_n}{dx} - B \frac{d\psi_n}{dx} = 0. \quad . \quad . \quad . \quad . \quad (32)$$

which on being combined with (30) to eliminate A and B gives as the equation to determine x_1 , and therefore λ ,

$$\frac{d}{dx} \left(\frac{d\phi_n}{dx} \frac{d\psi_n}{dx} \right) = 0. \quad . \quad . \quad . \quad . \quad (33)$$

By a process similar to that which was applied to (19) we find that (33) is equivalent to

$$0 = \frac{1}{(n+3)^2(n+4)} - \frac{x^2}{1!(n+3)^2(n+4)^2(n+5)(n+6)} \\ + \frac{x^4}{2!(n+3)^2(n+4)^2(n+5)^2(n+6)(n+7)(n+8)} - \dots,$$

which if n is integral may be written

$$0 = \frac{1}{(n+3)!(n+4)!} - \frac{x^2}{1!(n+4)!(n+6)!} \\ + \frac{x^4}{2!(n+5)!(n+8)!} - \dots \quad (34)$$

7. In the case of a wedge-shaped rod we have $n=0$. The equation to determine x_1 is

$$0 = \frac{1}{3!4!} - \frac{x^2}{1!4!6!} + \frac{x^4}{2!5!8!} - \frac{x^6}{3!6!10!} + \dots,$$

the lower roots of which are found to be

$$12.757, \quad 27.755, \quad 47.576, \quad 72.294.$$

$$\text{Also } u = C \left\{ \left(\frac{d\psi_0}{dx} \right)_{x_1} \phi_0(x) + \left(\frac{d\phi_0}{dx} \right)_{x_1} \psi_0(x) \right\} \quad . \quad . \quad . \quad (35)$$

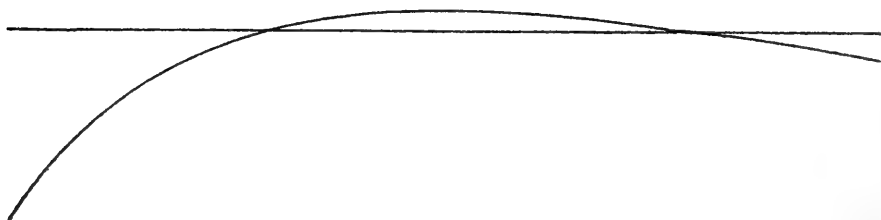
I find that the positions of the nodes, points of maximum excursion, and points of inflexion are as follows :—

First Mode ($x_1=12\cdot757$),
 $u=C\{11\cdot1754\psi_0(x) + \cdot0225089\phi_0(x)\}.$

	$x.$	$z/l.$
Nodes	3·75507	·294354
	10·25691	·804021
Loop	6·32451	·495768

See fig. 4.

Fig. 4.

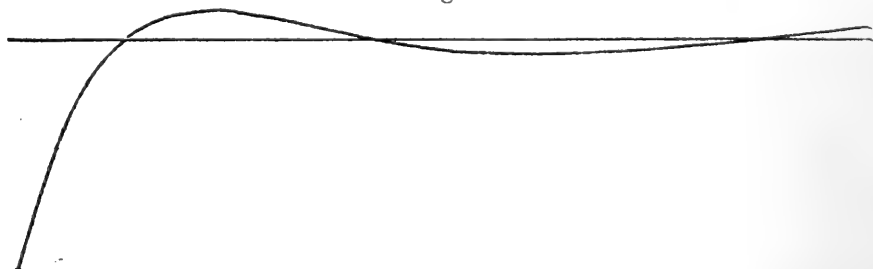


Second Mode ($x_1=27\cdot755$).
 $u=C\{138\cdot4027\psi_0(x) - \cdot00782072\phi_0(x)\}.$

	$x.$	$z/l.$
Nodes	3·66834	·132169
	12·41283	·447231
	23·56857	·849166
Loops	6·60227	·237877
	17·32316	·624146
Inflexion...	10·14996	·365699

See fig. 5.

Fig. 5.



Third Mode ($x_1=47\cdot576$).

$$u = C\{1921\cdot14\psi_0(x) + \cdot00379782\phi_0(x)\}.$$

	$x.$	$z/l.$
Nodes	3·67067	·077154
	12·30104	·258555
	26·00530	·546606
	41·71807	·876873
Loops	6·59346	·138588
	17·72714	·372606
	33·25672	·699023
Inflexions .	10·17758	·213923
	23·76647	·499548

See fig. 6.

Fig. 6.



Fourth Mode ($x_1=72\cdot294$).

$$u = C\{29003\cdot1\psi_0(x) - \cdot00218216\phi_0(x)\}.$$

	$x.$	$z/l.$
Nodes	3·67059	·050773
	12·30482	·170205
	25·87013	·357846
	44·46248	·615023
Loops	6·59377	·091208
	17·71200	·245000
	33·77604	·467203
	54·03317	·747409
Inflexions .	10·17658	·140767
	23·82147	·329509
	42·27130	·584714

See fig. 7 (p. 100).

Fig. 7.



8. To obtain the case of the conical rod we put $n=1$. The equation to determine x_1 , and therefore λ , is

$$0 = \frac{1}{4!5!} - \frac{x^2}{1!5!7!} + \frac{x^4}{2!6!9!} - \frac{x^6}{3!7!11!} + \dots, \quad (36)$$

the lower roots of which are

$$17.416, 35.027, 57.380.$$

Also we find
$$u = C \left\{ \left(\frac{d\psi_1}{dx} \right) x_1 \phi_1(x) + \left(\frac{d\phi_1}{dx} \right) x_1 \psi_1(x) \right\}. \quad (37)$$

It is found that the positions of the nodes and points of maximum excursion are as follows :—

First Mode ($x_1=17.416$).

$$u = C \{ 4.61034 \psi_1(x) + .00382017 \phi_1(x) \}.$$

	$x.$	$z/l.$
Nodes.....	6.72715	.386263
	14.68195	.843012
Loop	9.82786	.564301

Second Mode ($x_1=35.027$).

$$u = C \{ 52.6544 \psi_1(x) - .00103515 \phi_1(x) \}.$$

	$x.$	$z/l.$
Nodes.....	6.59080	.188163
	17.86855	.510138
	30.60030	.873620
Loops.....	10.18619	.290810
	23.34072	.666363

Third Mode ($x_1 = 57.380$).

$$u = C\{664.841\psi_1(x) + .000414102\phi_1(x)\}.$$

	$x.$	$z/l.$
Nodes.....	6.59385 17.70786 33.93229 51.29925	.114916 .308608 .591361 .894026
Loops.....	10.17632 23.83643 41.75737	.177349 .415413 .727735

9. *Free-supported Bar.*

Finally we may briefly notice the case in which the bar is supported at $z=l$. As before we have

$$u = A\phi_n(x) + B\psi_n(x).$$

The conditions to be fulfilled at a supported end are $\xi=0$ and $\omega\kappa^2\partial^2\xi/\partial z^2=0$, which in our case reduce to

$$u=0 \quad \text{and} \quad x^{n+3}\frac{d^2u}{dx^2}=0,$$

$$\text{and therefore yield } A\phi_n(x) + B\psi_n(x) = 0, \quad . \quad . \quad . \quad . \quad (38)$$

$$\text{and} \quad A\frac{d^2\phi_n}{dx^2} + B\frac{d^2\psi_n}{dx^2} = 0. \quad . \quad . \quad . \quad . \quad (39)$$

Eliminating A and B from (38) and (39) we have

$$\phi_n\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\phi_n}{dx^2} = 0,$$

which if n is integral gives as the equation from which x_1 , and therefore λ , is to be determined,

$$0 = \frac{1}{(n+2)!(n+4)!} - \frac{x^2}{1!(n+3)!(n+6)!} + \frac{x^4}{2!(n+4)!(n+8)!} - \dots \quad (40)$$

10. To obtain the case of the wedge-shaped bar put $n=0$. Equation (40) then becomes

$$0 = \frac{1}{2!4!} - \frac{x^2}{1!3!6!} + \frac{x^4}{2!4!8!} - \dots,$$

the lower roots of which are

$$10.902, 24.631, 43.204.$$

I find that the positions of the nodes, points of maximum excursion, and points of inflexion are as follows :—

		$x.$	$z/\bar{l}.$
First Mode.	Node	3·71776	·341016
	Loop	6·43209	·589990
Second Mode.	Nodes	3·66960 12·35145	·148981 ·501549
	Loops	6·59750 17·53168	·267853 ·771774
	Inflexion ...	10·16484	·412683
Third Mode.	Nodes	3·67062 12·30337 25·92098	·084960 ·284775 ·599968
	Loops	6·59365 17·71796 33·56639	·152617 ·410101 ·776928
	Inflexions...	10·17697 23·80026	·235557 ·550882

Fig. 8.

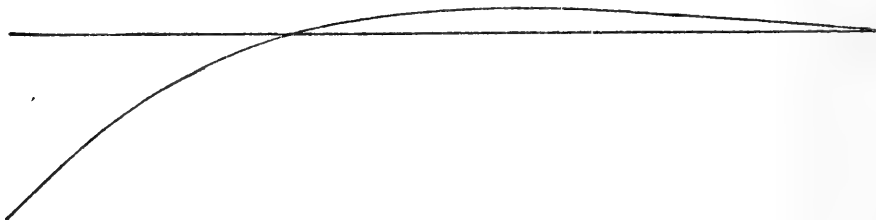
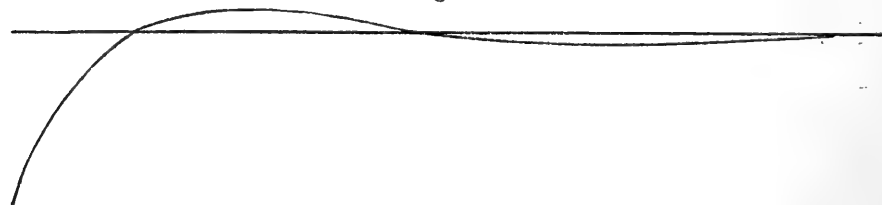


Fig. 9.



The results for the first and second modes are shown in figs. 8 and 9.

11. The case of the conical bar is obtained by making $n=1$. From (40) we then have

$$0 = \frac{1}{3!5!} - \frac{x^2}{1!4!7!} + \frac{x^4}{2!5!9!} - \frac{x^6}{3!6!11!} + \dots,$$

the lower roots of which are found to be

$$15.406, 31.750, 52.858.$$

The positions of the nodes and points of maximum excursion are found to be as follows :—

		$x.$	$z/l.$
First Mode.	Node	6.67792	.433462
	Loop	9.94075	.645252
Second Mode.	Nodes	6.59220 17.79314	.207628 .560413
	Loops	10.18177 23.55458	.320687 .741876
Third Mode.	Nodes	6.59380 17.71046 33.83296	.124746 .335057 .640073
	Loops	10.17648 23.82701 42.07101	.192525 .450774 .795925

APPENDIX.

Wave Motion in a Canal of Variable Section.

Take the x -axis parallel to the length of the canal, and let S denote the area of a cross-section, b the breadth at the surface, and η the difference between the ordinates of the free surface in the disturbed and undisturbed states. The equation of motion is then

$$\frac{\partial^2 \eta}{\partial t^2} = \frac{g}{b} \frac{\partial}{\partial x} \left(S \frac{\partial \eta}{\partial x} \right), \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{or if } \eta \propto \cos(\sigma t + \epsilon), \quad \frac{g}{b} \frac{d}{dx} \left(S \frac{d\eta}{dx} \right) + \sigma^2 \eta = 0. \quad . \quad (2)^*$$

* Lamb, Hydrodynamics, Art. 183 (4).

Consider the case of a canal of rectangular section, and let the depth h and the breadth b vary as x^m and x^n respectively. If h_0 and b_0 be the values of h and b at $x=a$, we have

$$h = h_0 \left(\frac{x}{a} \right)^m, \quad b = b_0 \left(\frac{x}{a} \right)^n,$$

$$S = hb = h_0 b_0 \left(\frac{x}{a} \right)^{m+n};$$

and therefore (2) reduces to

$$\frac{1}{x^n} \frac{d}{dx} \left\{ x^{m+n} \frac{d\eta}{dx} \right\} + \kappa^2 \eta = 0, \quad . \quad . \quad . \quad (3)$$

where $\kappa^2 = \sigma^2 a^m / g h_0,$

or $x^m \frac{d^2 \eta}{dx^2} + (m+n)x^{m-1} \frac{d\eta}{dx} + \kappa^2 \eta = 0. \quad . \quad . \quad . \quad (4)$

Writing $\frac{2}{2-m} x^{\frac{2-m}{2}} = \xi$, equation (4) reduces to

$$\frac{d^2 \eta}{d\xi^2} + \frac{2p}{\xi} \frac{d\eta}{d\xi} + \kappa^2 \eta = 0,$$

where $2p = \frac{2n+m}{2-m}$. If we now write $\eta = t / \xi^{p-\frac{1}{2}}$ the equation finally reduces to

$$\frac{d^2 t}{d\xi^2} + \frac{1}{\xi} \frac{dt}{d\xi} + \left\{ \kappa^2 - \frac{(p-\frac{1}{2})^2}{\xi^2} \right\} t = 0, \quad . \quad . \quad . \quad (5)$$

which is a Bessel's equation of order $(p-\frac{1}{2})$ or $(m+n-1)/(2-m)$.

In the case of $m=2$, the above transformations fail, but equation (3), which then becomes

$$x^2 \frac{d^2 \eta}{dx^2} + (n+2)x \frac{d\eta}{dx} + \kappa^2 \eta = 0,$$

is readily solved, being a homogeneous equation. It may be noticed, however, that when $m=2$ the solution becomes infinite for $x=0$, and therefore the origin must be excluded by means of a barrier from the stretch of canal considered.

Returning to (5), since m and n are both necessarily positive, and the solution has to be finite at the origin, a complete solution for our purposes is

$$t = C J_{p-\frac{1}{2}}(\kappa \xi),$$

or $\eta = \frac{C}{x^{\frac{m+n-1}{2}}} J_{\frac{m+n-1}{2-m}} \left(\frac{2\kappa}{2-m} x^{\frac{2-m}{2}} \right), \quad . \quad . \quad . \quad (6)$

where a numerical factor has been incorporated in the constant. If the canal be supposed to communicate at $x=a$ with an open sea, in which a tidal oscillation $\eta=A \cos (\sigma t+\epsilon)$ is maintained, we have on determining the constant in (6),

$$\eta=\frac{A J_{\frac{m+n-1}{2-m}}\left(\frac{2 \kappa}{2-m} x^{\frac{2-m}{2}}\right)}{x^{\frac{m+n-1}{2}}} \bigg/ \frac{J_{\frac{m+n-1}{2-m}}\left(\frac{2 \kappa}{2-m} a^{\frac{2-m}{2}}\right)}{a^{\frac{m+n-1}{2}}}. \quad (7)$$

It is now of interest to consider some special cases of (7).

(1) Let $m=0$, $n=1$. The depth now is constant and the breadth varies as the distance from the end $x=0$. Equation (7) then gives us

$$\eta=A \frac{J_0(\kappa x)}{J_0(\kappa a)} \cos (\sigma t+\epsilon).$$

(2) $m=1$, $n=0$. The breadth is constant and the depth varies as x . We then have

$$\eta=A \frac{J_0(2 \kappa \sqrt{x})}{J_0(2 \kappa \sqrt{a})} \cos (\sigma t+\epsilon).$$

(3) $m=\frac{1}{2}$, $n=\frac{1}{2}$. The breadth and the depth both vary as \sqrt{x} .

Hence

$$\eta=A \frac{J_0\left(\frac{4}{3} \kappa x^{3 / 4}\right)}{J_0\left(\frac{4}{3} \kappa a^{3 / 4}\right)} \cos (\sigma t+\epsilon).$$

(4) $m=0$, $n=2$. The depth is constant but the breadth varies as x^2 . We then have

$$\eta=A \frac{J_{\frac{1}{2}}(\kappa x)}{\sqrt{x}} \bigg/ \frac{J_{\frac{1}{2}}(\kappa a)}{\sqrt{a}} \cdot \cos (\sigma t+\epsilon).$$

But we know that $J_{\frac{1}{2}}(\theta) \sqrt{\left(\frac{1}{2} \pi \theta\right)}=\sin \theta$. Hence the above expression can be written

$$\eta=A \frac{\sin \kappa x}{\kappa x} \bigg/ \frac{\sin \kappa a}{\kappa a} \cdot \cos (\sigma t+\epsilon).$$

This shows that η vanishes for $\kappa x=s \pi$, where s is a positive integer.

(5) $m=1$, $n=\frac{1}{2}$. The depth now varies as x and the breadth as \sqrt{x} . Hence we have

$$\eta=A \frac{J_{\frac{1}{2}}(2 \kappa \sqrt{x})}{x^{1 / 4}} \bigg/ \frac{J_{\frac{1}{2}}(2 \kappa \sqrt{a})}{a^{1 / 4}} \cdot \cos (\sigma t+\epsilon).$$

This may also be written

$$\eta = A \frac{\sin(2\kappa\sqrt{x})}{2\kappa\sqrt{x}} \bigg/ \frac{\sin(2\kappa\sqrt{a})}{2\kappa\sqrt{a}} \cdot \cos(\sigma t + \epsilon),$$

which shows us that η vanishes for $2\kappa\sqrt{x} = s\pi$, where s is a positive integer.

(6) $m=1$, $n=1$. The depth and the breadth both vary directly as x . We then have

$$\eta = A \frac{J_1(2\kappa\sqrt{x})}{\sqrt{x}} \bigg/ \frac{J_1(2\kappa\sqrt{a})}{\sqrt{a}} \cdot \cos(\sigma t + \epsilon).$$

(7) $m=\frac{1}{2}$, $n=2$. The depth now varies as \sqrt{x} and the breadth as x^2 . Hence we have

$$\eta = A \frac{J_1(\frac{4}{3}\kappa x^{3/4})}{x^{3/4}} \bigg/ \frac{J_1(\frac{4}{3}\kappa a^{3/4})}{a^{3/4}} \cos(\sigma t + \epsilon).$$

(8) $m=1$, $n=2$. The breadth again varies as x^2 but the depth now varies as x . Therefore we have

$$\eta = A \frac{J_2(2\kappa\sqrt{x})}{x} \bigg/ \frac{J_2(2\kappa\sqrt{a})}{a} \cdot \cos(\sigma t + \epsilon).$$

We may note that if $m=1$, that is the depth varies as x , then equation (7) becomes

$$\eta = A \frac{J_n(2\kappa\sqrt{x})}{x^{n/2}} \bigg/ \frac{J_n(2\kappa\sqrt{a})}{a^{n/2}} \cdot \cos(nt + \epsilon).$$

X. *A Variant Proof of the Distribution of Velocities in a Molecular Chaos.* By PROFESSOR F. Y. EDGEWORTH, F.B.A., All Souls College, Oxford*.

THE received proofs of Maxwell's law involve the fundamental axiom of Probability, the stability of an average comparatively with its constituents. But the higher theory of Probability which deals with deviations from averages seems not to have been fully utilized. It follows from this theory that if there are a number of quantities from time to time assuming different values independently at random according to (almost) *any* law of frequency, then the average or sum or generally (almost) any linear function of these elementary quantities tends to fluctuate according to the *normal* (or "Gaussian") law of frequency. The randomness attributed to the elements is not incompatible

* Communicated by the Author.

with scientific order. The double aspect of law and chance is well illustrated by the sequence of digits in the development of mathematical constants when not periodical (and not commensurate with the arithmetical radix). For example, below are a set of forty-eight figures which were obtained as follows. The seventh digit in the logarithms of 101, 102 125 respectively having been noted, there was formed the (algebraic) sum of the differences between each digit and the mean of digits taken at random, viz. $4\cdot5$ (=the sum of the observed digits $-25 \times 4\cdot5$); and this aggregate was divided by 5. The result, $-1\cdot9$, having been recorded, another batch of twenty-five successive logarithms, beginning with that of 126, was similarly treated; and so on, for forty-eight batches of twenty-five elements, up to the logarithm of 1300. It will be seen that the group of compound quantities corresponds approximately to a normal error-curve for which the *mean* is zero and the *mean-square-of-deviation*, $8\cdot25$. Thus, whereas the *modulus* is $4\cdot062$, there ought to be half the total number of observations between the limits $\pm 1\cdot94$ ($=\cdot4769$ modulus); and four-fifths of the total number, say thirty-eight or thirty-nine, between the limits $\pm 3\cdot7$ ($=\cdot906$ modulus). In fact half the observations lie between $-1\cdot9$ and $+1\cdot7$; forty observations lie between $\pm 3\cdot7$.

The negative deviations from the Mean (zero), rearranged in the order of magnitude, are :

6·9, 6·5, 5·5, 3·5, 2·7, 2·7, 2·5, 2·5, 2·5, 2·3, 2·1, 1·9,
1·9, 1·7, 1·7, 1·5, 1·3, 1·3, 1·3, 1·3, 1·1, ·9, ·3.

The positive deviations from the Mean (zero) are :

·1, ·1, ·1, ·3, ·5, ·5, ·7, ·7, ·7, ·9, 1·1, 1·5, 1·5,
1·7, 1·9, 1·9, 2·3, 2·7, 2·9, 3·5, 4·9, 5·1, 5·3, 5·5, 6·5.

The character of the group would not have been sensibly altered if, instead of 25, we had used any other (tolerably large) number m , and divided the sum of deviations by \sqrt{m} . The correspondence with the normal law of frequency would be more perfect the larger m was; but the *mean* would still be zero, and the *mean square of deviation* $8\cdot25$. Nor would these characteristics be affected if we multiply any two assigned elements (*e. g.* the first and last) in each batch by $\sqrt{2} \sin \theta$ and $\sqrt{2} \cos \theta$ respectively. It comes to the same if we attach the sine and the cosine not to any assigned pair of elements but to any pair at random in each batch. Instead of $\sin \theta$ and $\cos \theta$ we might employ $\sin 2\theta$, $\sin 3\theta$... $\cos 2\theta$, $\cos 3\theta$... or their equivalents in terms of $\sin \theta$ and $\cos \theta$.

More generally, if $l, m, n \dots$ being any r (finite, not very unequal) factors with sum of squares equal to r , are sporadically attached to different elements in the successive batches, this modification of the elements will not sensibly alter the law of frequency for the compound. If the system of elements thus modified is similarly sprinkled with another, and another, set of similar factors $\lambda, \mu, \nu \dots$, the character of the compound still persists.

To apply this theory, let us begin by supposing the molecules to be perfectly elastic equal spheres. And let us simplify enunciation by conceiving a molecular chaos in *two* dimensions—as it were an enormous number of perfectly elastic billiard-balls repeatedly colliding with each other as they dash about at random over the smooth surface of an immense billiard-table with perfectly elastic cushions (compare Jeans, ‘Dynamical Theory of Gases,’ p. 4). The centre of gravity of the system may be supposed to be at rest. Let it be granted (*a*) (as usual, in accordance with the fact that the pressure of a gas at rest is equal in all directions) that the mean square of velocities resolved along each of two rectangular axes, OX and OY, is the same, (*b*) that there is reached a stable distribution of velocities, the same for velocities in either direction. Then, if possible, let that final law of frequency be other than the Gaussian law. At any time, T, after the state of complete chaos has been reached, consider the collision of two molecules of which the velocities are respectively (resolved in the direction of the two axes) u_s, v_s and u_t, v_t ; quantities which may be regarded as taken at random from the *melange* to which the final law of frequency is supposed to apply. The velocities after collision will depend not only on the velocities before collision, but also on the direction of the line joining the centres of the spheres at the moment of contact. Say that line makes the angle θ with the axis OX. Then the velocities of the ball, which before the collision were u_s, v_s , become after collision

$$\begin{aligned} u_s' &= (u_t \cos \theta + v_t \sin \theta) \cos \theta + (u_s \sin \theta - v_s \cos \theta) \sin \theta, \\ v_s' &= (u_t \cos \theta + v_t \sin \theta) \sin \theta - (u_s \sin \theta - v_s \cos \theta) \cos \theta. \end{aligned}$$

Likewise the expressions for u_t', v_t' are linear functions of the *four* velocities before the collision. Also other pairs of colliding particles acquire similarly compounded velocities. Thus after numerous collisions the velocity of a molecule in either direction may be regarded as a linear function of elements distributed according to a definite law of frequency,

and affected with factors such that the mean of the compounds is zero, while their mean square of deviation is constant. Therefore (as in the case of our digits sprinkled with sines and cosines) the final velocities (with mean and mean-square-of-error which will not be altered by continued collisions) will be distributed normally. The distribution at the time T was either not final, or not different from the normal.

It comes to the same if we place the epoch T *before* molecular chaos has been set up; and regard the u 's and v 's of colliding molecules as elements taken at random from an initial distribution of velocities which may be as different from the normal frequency as the distribution of digits (less by 4.5) above instanced. By parity of reasoning in the course of repeated collisions the system will work down to a stage in which the velocities are distributed according to the normal law. It may be observed that in this view of the proof the postulate (*b*) is replaced by one referring to an initial stage.

The reasoning is readily adapted to molecular motion in three dimensions; and to cases in which the centre of gravity is not at rest. The reasoning may be extended to molecules which are not spherical and not perfectly elastic; provided that the velocities consequent on repeated encounters continue to be (at least approximately) linear functions of the component velocities. When the mixture of molecules is not complete, as the stage of perfect chaos is being approached but is not yet reached, there is presumably fulfilled that approximation to the normal law of frequency which has been described as the Generalized Law of Error (see "The Law of Error," Cambridge Philosophical Transactions, 1905, and "The Law of Great Numbers," Journal of the Statistical Society, 1906, by the present writer).

XI. *Note on the Conduction of Heat along a Pipe through which Gas is Flowing, in its Relation to Measurements of the Specific Heats of Gases.* By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield*.

A FEW years ago the author measured the specific heats of Air and Carbon dioxide at constant pressure, and the results, which have since been confirmed by other investigators †, and which agree to one part in a thousand

* Communicated by the Author, having been read at the meeting of the British Association, 1912.

† Dugald Clerk, Report on Gaseous Explosions, B. A. Report, 1910; Scheele and Heuse, *Ann. d. Physik*, vol. xxxvii. Dec. 29, 1911.

with the theoretical value calculated from J. Joly's measurements of the specific heat at constant volume, give the specific heats of these gases about 2·5 per cent. higher than the values found by Regnault and many other investigators who followed him. In view of the great care with which Regnault's experiments were performed, it is natural, accepting the modern values as correct, to look for the explanation of the discrepancy as the outcome of some error inherent in the method adopted by Regnault. In my paper on the Measurements of the Specific Heats of Air and Carbon dioxide*, I advanced a suggestion to account for the error, and the object of the present paper is to record a simple experimental verification of that suggestion, and, incidentally, to point out how the error (which is a large one) may be estimated in any similar experiment in which it occurs.

Reviewing briefly the point in question, it will be remembered that in Regnault's experiments the alteration $\Delta\theta$ in the temperature of the calorimeter per minute due to radiation and to conduction through the pipe connecting the calorimeter to the heater, was written in the form $\Delta\theta = A - B\theta$, where θ is the excess of the temperature of the calorimeter over that of the room. The term A corresponds to the heat conducted through the connecting pipe from the heater to the calorimeter, and $B\theta$ to the heat loss by radiation from the calorimeter. Each of these terms corresponded to about 5 per cent. of the total energy supplied to the gas per minute. Regnault measured the constants A and B by noting the rate of rise of temperature of the calorimeter before and after the gas had passed through it. The error in question arises in assuming that the constant heat conduction through the pipe is the same when gas is flowing as when no gas is flowing. In fact, the hot gas keeps up the temperature of the pipe in the vicinity of the heater, and reduces the temperature gradient there. The result is that less heat is conducted from the heater into the pipe when the gas flows through, than when no gas is flowing. Of course, a great deal of heat is conducted by the pipe into the calorimeter when the gas is flowing, but the greater part of this comes from the gas itself. The fact that the average temperature of the pipe is higher when the gas is flowing also results in a greater radiation loss from the pipe. This error acts in the same direction as the other.

In the present experiment the gas was passed through a wide brass tube packed with copper gauze, and immersed in a heating bath provided with a stirrer. The wide brass tube

* Phil. Trans., A. vol. ccx. pp. 190-238.

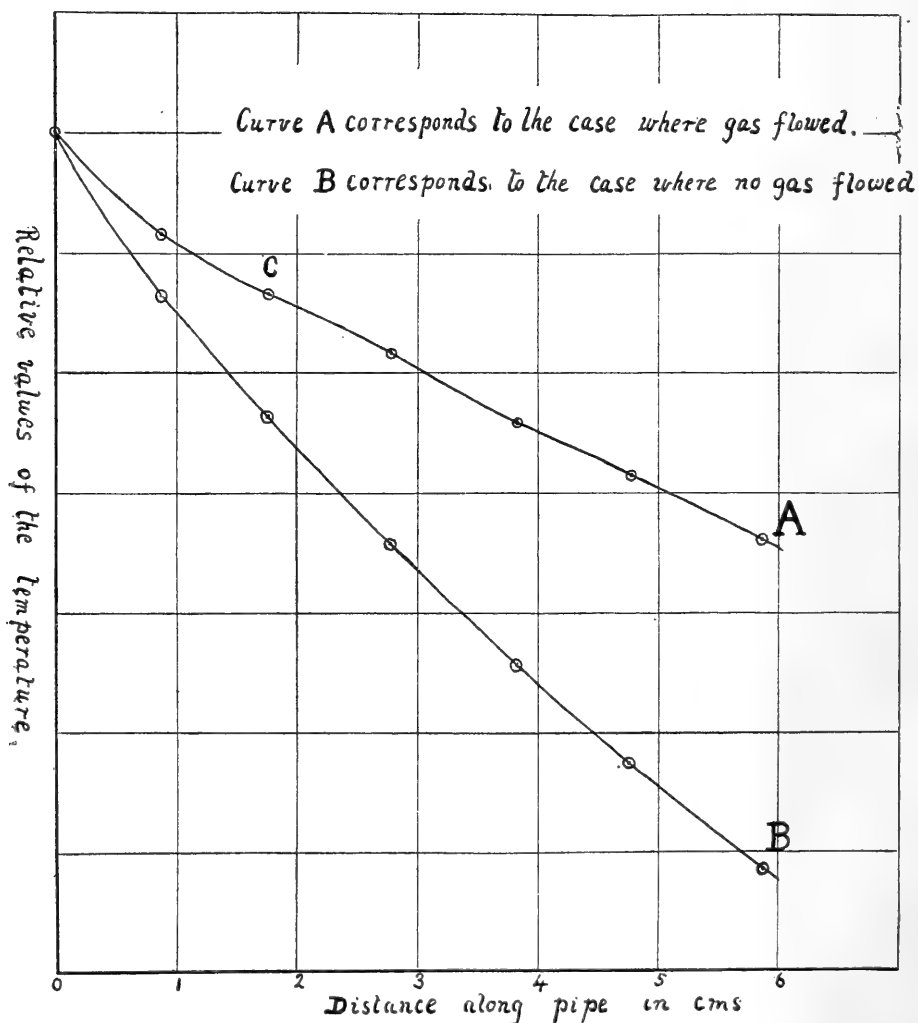
was continued into a copper tube 0.8 mm. in diameter, which passed through the wall of the heating bath and into a vessel of cold water which corresponded to the calorimeter of Regnault's experiment. The length of the pipe from heater to calorimeter was 10 cm., and the portion near the heater was surrounded by cork. The object of the experiment was to measure $-\left(\frac{\delta\theta}{\delta x}\right)_1$, the temperature gradient in the pipe in the vicinity of the heater when gas flowed, and the gradient $-\left(\frac{\delta\theta}{\delta x}\right)_2$ when no gas flowed through the pipe. Apart from certain minor considerations which will be referred to later, $\left(\frac{\delta\theta}{\delta x}\right)_1 / \left(\frac{\delta\theta}{\delta x}\right)_2$ represents the fraction of the measured heat conduction which should be taken if the apparatus were used for a specific heat determination with the corresponding rate of flow, and the heat conduction were measured in the manner adopted by Regnault.

If two german-silver wires are soldered to the copper tube near the heater, and connected to a galvanometer, we have a complete thermoelectric circuit, the german-silver being one element and the copper tube itself the other. The ratio of the deflexion δ_1 when gas flows to the deflexion δ_2 when no gas flows, gives the ratio of the temperature gradients referred to above. As a matter of fact, seven german-silver wires were soldered at different points extending to the end of the cork, *i. e.*, about half-way along the tube, and the deflexion corresponding to each adjacent pair was measured under the two conditions. The results were found not to vary very much with the rate of the flow, when that rate exceeded a certain minimum. The following results represent the mean for two experiments which agreed very well with each other, and corresponded to a rate of flow of about 0.5 litre per second. The numbers in the top line represent the various pairs of german-silver wires (counting from the heater) between which the temperatures were measured.

	1, 2	2, 3	3, 4	4, 5	5, 6	6, 7
Values of δ_2 ...	54.1	41.7	41.5	40.2	33.2	36.7
Values of δ_1 ...	33.5	21.0	18.7	23.0	17.5	22.2
Values of δ_1/δ_2 .	0.621	0.503	0.450	0.572	0.527	0.605

Great regularity cannot be expected, because the results depend to some extent on the closeness of fit of the cork, &c. The values of δ_1/δ_2 are considerably less than unity, as anticipated. Of course, if the temperature gradients had been measured farther along the pipe, *i.e.*, nearer to the calorimeter, we should have found values of δ_1/δ_2 greater than unity, for this ratio can only be diminished near the heater at the expense of being increased elsewhere.

By summing up the various differences in temperature, we can draw two curves illustrating the variations of temperature along the pipe for the two cases. These curves are shown in the figure, the temperatures being on the thermocouple



scale. The temperature corresponding to the calorimeter is at some unknown distance below the origin. If x represents a distance measured along the pipe $\frac{d^2\theta}{dx^2}$ is proportional to the

heat loss per square centimetre from the sides*. At the point C on the curve $\frac{d^2\theta}{dx^2}=0$, which means that at C the pipe is gaining as much heat from the gas as it is losing by radiation from its surface. At points to the left of C $\frac{d^2\theta}{dx^2}$ is positive, meaning that the pipe in this region is taking less heat from the gas than it is radiating from its surface. At points to the right of C, $\frac{d^2\theta}{dx^2}$ is negative, meaning that, owing to the greater difference in temperature between the gas and the pipe and the lower temperature of the latter, the pipe is taking in more heat from the gas than it is radiating from its surface. The smallness of the supply of heat from the gas to the pipe in the immediate vicinity of the heater results in δ_1/δ_2 for that region being larger than it is a little farther along the pipe. On the other hand, at greater distances from the heater δ_1/δ_2 starts to increase again, since the pipe must enter the calorimeter at the temperature of the latter. The minimum value of δ_1/δ_2 is to be found neither too near nor too far from the heater.

Now let us consider what fraction of the constant A occurring in Regnault's correction formula should be taken in a specific heat determination with the present apparatus. Consider any point P of the pipe. Let H be the heat conducted past this point per minute when no gas is flowing, and let ΔH be the amount which is radiated from the pipe between P and the calorimeter. The amount of heat entering the calorimeter is $H - \Delta H$. When gas flows through the pipe, the amount of heat conducted past P per minute is $H\delta_1/\delta_2$, and since the average temperature of the pipe between P and the calorimeter is higher than when no gas was flowing, the amount of heat entering the calorimeter exceeds that which the gas has lost in its fall in temperature from the heater to the calorimeter, by an amount which is less than $H\delta_1/\delta_2 - \Delta H$, and is therefore certainly less than $(H - \Delta H)\delta_1/\delta_2$. Hence the ratio of the amount of heat which gets from the heater to the calorimeter solely through the pipe when the gas is flowing, to the quantity which gets through when no gas is flowing, is certainly less than the minimum value of δ_1/δ_2 for the whole pipe, which in the present case amounts to about 0.45. It is interesting to observe that this is just about the value necessary to bring Regnault's experiments into agreement with my own, though, of course, no great significance can

* It is supposed that the pipe is thin-walled, so that there is no appreciable radial temperature variation.

be attached to this, in view of the fact that in the present experiments I have made no serious attempt to reproduce Regnault's conditions. A measurement of the minimum value of δ_1/δ_2 on the apparatus actually used by Regnault would probably, when used in conjunction with the values of A and B, found by him, cause his observations to lead to values of the specific heats much nearer the values now generally accepted*.

It may be remarked that in such an experiment as that of Regnault, a knowledge of the temperature distribution along the pipe would lead to an estimation of the correction for radiation from the pipe, as well as conduction through it, without any independent measurements of the emissivity of the surface, for suppose suffix *a* refers to the heater and suffix *b* to the calorimeter, and suppose that dashed letters refer to the case where no gas flows, and undashed letters to the case where the gas is flowing. If H is the total heat given out by the gas per minute due to its fall from the temperature of the heater to that of the calorimeter, Q the heat received by the calorimeter per minute, including the portion which is afterwards radiated from the calorimeter, $\bar{\theta}$ the mean excess temperature of the pipe above its surroundings, as determined from the curve, *p* the quantity by which $\bar{\theta}$ must be multiplied in order to obtain the heat radiated from the pipe, and *k* the quantity by which $-\frac{d\theta}{dx}$ must be multiplied in order to obtain the heat conducted past any cross-section of the pipe per minute, we have, when gas is flowing,

$$H - k\left(\frac{d\theta}{dx}\right)_a = Q - k\left(\frac{d\theta}{dx}\right)_b + p\bar{\theta}. \quad . \quad . \quad . \quad (1)$$

When no gas is flowing through the pipe we have,

$$-k\left(\frac{d\theta}{dx}\right)_a' + k\left(\frac{d\theta}{dx}\right)_b' = p\bar{\theta}', \quad . \quad . \quad . \quad (2)$$

$$-k\left(\frac{d\theta}{dx}\right)_b' = AM, \quad . \quad . \quad . \quad (3)$$

where A is Regnault's constant, measured in the manner adopted by him and M is the thermal capacity of the calorimeter and contents. The temperature gradients are all known from the curves, thus (3) gives *k*, *p* is obtained by substituting

* The alteration of the radiation from the pipe caused by the flow in Regnault's experiments was probably small, as owing to the short length of the pipe the whole radiation would be small.

in (2), so that all the quantities required by (1) in order to give H in terms of the measured quantity Q are known. Q has of course to be corrected for radiation from the calorimeter, but this presents no difficulty. The constant B occurring in Regnault's correction formula is correctly determined by his method, and is not affected by the flow. It is quite easy to extend the above argument to the case where the connecting pipe really consists of two pipes of different materials, as in some of Regnault's experiments.

Physical Laboratory,
The University, Sheffield.
Oct. 18, 1912.

XII. *The Photoelectric Properties of Thin Films of Platinum.*—Part II. By J. ROBINSON, M.Sc., Ph.D.*

Introduction.

1. IT was shown by Stuhlmann* that the photoelectric effect of thin films of different metals deposited on quartz depends on the thickness of the film, and on whether the film is on the side of the quartz facing the light (incident effect), or on the side away from the light (emergent effect). He measured the ionization currents in air, and found that when the films are thin enough the ratio $\frac{\text{emergent}}{\text{incident}} \left(\frac{E}{I} \right)$ currents is greater than unity, and for thicker films less than unity. For thin films the ratio is constant and equal to 1.14 for platinum.

In a former paper by the writer† it was shown that this dissymmetry observed by Stuhlmann can be separated into two quite distinct effects, as regards (1) the velocities of the electrons emitted, and (2) the actual numbers of electrons emitted. The films were deposited at a low pressure, and then a liquid-air vacuum was established and measurements made as quickly as possible afterwards. In this way it was hoped that true values for the velocities would be obtained. For both the photo-currents and the maximum velocities of the electrons, similar curves to that of Stuhlmann for the ratios $\left(\frac{E}{I} \right)$ ionizations were obtained as the thickness of the

* Communicated by the Author. An account of part of this paper was read at the British Association Meeting at Dundee, September, 1912.

† Phil. Mag. Aug. 1910, p. 331.

‡ Phil. Mag. April 1912, p. 542.

film was altered, *i. e.* for thin films the emergent velocities and currents were larger than the incident velocities and currents, and *vice versa* for thick films. It was also found that the dissymmetry for the velocities was not so marked as for the currents.

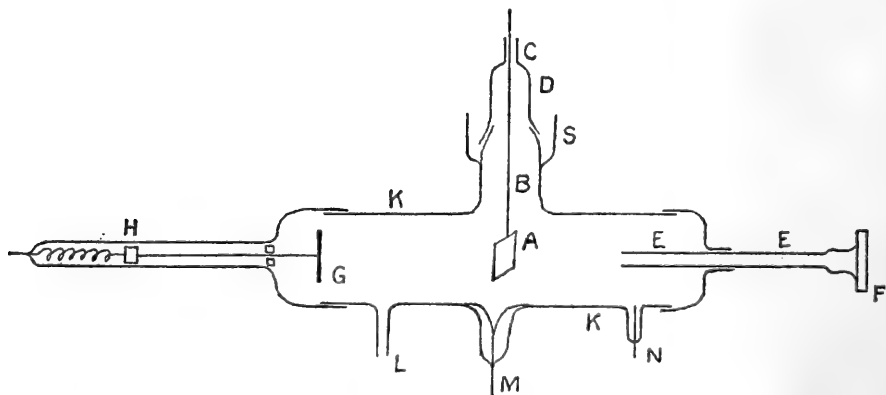
2. The present investigation was undertaken to get more knowledge of these effects. The points investigated fall under the four heads :—

- (a) There is a certain thickness of film for which the ratio $\frac{E}{I}$ currents=unity, and also a thickness for which $\frac{E}{I}$ velocities=unity. It was desired to find whether for the same source of light these two thicknesses of film are the same.
- (b) The variation of the actual magnitude of the photocurrent (incident and emergent) was investigated for different thicknesses of film.
- (c) Whether the dissymmetry is a function of the actual magnitude of the velocity of the emitted electrons.
- (d) Whether the angle of incidence and the orientation of the plane of polarization of the light influences the dissymmetry.

3. Apparatus.

The apparatus used was similar to that described in the forementioned paper. Modifications were introduced to make still more sure that the effect of reflected light was reduced to a minimum, and that the film was uniform.

Fig. 1.



These improvements consisted in making the tube KK (fig. 1) wider (7 cm. diameter), the inlet for the light narrower, and the platinum electrode G larger. As before

the walls of the vessel were coated with platinum before commencing the actual experiments, and the potential of the walls controlled by the wire M which was made to touch the platinized walls. The quartz plate A was 1.5 mm. thick, and 2.5 cm. long by 2 cm. wide. It was attached rigidly to the rod B, insulated by an amber plug C, and was capable of rotation about B as axis by the ground joint S. To deposit a film on the quartz plate A, the platinum electrode G was moved up to a fixed distance of 1 inch from it, and a discharge passed from an induction-coil, using G as cathode and an insulated wire at N as anode. This was done at a low pressure, and in most cases before depositing the discharge was passed for a few hours with G far removed from the quartz plate A which was placed with its plane parallel to the axis of the tube KK. This precaution was taken so as to get rid of any impurities on the surface of the platinum electrode, and to get it into the condition that it has stopped giving out gas*. The gas given out by the platinum was pumped away by a Gaede pump, and only when the amount given out per minute was small was a film deposited.

After depositing a film, a liquid air vacuum was obtained and measurements made. Then the film was thickened slightly and the measurements repeated, and so on till the film was so thick that the emergent effect was small.

Electrical contact with the film was made by first of all depositing a thick film of platinum on one end of the quartz plate. Tinfoil was laid over part of this, and the plate held firmly in a clamp which was soldered to the rod B. Platinum was deposited over this whole system. In some experiments the edge of the plate was silvered instead of being thickly coated with platinum.

The tube EE to admit the light was narrow so that light fell only on the centre of the film.

The rod B was connected in the ordinary way to one pair of quadrants of a Dolezalek electrometer. Measurements of the velocities of the electrons were made by earthing the walls of the vessel and finding the maximum potential acquired by the film. In some cases the velocities were also measured by finding the retarding potential that must be applied to the walls to prevent a photoelectric leak. The currents were measured by charging the walls to a potential of + 60 volts. The quadrants were joined through a high resistance of xylol and alcohol of 10^{10} ohms †,

* Hodgson, *Phys. Zeit.* 1912, p. 595.

† Campbell, *Phil. Mag.* Aug. 1911, p. 301.

and the steady deflexion read. On certain occasions this high resistance was dispensed with, and the leak measured directly.

As source of light a quartz mercury lamp was used. For some experiments a spark was also used.

4. *Corrections for Velocity Measurements.*

Some attention has recently been given to accurate measurements of the photoelectric velocities. Hughes* has shown that by distilling metals in vacuum, velocities can be measured accurately, and quite free from the errors introduced by surface films. For the purposes of the present investigation, the method for obtaining films, that of sputtering, is preferable to the distillation method, for it is easier to estimate the thickness of sputtered films, and possibly they may be of more uniform thickness over the whole of the quartz plate than if they had been distilled. An objection might be raised to the method of sputtering because the electric discharge may cause some kind of polarization of the film. Hughes† refers to such an influence of the discharge on thick electrodes, where it is possible to increase the maximum potential attained under exposure to light by using the electrode as a cathode in a discharge for a short time.

In the present experiments consistent values for the maximum potential were obtained for any one film. The velocities generally varied from film to film, but with very few exceptions they ranged from 2·3 to 2·9 volts. These do not differ much from the velocities given by Hughes for most of the metals that he distilled, and as he proved that the distillation method gave films free from gas layers, we are justified in concluding that the present method achieves the same result.

It is not in the scope of the present work to investigate the actual distribution of velocities, although the apparatus was designed in such a way as to make this possible if necessary. A disturbing factor in such investigations, and as was suggested by V. Baeyer‡ also in velocity measurements, is the reflexion of electrons from the walls of the vessel. If this has to be taken into account, we must know how the emission of photoelectrons depends on the angle of emission. Hughes§ came to the conclusion that the emission is the same for all angles, but this is not in harmony with some measurements made by the writer on

* Phil. Trans. A, vol. 212. p. 205 (1912).

† Proc. Camb. Phil. Soc. xvi. p. 167 (1911).

‡ *Verh. d. deutsch. Phys. Ges.* x. p. 96 (1908).

§ *Loc. cit.*

different metals *. It was shown that the greatest emission is normal to the electrode, and as the angle increases the emission diminishes. This point need not be considered further with regard to the velocity measurements, as it seems unlikely that reflected electrons can alter the maximum potential attained by the radiated films †.

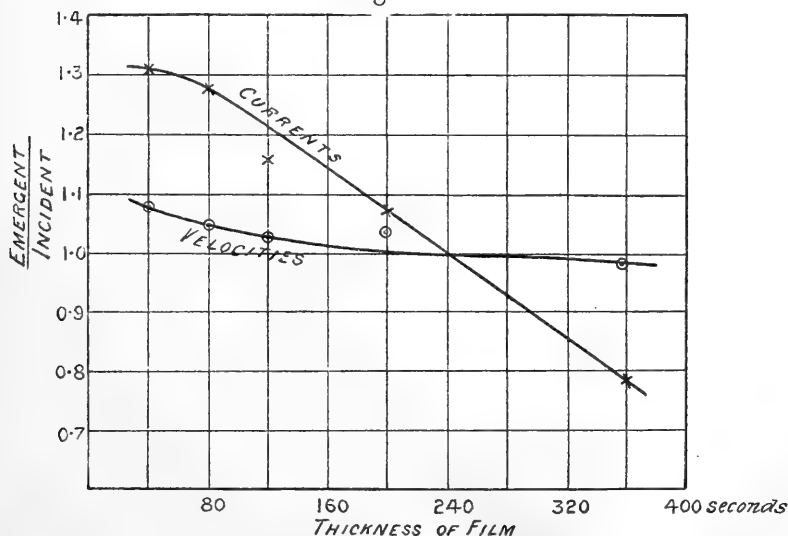
5. Measurements of the Ratios $\frac{E}{I}$.

The results for one series of experiments to find how the ratios $\frac{E}{I}$ currents and $\frac{E}{I}$ velocities vary with the thickness of the film are shown in Table I. The relative

TABLE I.

Thickness of Film.	$\frac{E}{I}$ currents.	$\frac{E}{I}$ velocities (in volts).
40 seconds	1.311	1.071
80 " 	1.281	1.041
120 " 	1.154	1.022
200 " 	1.063	1.033
360 " 	0.787	0.977

Fig. 2.



thicknesses of the films are given in terms of the time of deposit. The results of this table are shown graphically in fig. 2, where the ratios $\frac{E}{I}$ currents and $\frac{E}{I}$ velocities are

* *Ann. der Phys.* Bd. xxxi. p. 791 (1910).

† Ladenburg, *Phys. Zeit.* viii. p. 590 (1907); Hughes, *loc. cit.*

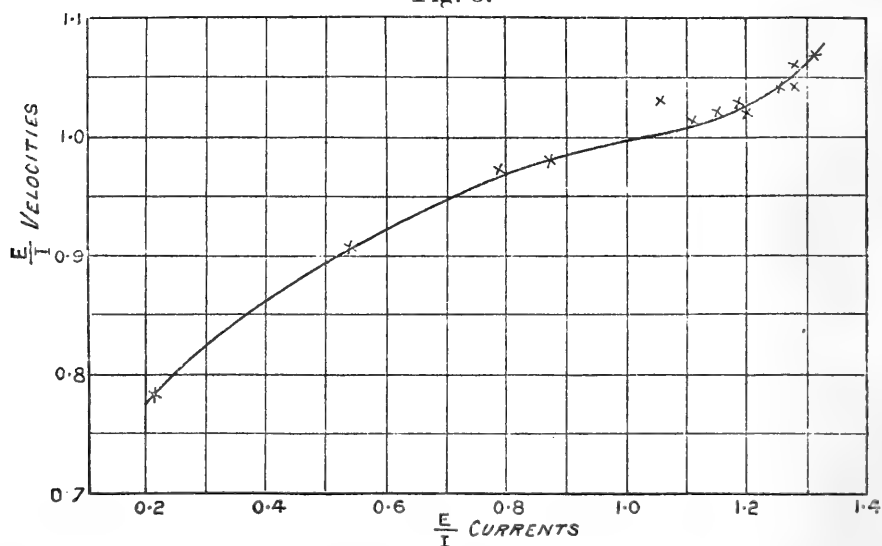
both plotted as ordinates against the thickness of the film. The two curves pass through the ratio unity together. The larger dissymmetry for currents than for velocities is well marked.

In order to determine more accurately whether the curves actually do pass through the value unity together, the results for a number of series of experiments are given together in Table II. The films are numbered in the order in which they

TABLE II.

Number of Film.	$\frac{E}{I}$ currents.	$\frac{E}{I}$ velocities (in volts).
11th	1.311	1.071
16th	1.281	1.062
12th	1.281	1.042
9th	1.259	1.049
7th	1.230	1.035
10th	1.200	1.020
1st.	1.185	1.030
13th	1.154	1.022
8th	1.116	1.014
14th	1.063	1.033
3rd	0.870	0.980
15th	0.787	0.977
2nd	0.570	0.915
4th	0.540	0.903
5th	0.206	0.784

Fig. 3.



were made. In fig. 3 the ratios $\frac{E}{I}$ currents are plotted as abscissæ and the corresponding ratios $\frac{E}{I}$ velocities as

ordinates. A smooth curve drawn through the points is found to pass as nearly as possible through the point 1, 1. Hence we find that the ratios $\frac{E}{I}$ currents and $\frac{E}{I}$ velocities are unity for the same thickness of film.

6. *Actual Magnitudes of the Photo-Currents.*

No attempt was made in the experiments just described to compare the actual magnitudes of the photo-currents for different film thicknesses, but it was noticed that these currents were certainly not proportional to the thickness of the film. Attention was now directed to this point. It was found to be unnecessary to correct for any variations in the intensity of the mercury lamp used, as this formed a very constant source of ultra-violet light. From a large number of experiments the same general results were obtained. A typical set is given in Table III. The emergent and incident currents are both plotted against the thickness of the film in fig. 4 (p. 122).

TABLE III.

Thickness of Film.	Photo-Currents.		$\frac{E}{I}$.
	Emergent E.	Incident I.	
20 seconds	5.4	3.8	1.21
40 ,, 	6.5	4.7	1.22
60 ,, 	11.5	8.5	1.27
100 ,, 	378	310	1.21
140 ,, 	230	197	1.16
180 ,, 	198	180	1.10

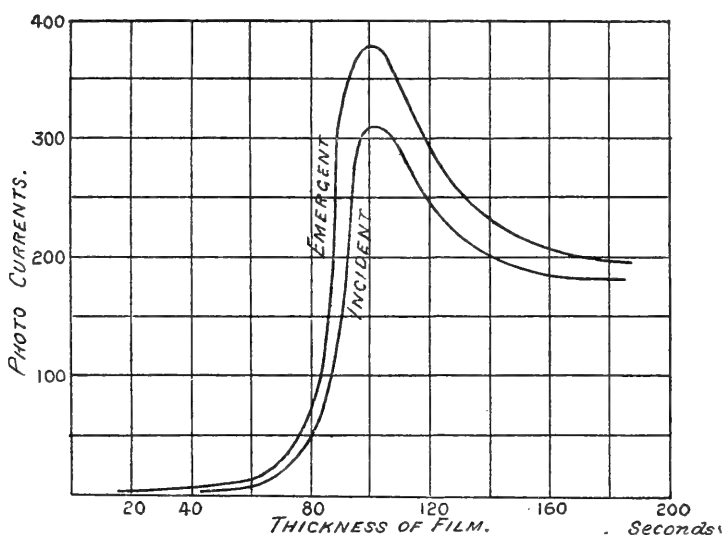
The most striking point about these results is the sudden increase in current at a certain thickness of film. An estimate of this thickness was obtained in the following way:—

After the photoelectric measurements were completed, the discharge was passed for a definite time to obtain a thicker film for which the specific resistance is known fairly accurately*. The resistance of this thick film was measured and its thickness calculated, making use of Paterson's values. From the relative times of deposit, the thickness of the film

* Paterson, Phil. Mag. iv. p. 652 (1902).

at which the sudden increase in current takes place was found to be 10^{-7} cm.

Fig. 4.



Another point of interest is the decrease in the magnitude of the currents for films thicker than 10^{-7} cm. It was at first thought that this diminution was spurious, and that it was due to the films beginning to absorb any traces of gas left in the apparatus. The consistency with which this effect was obtained in later experiments leads to the belief that it is not spurious, and that it is in some way connected with the sudden rise in current preceding it.

Still another point of interest is the fact that for films thinner than 10^{-7} cm. the ratio $\frac{E}{I}$ currents is practically constant, and that it only begins to diminish when the sudden rise in the actual magnitude of the currents takes place.

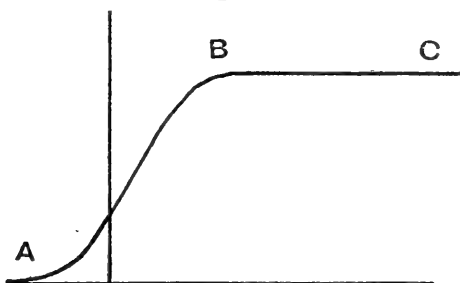
7. Maximum Values of the Ratio $\frac{E}{I}$.

The constant value of the ratio $\frac{E}{I}$ currents for films thinner than the critical thickness 10^{-7} cm. was well marked in all the experiments performed. This ratio was found here to be at least 1.22, whilst Stuhlmann did not obtain experimental values greater than 1.14. This difference is so considerable that it was necessary to inquire whether there was some flaw in my apparatus. One of the films which gave a ratio 1.26 was taken, and the conditions of the experiment

altered in various ways to find whether the ratio could be changed. Measurements of $\frac{E}{I}$ currents were made :—

- 1st. With the apparatus as already described, just after depositing a film.
- 2nd. At atmospheric pressure, and at various pressures down to a liquid-air vacuum.
- 3rd. By varying the potential of the walls, but so as to be always high enough for the current to be on the part BC of the distribution curve.

Fig. 5.



- 4th. After standing in air for a few days.
- 5th. After removing the platinum electrode G from the apparatus altogether to find whether light reflected from it had an influence.
- 6th. With the platinized walls covered with soot to be absolutely sure that reflected light from the walls had no influence.

None of these modifications produced any appreciable change in the ratio 1.26, so that the conclusion can be drawn that this maximum ratio $\frac{E}{I}$ can have larger values than 1.14 given by Stuhlmann.

8. *Influence of different sources of Light.*

It was at first intended to investigate the influence of the wave-length of the light used on the dissymmetry. It is very probable that this has some influence, for the velocity of the photoelectrons depends on the frequency. Millikan* has recently shown that there is a method for varying the velocities of the photoelectrons which gives much wider ranges than can be obtained by sifting out the different frequencies from a mercury lamp. Whilst the arc can only produce velocities up to about 3 volts, by using a spark as source of light, velocities can be obtained as high as 500 volts. If the velocities of the electrons affect the dissymmetry, this will be

* *Verh. d. deutsch. Phys. Ges.* No. 14, p. 712 (1912).

detected most quickly by comparing the effects due to the light from a spark and from a mercury arc *.

A spark was obtained between brass terminals, and was excited by an induction-coil through the primary of which an alternating current was sent. The capacity in parallel with the spark-gap was varied, and Millikan's results verified that in this way the photo velocities could be altered considerably. The spark-gap was arranged between the mercury lamp and the photoelectric cell so that the photo-current from each could be measured at will. The intensity of light from the spark was also very constant so that no corrections for variation in intensity were necessary. A liquid-air vacuum was not obtained, but the pressure was kept as low as possible by a Gaede pump. The orders of the velocities obtained were 1-2 volts from the arc, and 50 volts from the spark.

A whole series of films was investigated as in the preceding sections, and the photo-currents (incident and emergent) measured for each source of light. In Table IV. the actual

TABLE IV.

Thickness of Film.	Arc.			Spark.		
	Currents.		$\frac{E}{I}$	Currents.		$\frac{E}{I}$
	E.	I.		E.	I.	
20 seconds ...	3	2	1.16	2	1.5	1.27
40 ,, ...	4	2		
60 ,, ...	37	32	1.16	32	27	1.20
80 ,, ...	560	480	1.17	185	148	1.23
110 ,, ...	440	430	1.024	128	119	1.075
140 ,, ...	250	310	0.79	84	99	0.85
	Velocities.		$\frac{E}{I}$	Velocities.		$\frac{E}{I}$
	E.	I.		E.	I.	
140 seconds ...	1.5 Volt.	1.8	0.83	51 Volts.	54	0.94

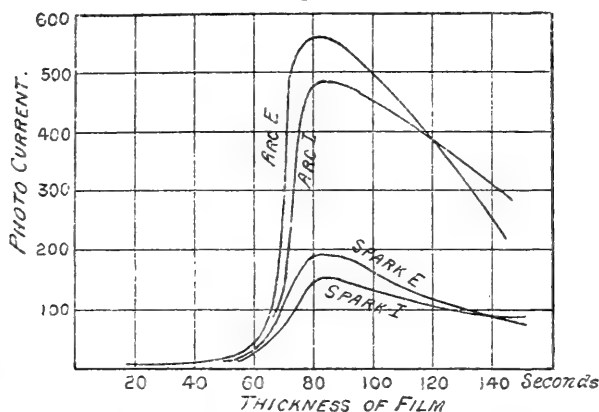
magnitudes of the currents are given in scale-divisions of the electrometer, as well as the ratios $\frac{E}{I}$ currents. The results

* In making measurements on this point, I was assisted by Mr. J. W. Buckley, of Sheffield University, to whom I express my best thanks.

are plotted to show the influence of the thickness of the film on

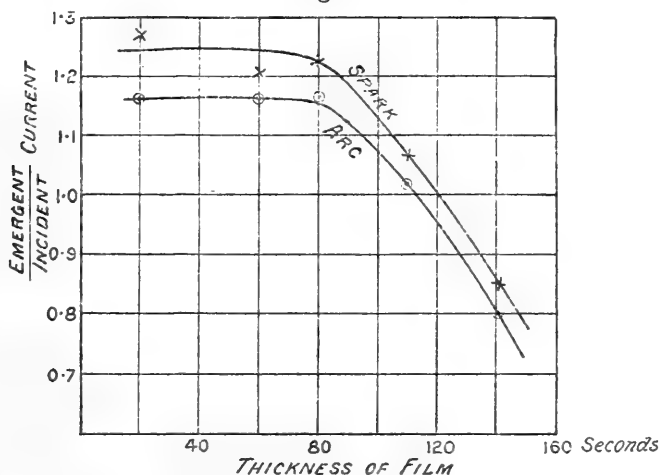
- (a) The actual magnitude of the currents (fig. 6) ;
- (b) The dissymmetry (fig. 7).

Fig. 6.



From fig. 6 it is seen that for both sources of light there is a certain thickness of film for which the photo-current begins to increase rapidly, and that this thickness is the same

Fig. 7.



for both sources. The relative increase in current is larger for the arc than for the spark. As before, a diminution of the photo-currents sets in after the sudden increase. Fig. 7 shows that the dissymmetry is obviously a function of the velocity of the electrons emitted, and that the larger the velocity, the larger is the dissymmetry. Other inferences that can be drawn from these results are :—

- (a) The thickness of film which makes the emergent current equal to the incident is greater the greater the maximum velocity of emission.

(b) Although the velocities are only given for one film, the dissymmetry is not so marked as for the currents.

(c) The maximum value of the ratio $\frac{E}{I}$ currents for the arc is now smaller than in the preceding experiments, and now they agree more nearly with the value given by Stuhlmann. As the apparatus was not altered at all, we must conclude that the films are modified by allowing the spark radiations to fall on them, and in such a way as to diminish the ratio $\frac{E}{I}$ as measured with the arc as source of light.

9. *Influence of the angle of incidence and the orientation of the plane of polarization of the light on the dissymmetry.*

In the experiments described up to the present only normal incidence of light was used. If the apparatus described is used for oblique incidence, then more attention ought to be directed to the influence of reflected light. Because of this, only measurements of the photo-currents were made, and no attention paid to the velocities. The walls of the vessel were blackened and kept at a potential of +60 volts. To polarize the ultra-violet light, Prof. W. M. Hicks kindly placed a calcite polarizer at my disposal.

The actual magnitudes of the currents were found to increase slightly as the angle of incidence was increased up to 45° , whether total light or light polarized parallel to or perpendicular to the plane of incidence was used. On the other hand, it was not found possible to establish an influence of the plane of polarization on the dissymmetry, as Table V. shows. The variations are small and irregular, so that they are most probably due to experimental errors.

TABLE V.

Thickness of Film.	Angle of Incidence.	$\frac{\text{Emergent}}{\text{Incident}}$ Currents.	
		E \parallel	E \perp
< 10^{-7} cm. ...	0°	1.14	1.15
	32°	1.12	1.145
> 10^{-7} cm. ...	0°	0.85	0.83
	32°	0.84	0.85

Discussion.

10. If we wish to explain the variation of the magnitude of the photo-current with the thickness of film, we must also take into account some results recently given by Dyke * on the variation of the photo velocities with the film thickness. His results are given only for the incident effect. Velocity measurements involve so many difficulties that no regular curves were obtained, but a general statement of Dyke's results is that for films thinner than 10^{-7} cm. the velocities are high, and for thicker films much lower. This thickness 10^{-7} cm. is also a critical thickness for the velocities, which undergo a sudden decrease here.

We will consider the merits of certain possible explanations of these photoelectric phenomena at the thickness of film 10^{-7} cm.

(a) It was shown by Paterson † that the specific resistance of thin films of platinum depends on the thickness. As the thickness diminishes from 10^{-6} cm. the specific resistance remains fairly constant till the thickness 10^{-7} cm. is reached, when it begins to increase rapidly. As this sudden change in specific resistance occurs for the same thickness as the change in the photoelectric effects, it might be suggested that the high resistance of films thinner than 10^{-7} cm. accounts for the small values of the photo-currents observed. This is, however, improbable, for when measurements of the current were made by the leakage method no lag of the electrometer needle was observed, and such would certainly have been observed if the films had an enormously high resistance. The readings of the currents were always steady and very consistent for the thinnest films.

(b) Again, no satisfactory explanation can be found by considering the films to be discontinuous. Such discontinuities obviously will exist for very thin films, but as long as there is some metal on the quartz plate, the film will conduct if there is no break right across it of more than about .001 inch in width. Wood ‡ has recently shown that conduction can take place between two metals kept at this distance apart. Discontinuities might exist so that the film appears something like a draughts-board. As more metal is deposited the empty spaces left get gradually filled up. Hence the area of metal exposed to the light might alter with the time of deposit. It is, however, difficult to see how an explanation can be reached along this direction.

* *Phys. Rev.* xxxiv. p. 459 (1912).

† *Loc. cit.*

‡ *Phil. Mag.* Aug. 1912, p. 316.

(c) The effects do not seem to be due to gas layers at the surface of the films. In most of the experiments when the greatest precautions were taken, there were most probably no such gas films. Had there been any they would most probably have influenced thin films and thick films alike.

(d) Possibly platinum films can only absorb gas when their thickness is greater than 10^{-7} cm. If we make this assumption, and assume besides that the photoelectric effect is due to absorbed gas as well as to the metal, then the sudden increase in current can be explained. There would also be many more molecules about in proportion to the thickness at 10^{-7} cm. than for thinner films, so that the photoelectrons would have their energy reduced by collision. Hence we might account for a decrease in velocity also. But although the photoelectric effects may be in harmony with this view, it is difficult to see why the specific resistance should diminish so much when gas is absorbed.

(e) There may be some alteration in the power of films to absorb light at 10^{-7} cm. We might suppose that there is a sudden increase in the absorption of light and so account for the sudden rise in current, but such an assumption would not be in harmony with the diminution of velocity, for it is generally supposed that the photo velocities are independent of the intensity of light, and of the amount of light absorbed.

(f) An explanation which is in harmony with all the facts known at present is the following:—

Let us suppose that the photoelectrons have the power of ionizing molecules of platinum by colliding with them. Then there will be two kinds of electrons in the photoelectric effect of thick metals: "primary," which are produced by light falling on molecules, and "secondary," which are produced by the collision of the primary electrons and molecules. To have both kinds of electrons in a film the thickness must be greater than a certain quantity λ , which we may call the mean free path of the electrons. For films thinner than λ we have only primary electrons, and for those thicker than λ , both primary and secondary. This accounts for the sudden increase in photo-current if the thickness at which it takes place is equal to the mean free path of electrons in platinum. An estimate of this quantity was given by Paterson * from measurements of the Hall effect, and he found λ of the order of 10^{-7} cm., which is the critical film thickness for the photoelectric phenomena.

* *Loc. cit.*

If primary electrons can produce secondaries by collision, then we ought to expect a diminution in the velocity of the electrons at 10^{-7} cm., which is what Dyke found.

The fact that the critical thickness is the same for the slow electrons produced by the arc and the quicker electrons due to the spark, is also in harmony with this view, for the mean free path of the electrons does not vary much with their velocity.

Again, for films thinner than the mean free path, the photo-currents will not be influenced by the absorption of electrons, which can only take place when the electrons come near to the molecules. This explains why the ratio $\frac{E}{I}$ currents is constant for thicknesses up to 10^{-7} cm. For thicker films, absorption will take place so that the ratio $\frac{E}{I}$ begins to diminish.

11. *Minimum Energy for Ionization.*

It is necessary to consider whether slow photoelectrons have sufficient energy to ionize molecules of platinum. Estimates of the minimum amount of energy required to ionize a molecule have been given by different writers. Hughes* estimates this quantity to be that of an electron of 8 volts velocity for oxygen.

The similarity of the curves for the arc and the spark in fig. 6 suggests that their characteristics have the same origin. There is no doubt that the 50 volt electrons produced by the light of the spark can ionize, and as all the other facts agree with this ionization theory, we conclude that it is possible that the slow photoelectrons due to the arc also have sufficient energy to ionize.

The method employed by Hughes to calculate the minimum amount of energy required to ionize a molecule of oxygen is interesting, and it can readily be applied to the present problem. He found that to ionize oxygen by light, the wave-length must not be longer than λ 1350. He showed how to represent the velocity of photoelectrons as a function of the frequency of the light. If V is the velocity in volts, and n is the frequency of the light,

$$V = kn - V_0,$$

where k and V_0 are constants for each substance. As λ 1350 is the wave-length limit for oxygen, an electron emitted by light of this wave-length would just emerge from

* *Loc. cit.*

the molecule, and thus $V=0$. V_0 is the energy that an electron must acquire in order just to emerge from a molecule. Hence, for oxygen, $V_0=kn$, where n is the frequency corresponding to λ 1350.

He did not investigate the law for platinum, but he showed that it holds rigorously for a large number of metals and also that k does not vary much from metal to metal. We will take k for platinum to be the mean for the different metals investigated, i. e. $k=3.62 \times 10^{-15}$, and assume that the longest wave-length which is capable of producing a photoelectric effect in platinum is $\lambda=3400$, which was near the wave-length limit for cadmium.

This gives $V_0=3.25$ volts, which gives the minimum energy to produce a photoelectron in platinum. If there are electrons in the metal with velocities larger than this, then it will be possible to produce secondary electrons by collision. By the application of the law $V=kn-V_0$ we can easily find whether there are electrons present with velocities greater than 3.25 volts. By assuming a high enough value for n , and this is only limited by the temperature of the lamp and the absorption of quartz, electrons can be found with velocities greater than 3.25 volts. This limitation of quartz on the frequency may prove a drawback. For instance, if λ 1849 is the shortest wave-length which falls on the film, we find V to be 2.65 volts, which is less than the minimum to produce ionization. [This theoretical value for the maximum velocity agrees fairly well with the actual values observed, see § 4.]

The discovery of Dyke enables us to get over this difficulty. For thin films the maximum velocity is much larger than for thick films, and Hughes's results only apply to thick films. If we take a moderate estimate of the ratio of the velocities for thin films to those for thick films as 3, from Dyke's results, there will be electrons in ordinary thick metals with velocities of 2.65×3 volts, which is well outside the limit of 3.25 volts required for ionization to be possible.

12. The decrease in magnitude of the photo-currents following after the sudden increase can possibly be explained by an absorption of the electrons. The incident current does not decrease as much as the emergent, for the ratio $\frac{E}{I}$ diminishes. If the experiments had been extended to much thicker films, possibly the incident current would have been found to increase again; for Ladenburg showed

that as the thickness of nickel increases up to about 8 wave-lengths, the incident photo-current increases. It attains its maximum value when all the light is absorbed.

Another estimate of the maximum depth for platinum at which light can produce a photoelectric effect can be obtained from measurements of the emergent current. We find by extrapolation in fig. 2 that the emergent current would be zero at about 5×10^{-6} cm. This means that the light can produce electrons only to a depth less than 5×10^{-6} cm. This estimate of the maximum depth to which light can produce electrons is much smaller than that of Ladenburg, who found it to be 8 wave-lengths, or of the order of 10^{-4} cm. This discrepancy may be due to the fact that the estimates are given for different metals.

13. As to the causes of the dissymmetrical effect it is very difficult to suggest a satisfactory explanation. As more electrons emerge in the direction of the light, and as they have a larger velocity in this direction, there must be some influence at work in the actual process of causing electrons to leave the molecules, which tends to make them emerge more readily in the direction of the light. If this were not the case, and if electrons emerge from molecules equally in all directions, then we should be left with the task of explaining the dissymmetry by the pressure of light on the electrons after they have emerged from the molecules. Such a consideration does not appear to account for the magnitude of the dissymmetry.

It may be asked why the emergent velocity diminishes as the thickness of the film increases. All the films used were semitransparent. Hence some light gets right through the films, and as these films absorb all wave-lengths uniformly* some ultra-violet light also gets right through. If the general view is correct that the velocity of photoelectrons is independent of the intensity of the light used, then we ought not to expect the emergent velocity to diminish so long as some light goes right through the films. As the emergent velocity does diminish we may account for it by some assumption as:—

- (a) Perhaps light must have a certain minimum intensity to produce electrons ;
- (b) Possibly the velocity of the electrons is a function of the intensity of the light ;

* Robinson, Phil. Mag. April 1912, p. 549.

- (c) Possibly some part of the photoelectric effect is due to some other radiation accompanying ultra-violet light, which radiation is more easily absorbed by platinum than light. Millikan's* work seems to show that this is not very probable.

Prof. C. H. Lees suggested another possibility to me, that the form of the light-waves may have an influence on the dissymmetry. It is supposed that light-waves are modified in going through matter. Some experiments were performed by Stuhlmann† which seem to support this view. He showed that the dissymmetry was much less marked when the light had to pass through a greater thickness of quartz, and explained this by the absorption of light by quartz. As quartz does not absorb ultra-violet light appreciably, it seems probable that the view here suggested might have some bearing on the dissymmetry.

14. *Summary of Results.*

1. $\frac{E}{I}$ currents and $\frac{E}{I}$ velocities are both unity for the same thickness of film.
2. The dissymmetry for velocities is not so strongly marked as for currents.
3. As the thickness of film increases through 10^{-7} cm., the photo-current increases suddenly.
4. The ratio $\frac{E}{I}$ currents is constant for films thinner than 10^{-7} cm. and begins to diminish after the sudden increase in current has set in.
5. Radiations from the spark produce much quicker electrons than those from the arc.
6. The dissymmetry is more strongly marked the quicker the electrons produced.
7. It has been shown that it is possible that photoelectrons possess sufficient energy to ionize molecules of platinum, and that it is this which leads to the best explanation of the sudden rise of photo-current at 10^{-7} cm.
8. The thickness of film which gives the sudden rise in current is the same for slow and quick moving electrons.
9. The orientation of the plane of polarization of the light has no influence on the dissymmetry.

East London College,
Oct. 24th, 1912.

* *Loc. cit.*

† *Loc. cit.*

XIII. *The Influence of Pressure on the Surface Friction of Ice.* By HENRY MORPHY, B.A.*

THIS investigation was undertaken at the suggestion of Dr. Joly, who thought that it might be of interest in connexion with his theory of skating. This theory being, as is well known, that skating is rendered possible by the formation of a film of water, between skate and ice, owing to the melting of the latter under pressure.

The experimental determinations consisted in the measurement of the coefficient of statical friction between the runners of a small sleigh, carrying a variable load, and the surface of ice kept at constant temperature.

In some preliminary experiments difficulty was encountered in measuring the correct surface temperature of the ice, which was formed in a shallow trough, surmounting a flat copper box, through which a current of freezing-mixture was passed. With this apparatus it was impossible to eliminate surface radiation, and hence, owing to the blanketting effect of the sleigh, the temperature beneath its runners would vary. As it was desirable to know definitely the surface temperature of the ice and essential to ensure its being dry, this apparatus was abandoned and the following, in which the ice was formed in a constant temperature enclosure, was adopted.

A glass gas chimney 8 inches long by 2 inches diameter was closed at the ends with rubber disks covered by brass disks which were bolted together by two long tie-rods, passing through lugs in the brass. Through the centre of one brass disk a $\frac{1}{2}$ -inch brass tube 8 inches long was soldered, being flush with the inner side of the brass. A piece of $\frac{1}{4}$ -inch brass tube was similarly fitted into the same disk close to the larger tube. These two tubes were cemented into a circular disk of pitch pine 5 inches in diameter, leaving 4 inches between brass disk and wood. This wooden disk enabled the whole to be fastened into the constant temperature enclosure, which was simply a rectangular box of pitch pine, fitted with glass windows for purposes of observation, and having two brass tubes for the circulation of the freezing-mixture. This box was placed on a platform which could be tilted to any angle. Horizontal and vertical scales enabled the tangent of the angle to be read.

A small sleigh was made from sheet aluminium, having

* Communicated by Prof. Joly, F.R.S.

two parallel runners polished with fine emery and carrying a glass tube which could be loaded at will with lead shot. By means of a steel rod, passing through the $\frac{1}{4}$ -inch brass tube and suitably bent, the sleigh could be lifted and moved from place to place within the gas chimney.

A continuous current of freezing-mixture (water with excess of ice and salt) was circulated through the wooden box by a small pump driven off an electric motor. The ice temperature was read by a copper-platinoid thermocouple consisting of one pair of junctions in series with a suspended-coil galvanometer. The second junction was kept in melting ice. Resistance was added to the circuit to reduce the sensitiveness until the deflexion registered $0^{\circ}05$ C. per scale-division.

The following procedure was adopted in carrying out an experiment. The sleigh was placed in the gas chimney. The ends were bolted on and the whole was bolted into the wooden box. A large rubber ring formed a water-tight joint between the latter and the wooden disk. The sleigh being raised to the top of the tube, distilled water was introduced so as to fill the latter about one-third. This water was frozen solid by the circulation of freezing-mixture. The humped surface of the ice first formed necessitated reflooding and refreezing before a flat ice surface was obtained. The sleigh was then lowered and the platform tilted until the angle of statical friction was found. The sleigh could be pulled up the inclined ice surface by a fine silk thread passing through the $\frac{1}{2}$ -inch brass tube. The sleigh was now raised from the ice and a number of lead shot were introduced. The thermocouple junction was placed amongst the shot. When their temperature had fallen to that of the enclosure, the sleigh was again lowered and the angle of friction was again determined. This process was repeated again and again with the addition of lead shot each time. The angle of friction was found to remain constant until a certain stage of the loading, when it suddenly fell to about half of its original value. It then remained constant for further increases in the load.

These results, which confirmed those obtained previously with less satisfactory apparatus, are shown in the table below. In the first column is shown the load, *i.e.*, the weight of sleigh + weight of shot added. In the second and third columns are shown, respectively, the coefficient and angle of friction, whilst the fourth gives the temperature of the ice as determined from the galvanometer deflexions.

Load.	Tan γ .	γ .	Temp.
5.68 grams.	$0.36 \pm .01$	$20^\circ \pm 30'$	$-5^\circ.65$ C.
10.39 "	" "	" "	$-5^\circ.65$
11.96 "	" "	" "	$-5^\circ.75$
12.74 "	" "	" "	$-5^\circ.60$
13.53 "	" "	" "	$-5^\circ.65$
14.31 "	" "	" "	$-5^\circ.65$
15.10 "	$0.17 \pm .01$	$9^\circ.30' \pm 30'$	$-5^\circ.60$
16.67 "	" "	" "	$-5^\circ.55$
19.81 "	" "	" "	$-5^\circ.60$
24.52 "	" "	" "	$-5^\circ.60$
5.68 "	$0.36 \pm .01$	$20^\circ \pm 30'$	$-5^\circ.60$

These experiments were repeated on another occasion with the same result and similar results had been obtained with different apparatus.

As a result of the investigation the following points are clearly shown:—

(1) The coefficient of friction for ice at constant temperature may have either of two constant values according to the pressure per unit surface of contact.

(2) For small pressures, and up to a certain well defined limit of pressure, the coefficient is fairly large, having the value $0.36 \pm .01$ in the case investigated.

(3) For pressures greater than the above limit the coefficient is relatively small, having the value $0.17 \pm .01$ in the case investigated.

In conclusion it remains for the writer to express his thanks to Dr. Joly both for suggesting the work and also for his kind interest during its progress.

The Physical Laboratory,
Trinity College, Dublin.
Nov. 13, 1912.

XIV. *Second Memoir on Quaternionic Relativity.* By L. SILBERSTEIN, Ph.D., University Lecturer in Natural Philosophy, Rome*.

IN my first paper on this subject† I developed the fundamental relativistic formulæ in quaternionic language along with their application to the system of differential equations of the electron theory, and have given, finally,

* Communicated by the Author.

† Phil. Mag. vol. xxiii. May 1912 (written Nov. 1911).

some short expressions for the *ponderomotive* force combined with its activity, which union I called the *force-quaternion* and denoted by P_e . One of these forms has been :

$$P_e = \frac{1}{2}\{D\mathbf{F} \cdot \mathbf{F} - \mathbf{G} \cdot D\mathbf{F}\}, \quad . \quad . \quad . \quad . \quad (1)$$

loc. cit. (28), p. 808. I hoped then to be able to prove that this particular form is apt to show the properties of the corresponding stress, and of the density and flux of electromagnetic energy. In fact, I found since, that the above formula gives all of these in an unexpectedly simple way, if subjected to a somewhat peculiar but slight transformation, of a purely formal character. The formula (1) so transcribed proved then to be very convenient for further application, inasmuch as it led to very simple formulæ for the relativistic transformation of stress and of density and flux of energy*.

To show this, along with some allied matter, will be the subject of the present paper.

1. *Simplified form of the force-quaternion.*—In order to give to the second term of the right side of the above formula (1) a form similar to the first term and guided by the principle of alternation† (as explained in my first paper), I recurred, after several trials of other forms, to the peculiar form

$$\mathbf{G}[D]\mathbf{F},$$

in which the differential operator D is intended to act *both forward and backward*, and which I define explicitly by

$$\mathbf{G}[D]\mathbf{F} = \mathbf{G}D \cdot \mathbf{F} + \mathbf{G} \cdot D\mathbf{F}, \quad . \quad . \quad . \quad . \quad (2)$$

the dots symbolizing always separators, *i. e.* stopping D 's differentiating power. What is still to be explained in this symbolism, to make it entirely clear, is only the meaning of $\mathbf{G}D$, which is unusual inasmuch as the operator D *follows* the entity operated on‡. The way how $\mathbf{G}D$ is to be defined naturally suggests itself : If D were an ordinary quaternion,

* The corresponding set of formulæ has been communicated by the author to the *Societas Scientiarum Varsoviensis* in December 1911.

† Remember that the electromagnetic bivector \mathbf{F} is a (scalarless) *left quaternion* and the complementary \mathbf{G} a (scalarless) *right quaternion*.

‡ The reader must not be afraid of this departure from convention. Oliver Heaviside says, in a similar situation, simply : "A cart may be pulled or pushed." *Electromagnetic Theory*, vol. ii. p. 218. Besides, J. W. Gibbs taught us to employ linear vector operators as *prefactors* and as *postfactors*.

with s , \mathbf{w} as its scalar and vector parts, respectively, we should have

$$\mathbf{G}s + \mathbf{G}\mathbf{w} = \mathbf{G}s + \nabla\mathbf{G}\mathbf{w} - (\mathbf{G}\mathbf{w}) = s\mathbf{G} - \nabla\mathbf{w}\mathbf{G} - (\mathbf{w}\mathbf{G});$$

writing here $\partial/\partial l$ instead of s and ∇ instead of \mathbf{w} , the required definition of $\mathbf{G}\mathbf{D}$ will be

$$\mathbf{G}\mathbf{D} = \frac{\partial \mathbf{G}}{\partial l} - \text{curl } \mathbf{G} - \text{div } \mathbf{G}. \quad . \quad . \quad . \quad . \quad (3)$$

Observe that $\mathbf{D}\mathbf{G}$ could not be used at all, for \mathbf{G} is *right-handed*, so that $\mathbf{D}\mathbf{G}$ would be torn asunder by the relativistic transformation.

Now to see the utility of $\mathbf{G}\mathbf{D}$ let us compare it with $\mathbf{D}\mathbf{F}$, which appears in (1). Since, by (VI. *a*), $\mathbf{D}_c\mathbf{G} = \mathbf{C}_c$, we have by the elementary rule, by which the conjugate of a product of quaternions is the product of their conjugates in the reversed order, $\mathbf{C} = \mathbf{G}_c\mathbf{D} = -\mathbf{G}\mathbf{D}$. But, by (VI.), $\mathbf{C} = \mathbf{D}\mathbf{F}$. Thus

$$\mathbf{D}\mathbf{F} = -\mathbf{G}\mathbf{D}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and using this in (1) we obtain the required expression for the *force-quaternion*

$$\mathbf{P}_e = -\frac{1}{2}\mathbf{G}[\mathbf{D}]\mathbf{F}. \quad . \quad . \quad . \quad . \quad (\text{XV.})^*$$

Thus, $\mathbf{G}[\]\mathbf{F}$, when applied to \mathbf{D} , or rather, when exposed to the bilateral action of \mathbf{D} , gives the force-quaternion; and this being the case, it has been easy to guess that the same operator $\mathbf{G}[\]\mathbf{F}$, when applied to a *vector*, say to the unit surface-normal \mathbf{n} , should give us the corresponding stress and the component of the energy flux relativistically associated with it†. This supposition proved, on trial, to be correct, and having once verified it, the systematical deduction from (XV.) of the energy, stress, &c., as shown in the next section, has been a matter of course.

2. *Properties of the operator $\mathbf{G}[\]\mathbf{F}$. Stress, electromagnetic momentum, flux and density of energy.*—To see the properties of the above operator, develop the right side of (XV.), remembering that

$$\mathbf{P}_e = \rho \left\{ \frac{1}{c}(\mathbf{p}\mathbf{E}) + \mathbf{E} + \frac{1}{c}\mathbf{V}\mathbf{p}\mathbf{M} \right\} = \frac{1}{c}(\mathfrak{F}\mathbf{p}) + \mathfrak{F},$$

\mathfrak{F} being the ponderomotive force (per unit volume), and

* The Roman numerals, reserved for the more essential formulæ, are here continued from the first paper.

† Especially as I have already remarked (*Ann. der Physik*, vol. xxii. 1907) that $\mathbf{G}[\]\mathbf{F}$, when applied to a *scalar*, or simply $\mathbf{G}\mathbf{F}$, gives the resultant flux and the density of energy.

($\mathfrak{F}\mathbf{p}$) its activity ; then

$$\frac{\iota}{c}(\mathfrak{F}\mathbf{p}) = -\frac{1}{2}\mathbf{S}\mathbf{G}[\mathbf{D}]\mathbf{F} = \frac{1}{2}\frac{\partial}{\partial t}(\mathbf{G}\mathbf{F}) - \frac{1}{2}\text{div } \mathbf{V}\mathbf{G}\mathbf{F}, \quad (5)$$

$$\mathfrak{F} = -\frac{1}{2}\mathbf{V}\mathbf{G}[\mathbf{D}]\mathbf{F}, \quad (6)$$

whence

$$(\mathfrak{F}\mathbf{p}) = -\frac{1}{2}\frac{\partial}{\partial t}(\mathbf{G}\mathbf{F}) + \frac{\iota c}{2}\text{div } \mathbf{V}\mathbf{G}\mathbf{F} = -\frac{\partial u}{\partial t} - \text{div } \mathfrak{P},$$

the scalar u and the vector \mathfrak{P} being given by

$$\left. \begin{aligned} u &= \frac{1}{2}(\mathbf{G}\mathbf{F}) = \frac{1}{2}(\mathbf{E}^2 + \mathbf{M}^2) \\ \mathfrak{P} &= -\frac{\iota c}{2}\mathbf{V}\mathbf{G}\mathbf{F} = c\mathbf{V}\mathbf{E}\mathbf{M} \end{aligned} \right\} \quad (7)$$

Thus, the scalar part of the equation (XV.) expresses the conservation of energy, leading to the flux of energy or the Poynting-vector, \mathfrak{P} , and to the density of electromagnetic energy, u .

Both of the equations (7) may be condensed into one single quaternionic formula

$$\frac{1}{2}\mathbf{G}\mathbf{F} = -u + \frac{\iota}{c}\mathfrak{P}^*, \quad (\text{XVI. } a)$$

thus giving us one of the properties of $\mathbf{G}[\]\mathbf{F}$.

To obtain another property of this operator develop the vector part of (XV.), *i. e.* (6). Then

$$\mathfrak{F} = -\frac{1}{2}\mathbf{V}\mathbf{G}\left[\frac{\partial}{\partial t}\right]\mathbf{F} - \frac{1}{2}\mathbf{V}\mathbf{G}[\nabla]\mathbf{F};$$

here, the first term on the right is seen, by (2), to be simply identical with

$$-\frac{1}{2}\frac{\partial}{\partial t}\mathbf{V}\mathbf{G}\mathbf{F} \text{ or } -\frac{1}{c^2}\frac{\partial \mathfrak{P}}{\partial t},$$

so that we have only to develop the second term, which (since it will turn out to be the Maxwellian ponderomotive force) we shall denote by \mathbf{F}_{Mxw} . Thus

$$\mathfrak{F} = \mathfrak{F}_{\text{Mxw}} - \frac{1}{c^2}\frac{\partial \mathfrak{P}}{\partial t}, \quad (8)$$

where we recognize already in \mathfrak{P}/c^2 the electromagnetic momentum (per unit volume) and where

$$\mathfrak{F}_{\text{Mxw}} = -\frac{1}{2}\mathbf{V}\mathbf{G}[\nabla]\mathbf{F}. \quad (9)$$

* It is hardly necessary to warn the reader that $\mathbf{G}\mathbf{F}$ is *not* a physical quaternion.

Now, the vector part of the product of any three vectors $\mathbf{A}, \mathbf{B}, \mathbf{C}^*$ is easily proved to be

$$\begin{aligned} \mathbf{VABC} &= \mathbf{B(CA)} - \mathbf{C(BA)} - (\mathbf{CB})\mathbf{A} \} \\ &= \mathbf{B(CA)} - (\mathbf{AB})\mathbf{C} - \mathbf{A(BC)} \} \end{aligned} \quad (10)$$

which is here written in a twofold manner on purpose. Taking $\mathbf{G}, \mathbf{F}, \nabla$ instead of $\mathbf{A}, \mathbf{C}, \mathbf{B}$ and using, with due caution, the first and the second form of (10), respectively, we obtain

$$\begin{aligned} \mathbf{VG} \nabla \cdot \mathbf{F} &= \nabla(\mathbf{G} \cdot \mathbf{F}) - \mathbf{F} \cdot \text{div } \mathbf{G} - (\mathbf{F} \cdot \nabla)\mathbf{G}, \\ \mathbf{VG} \cdot \nabla \mathbf{F} &= \nabla(\mathbf{F} \cdot \mathbf{G}) - \mathbf{G} \cdot \text{div } \mathbf{F} - (\mathbf{G} \cdot \nabla)\mathbf{F}, \end{aligned}$$

where none of the separating dots is superfluous: in the first formula it is \mathbf{G} only which is exposed to the action of the differential operators as if \mathbf{F} were constant, and *vice versa* in the second formula. Taking their sum, the first terms of the right-hand sides give us the *full* gradient of the scalar product (\mathbf{GF}) , *i. e.* $\nabla(\mathbf{GF})$ without dot, so that

$$\begin{aligned} \mathbf{VG}[\nabla]\mathbf{F} &= \nabla(\mathbf{GF}) - \mathbf{F} \cdot \text{div } \mathbf{G} - \mathbf{G} \cdot \text{div } \mathbf{F} - (\mathbf{F} \cdot \nabla)\mathbf{G} - (\mathbf{G} \cdot \nabla)\mathbf{F} \\ &= \mathbf{i} \left\{ \frac{\partial}{\partial x}(\mathbf{GF}) - \text{div}(\mathbf{FG}_1 + \mathbf{GF}_1) \right\} + \mathbf{j}\{\dots\} + \mathbf{k}\{\dots\} \\ &= \mathbf{i} \text{div} \{(\mathbf{GF})\mathbf{i} - \mathbf{F}(\mathbf{Gi}) - \mathbf{G}(\mathbf{Fi})\} + \dots \end{aligned}$$

Thus (9) takes the form

$$\mathfrak{F}_{\mathbf{Mxw}} = -\mathbf{i} \text{div } \mathbf{f}_1 - \mathbf{j} \text{div } \mathbf{f}_2 - \mathbf{k} \text{div } \mathbf{f}_3, \quad (9a)$$

where the vectors $\mathbf{f}_1, \mathbf{f}_2, \mathbf{f}_3$, constituting a self-conjugate *stress*, are given by

$$\mathbf{f}_1 \text{ or } \mathbf{fi} = \frac{1}{2}\{(\mathbf{GF})\mathbf{i} - \mathbf{F}(\mathbf{Gi}) - \mathbf{G}(\mathbf{Fi})\}, \text{ \&c.,}$$

or, \mathbf{n} being any (say unit-) vector, by

$$\mathbf{f}_n = \mathbf{fn} = \frac{1}{2}(\mathbf{GF})\mathbf{n} - \frac{1}{2}\mathbf{F}(\mathbf{Gn}) - \frac{1}{2}\mathbf{G}(\mathbf{Fn}), \quad (11)$$

or, finally, by the dyadic †

$$\mathbf{f} = \frac{1}{2}(\mathbf{GF}) - \frac{1}{2}\mathbf{F}(\mathbf{G} \quad - \frac{1}{2}\mathbf{G}(\mathbf{F} \quad \dots \quad (11a)$$

This stress, represented by the linear vector operator \mathbf{f} , is,

* Which may be *ordinary-* or *bivectors*.

† Here, and in what follows, \mathbf{f} is a dyadic or a linear *vector operator*, which may be called the *stress-operator*, and which, when applied to the unit surface-normal \mathbf{n} , gives the corresponding *pressure-vector* \mathbf{f}_n .

obviously, the well-known *Maxwellian stress** (*pressure proper being considered positive, and tension proper negative*).

But what we are here mainly concerned with, is another form of this stress, showing the utility of the operator $\mathbf{G}[\]\mathbf{F}$. Now, recurring again to (10), we obtain at once, instead of (11),

$$f\mathbf{n} = \frac{1}{2}V\mathbf{G}\mathbf{n}\mathbf{F}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the desired form. Moreover, we have for the scalar part of the same triple product

$$S\mathbf{G}\mathbf{n}\mathbf{F} = S\mathbf{G}V\mathbf{n}\mathbf{F} = -(\mathbf{G}V\mathbf{n}\mathbf{F}) = (\mathbf{n}V\mathbf{G}\mathbf{F}),$$

i. e., by (7) or (XVI.a),

$$\frac{1}{c}S\mathbf{G}\mathbf{n}\mathbf{F} = \frac{\iota}{c}(\mathfrak{P}\mathbf{n}).$$

Consequently, the full quaternionic product will be

$$\frac{1}{2}\mathbf{G}\mathbf{n}\mathbf{F} = \frac{\iota}{c}(\mathfrak{P}\mathbf{n}) + f\mathbf{n}, \quad . \quad . \quad . \quad (XVI.b)$$

which is the second property of our operator.

Both of its properties, as expressed by the formulæ (XVI.a) and (XVI.b), may be combined into one, by adding these formulæ together side by side, after having multiplied the former by a quite arbitrary scalar s . Then we shall have $\mathbf{G}[\]\mathbf{F}$ as applied to a full quaternion $s + \mathbf{n}$. Take for this purpose, say, a purely *imaginary* scalar $s = \iota\sigma$, so that

$$k = \iota\sigma + \mathbf{n} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

will be a special physical quaternion, cov. q . Then we shall have

$$\frac{1}{2}\mathbf{G}k\mathbf{F} = \frac{\iota}{c}\{(\mathfrak{P}\mathbf{n}) - c\sigma u\} + f\mathbf{n} - \frac{\sigma}{c}\mathfrak{P}, \quad . \quad (XVI.)$$

a formula which will be useful for our subsequent considerations. This expression is, obviously, like k itself, a genuine *physical quaternion*, namely covariant with q †.

* In fact, developing (11) we obtain at once

$$f\mathbf{n} = u\mathbf{n} - \mathbf{E}(\mathbf{E}\mathbf{n}) - \mathbf{M}(\mathbf{M}\mathbf{n}), \quad u = \frac{1}{2}(E^2 + M^2),$$

which is the usual form of Maxwell's stress. Cfr. also (7).

† For it has a real vector and an imaginary scalar part, like $q = l + \mathbf{r}$, and, since $\mathbf{G}' = Q\mathbf{G}Q_c$, $\mathbf{F}' = Q_c\mathbf{F}Q$, $k' = QkQ$,

$$\mathbf{G}'k'\mathbf{F}' = Q\mathbf{G}k\mathbf{F}Q.$$

Notice that \mathbf{n} is a unit vector of quite *arbitrary* direction, while σ is a real but otherwise *arbitrary* scalar.

Resuming the results of the present and the foregoing section we can now say shortly that one and the same operator

$$\mathbf{G}[\]\mathbf{F}$$

furnishes us the *force-quaternion*, the *corresponding stress and the flux and density of energy*, according as we fill out the vacant place $[\]$ by \mathbf{D} , or by a simple vector or a simple scalar, respectively. (Formulæ XV. and XVI.a, XVI.b or their combination XVI.)

Thus, our operator $\mathbf{G}[\]\mathbf{F}$ does all the offices of Minkowski's matrix S of 4×4 elements* or Sommerfeld's and Laue's "world-tensor," the procedure however being in our case, I daresay, a great deal simpler. Especially simple is the structure of our operator, as compared with that of the "world-tensor"; for, while in $\mathbf{G}[\]\mathbf{F}$ both of the bivectors are ordinary quaternionic factors, Sommerfeld's "tensor" (*Ann. d. Physik*, vol xxxii. p. 768) or, as written by Laue,

$$T = [\mathfrak{M}\mathfrak{M}],$$

is derived from the "Sechservector" \mathfrak{M} in a very complicated way. In fact, the definition of this symbol is actually given by Lane's formula (80) (*Relativitätsprinzip*, p. 74), which contains for one only of the elements of the "tensor," T_{jk} , not less than 16 products, while the whole "tensor" consists (in the symmetrical case) of ten of such elements or components.

The utility of $\mathbf{G}[\]\mathbf{F}$ will appear also from what follows. A similar investigation of the properties of the operator $\mathbf{F}[\]\mathbf{G}$, as applied, of course, to \mathbf{D}_c , k_c^* , instead of \mathbf{D} , k , is left to the reader.

3. *The relativistic transformation of stress and flux and density of energy.*—It is well known that, using the "world-tensor," the stress components, &c., constituting its ten elements, are transformed as the squares and products of the coordinates of a point of the four-dimensional "world," i. e. f_{11} as x^2 , f_{12} as xy , and so on. The corresponding formulæ are fairly complicated and rather hard to read and more so to remember†. The formulæ of transformation

* S is the "product" of two "alternating" matrices, each consisting of 4×4 elements; *cfr.* Minkowski, *Gotting. Nachr.* 1908, § 13. For the "vacuum" Sommerfeld's S , being generally non-symmetrical, becomes a symmetrical matrix.

† See for example Laue's (78), p. 74, *loc. cit.*

thus obtained separately for the components are but afterwards combined into vector equations.

Now the quaternionic method of treatment seems in this respect also to be more convenient and more transparent. In fact, since we know already, by formula (XVI.), that

$$Z = \frac{t}{c} \{ (\mathfrak{P}\mathbf{n}) - c\sigma u \} + f\mathbf{n} - \frac{\sigma}{c} \mathfrak{P} \quad . \quad . \quad . \quad (14)$$

is a *physical quaternion*, cov. q , we have, by the same formula,

$$QZQ = \frac{1}{2} \mathbf{G}' k' \mathbf{F}', \quad . \quad . \quad . \quad . \quad (15)$$

where, by (13),

$$k' = QkQ, \text{ say } = \iota\sigma' + \mathbf{N}' = \iota\sigma' + \mathbf{N}'\mathbf{n}',$$

$$\sigma' = \gamma[\sigma - \beta(\mathbf{n}\mathbf{i})]; \quad \mathbf{N}' = \mathbf{n}[(\gamma - 1)(\mathbf{n}\mathbf{i}) - \sigma \cdot \beta\gamma]\mathbf{i}. \quad (16)$$

(Here \mathbf{i} is written instead of the original \mathbf{u} , so that now the velocity of the system S' relatively to S is $\mathbf{v} = v\mathbf{i} = c\beta\mathbf{i}$.)

Thus, by (15),

$$QZQ = \frac{\iota\sigma'}{2} \mathbf{G}'\mathbf{F}' + \frac{\mathbf{N}'}{2} \mathbf{G}'\mathbf{n}'\mathbf{F}';$$

but, by (XVI.a), (XVI.b), the right-hand side of this equation is

$$\iota \left\{ \frac{1}{c} (\mathfrak{P}'\mathbf{N}') - \sigma'u' \right\} + f'\mathbf{N}' - \frac{\sigma'}{c} \mathfrak{P}',$$

whereas QZQ equals, by (14),

$$\iota\gamma \left\{ \frac{1}{c} \mathfrak{P}_n - \sigma u - \beta \left(f_{n1} - \frac{\sigma}{c} \mathfrak{P}_1 \right) \right\} + f\mathbf{n} - \frac{\sigma}{c} \mathfrak{P}$$

$$+ \mathbf{i} \left\{ (\gamma - 1) \left(f_{n1} - \frac{\sigma}{c} \mathfrak{P}_1 \right) - \beta\gamma \left(\frac{1}{c} \mathfrak{P}_n - \sigma u \right) \right\}.$$

Hence, by comparing separately the scalar and the vector parts, we obtain the following two relations

$$\gamma \left(\frac{\mathfrak{P}_n}{c} - \sigma u \right) - \beta\gamma \left(f_{n1} - \frac{\sigma}{c} \mathfrak{P}_1 \right) = \frac{(\mathfrak{P}'\mathbf{N}')}{c} - \sigma'u', \quad . \quad . \quad . \quad (17a)$$

$$f\mathbf{n} - \frac{\sigma}{c} \mathfrak{P} + \mathbf{i} \left\{ (\gamma - 1) \left(f_{n1} - \frac{\sigma}{c} \mathfrak{P}_1 \right) - \beta\gamma \left(\frac{\mathfrak{P}_n}{c} - \sigma u \right) \right\} = f'\mathbf{N}' - \frac{\sigma'}{c} \mathfrak{P}'$$

$$. \quad . \quad . \quad (17b)$$

Now, these being valid for *any* σ (and for all directions of \mathbf{n}),

take first $\sigma=0$, and then $\sigma=1$, and remember that, by (16),

$$\begin{aligned}\sigma'_0 &= -\beta\gamma(\text{in}); \quad \sigma'_1 - \sigma'_0 = \gamma; \quad \mathbf{N}'_1 - \mathbf{N}'_0 = -\beta\gamma\mathbf{i}; \\ \mathbf{N}'_0 &= \mathbf{n} + (\gamma - 1)\mathbf{i}(\text{in}) = \gamma \frac{1}{\epsilon} \mathbf{n},\end{aligned}$$

where ϵ is a *linear vector operator*, stretching every vector normal to the direction of motion in the ratio $\gamma : 1$ and not affecting vectors parallel to that direction, or in dyadic form

$$\epsilon = \mathbf{i}(\mathbf{i} + \gamma\mathbf{j}(\mathbf{j} + \gamma\mathbf{k}(\mathbf{k} \dots \dots \dots (18)$$

Of the four relations, obtained in this way from (17 a), (17 b), one, namely that which contains $\mathfrak{P}_n - c\beta f_{n1}$, is a consequence of the three others (one of which contains the resultant \mathfrak{P}).

These three relations, after a slight rearrangement of terms and without splitting in Cartesians, give us the required *relativistic transformation of the density and flux of energy and of the stress* in the remarkable form

$$\left. \begin{aligned}\frac{1}{\gamma^2}u &= u' + \frac{2}{c^2}(\mathfrak{P}'\mathbf{v}) + \frac{1}{c^2}(\mathbf{v}f'\mathbf{v}) \\ \frac{1}{\gamma^2}\epsilon\mathfrak{P} &= \mathfrak{P}' + \left[\frac{1}{c^2}(\mathbf{v}\mathfrak{P}') + u' + f'\right]\mathbf{v} \\ \frac{1}{\gamma^2}\epsilon f &= f'\frac{1}{\epsilon} + \frac{1}{c}[\mathfrak{P}' + u'\mathbf{v}](\mathbf{v} + \frac{1}{c^2}\mathbf{v}\left(\frac{1}{\epsilon}\mathfrak{P}'\right)\end{aligned}\right\}, \quad . \quad (\text{XVII.})$$

ϵ being the operator explained in (18).

The three formulæ in (XVII.), one being scalar, one vectorial, and one dyadic, are completely equivalent to Laue's *ten* ($=1+3+6$) transformational formulæ (102) *, which the reader may verify at once, by expanding the second and third of (XVII.) and remembering that f' , like f , being a linear operator, $f'\mathbf{v} = v f' \mathbf{i} = v \mathbf{f}'_1, (\mathbf{v}f'\mathbf{v}) = v^2 f'_{11}$, and so on.

To obtain u', \mathfrak{P}', f' in terms of u, \mathfrak{P}, f , we have only to transfer the dashes to the symbols without dashes and to write $-\mathbf{v}$ instead of \mathbf{v} , leaving the coefficient γ and the dyadic ϵ unchanged.

Of particular interest, especially as regards its application to relativistic dynamics, is the case in which the *flux of energy*, and consequently also the electromagnetic momentum, *vanishes* for one of the two systems S, S' , we are comparing;

* Laue, *loc. cit.* p. 87.

say $\mathfrak{P}'=0$. Then the formulæ (XVII.) are considerably simplified, giving for the S -point of view :

$$\left. \begin{aligned} \frac{1}{\gamma^2} u &= u' + \frac{1}{c^2} (\mathbf{v} f' \mathbf{v}) \\ \frac{1}{\gamma^2} \epsilon \mathfrak{P} &= u' \mathbf{v} + f' \mathbf{v} \\ \frac{1}{\gamma^2} \epsilon f &= f' \frac{1}{\epsilon} + \frac{u'}{c^2} \mathbf{v}(\mathbf{v}) \end{aligned} \right\} \quad \text{. . . (XVII.a)}$$

Remembering that $\frac{1}{\epsilon} \mathbf{v} = \mathbf{v}$, we may write also, somewhat more conveniently,

$$\mathfrak{P} = \gamma^2 \left[u' \mathbf{v} + \frac{1}{\epsilon} f' \mathbf{v} \right],$$

and similarly for the third of the above formulæ. But as a matter of fact the operator ϵ , of quite simple structure, makes no difficulty, wherever it stands. Moreover, its appearance in our formulæ has nothing artificial about it, since it corresponds, in fact, to the very nature of the transformation which is fundamental for the whole theory of relativity.

November, 1912.

XV. *The Asymmetric Emission of Secondary Rays.* By
O. W. RICHARDSON, *Professor of Physics, Princeton University* *.

IN 1908 Bragg † showed that when γ rays passed normally through a thin plate of matter the ionization produced by the β secondary rays thus stimulated was greater on the emergent than on the incident side : C. D. Cooksey ‡ showed that similar effects were caused by the electronic emission from thin plates illuminated by Röntgen rays. It was first shown by O. Stuhlmann §, and about the same time, independently, by R. D. Kleeman ||, that when thin films of metals are traversed normally by ultra-violet light, the number of electrons emitted on the emergent is greater than

* Communicated by the Author.

† *Nature*, vol. lxxvii. p. 270, Jan. 23, 1908; *Phil. Mag.* vol. xvi. p. 918 (1908).

‡ *Nature*, vol. lxxvii. p. 509 (1908).

§ *Nature*, May 12, 1910; *Phil. Mag.* vol. xx. p. 331 (1910), vol. xxii. p. 854 (1911).

|| *Nature*, May 19, 1910; *Proc. Roy. Soc. A.* vol. lxxxiv. (1910).

that on the incident side. A similar asymmetry in the distribution of the X type of secondary rays produced by the absorption or stoppage of Röntgen, γ , β , and cathode rays has been demonstrated by the experiments of Bragg and his pupils, and of Kaye, Stark, Crowther, Gray, and other investigators.

This type of effect was first predicted by Bragg as a consequence of his view that the γ and Röntgen rays were uncharged material particles in rapid motion, and its existence has consequently been held to favour Bragg's theory. The occurrence of similar effects with light would, by a like argument, lead to the conclusion that it also consists of a shower of material particles. In fact, the greater number of Bragg's reasons for favouring the material constitution of γ and Röntgen rays apply also to light. Most writers seem to accept the principle that light and X radiations, as it is convenient to call radiations which behave physically in a manner similar to the γ and Röntgen rays, differ only in degree and not in kind. The explanation then usually offered* to account for these asymmetric effects in secondary emission is that the energy in the radiations is not continuously distributed, but exists in a very concentrated form in limited regions. In this way a single electron may be made to receive the major part of both the energy and momentum in a radiation unit. As the case against such a view of the nature of light is at least arguable, it is worth while to examine the question from a rather wider standpoint, to see if an estimate of the maximum effects to be observed may be obtained without making any definite hypothesis about the structure of the radiation. I shall practically confine myself to the secondary emission of electrons under the influence of radiations of the X type and light.

A general review of the phenomena grouped under the emission of electrons caused by radiation and under the temperature variation of the radiation from a black body, supports the view that the action between the radiation and the matter is primarily between radiation and electrons, and that this action goes on in a manner which may be treated as continuous, in the case of any particular electron, until the latter reaches a certain condition. This condition is followed by an act of a different character, which we may term disruption; the act of disruption terminates the continuity of the preceding processes and is succeeded by a new

* Stark, *Phys. Zeits.* vol. x. p. 579 (1909).

cycle of, in general, similar events. The condition for disruption is that the energy of the electron should be an integral multiple of $h\nu$, where ν is the frequency of the radiation and $h=6.55 \times 10^{-27}$ erg sec. In a large number of cases it is probable that integral multiples other than unity may be left out of consideration without serious error. According to a theory of black body radiation recently developed by Planck *, this is always the case when the intensity of the primary radiation is sufficiently small. I shall suppose the act of disruption to result in the liberation of an electron to such an extent that it no longer forms part of the dynamical system to which it originally belonged. In favourable cases the electron may be expelled from the matter and appear as an emitted electron, or secondary radiation of the β or electronic type. This will invariably be the case if ν is sufficiently large and the layer of matter which absorbs the radiation is sufficiently thin. I shall assume that up to the instant of disruption no part, either of the momentum or of the energy which any particular electron receives from the radiation, is communicated to the rest of the matter. The acquisition of energy and momentum by the matter as a whole then takes place through the acts of the disrupted electrons. This assumption may not invariably be fulfilled, but it will probably lead to a correct estimate of the maximum amount of asymmetry to be found in the most favourable cases.

Consider the case of X radiation or light, incident normally on a thin slab of absorbing material. In general, absorption may occur through the operation of processes of very different nature, for example, conduction as opposed to resonance effects; but we shall suppose that the only type of absorption which we need to consider is that which results finally in electronic disruption. We shall fix our attention on the state of things which exists after the slab has been illuminated for some time; so that there is no further accumulation, in the slab, of energy abstracted from the incident beam. Under these circumstances the energy absorbed from the incident radiation will appear, at any rate in the first instance, as the kinetic energy $h\nu$ which the disrupted electrons possess at the instant of disruption. Thus if there are N of them disrupted in unit time, the energy absorbed from the radiation is $Nh\nu$. We are here supposing that some suitable means of return is provided for the electrons, so that the number present in the slab at any instant preserves the same average value. It is clear also

* *Ann. der Phys.* vol. xxxvii. p. 642 (1912).

that under the supposed conditions the average energy of the electrons instantaneously present in the slab remains invariable. It is important to observe that the energy $h\nu$ which we have to consider here, is that which the disrupted electrons possess before, not after, they leave the slab.

But the incident beam is depleted of momentum as well as energy. Without committing ourselves for the moment as to the nature of this momentum, let us suppose that when the incident beam loses an amount E of energy it loses an amount λE of momentum. On the electromagnetic theory

λ is constant and equal to $\frac{1}{c}$, where c is the velocity of light *in vacuo*. According to the hypotheses which we have adopted, the whole of this momentum is conveyed in the first instance to the undisrupted electrons. Now consider the increase of momentum of the slab and contained electrons in any small interval of time. It arises from:—(1) the momentum of electrons which come into the slab, (2) the momentum, reckoned negatively, of the disrupted electrons, and (3) the momentum accumulated during the interval by the electrons present in the slab. Since the average state of the electrons instantaneously present does not change with time, it follows that the difference of (1) and (2) is equal to (3). When (1) is zero, (3) is the momentum derived from the radiation, if the principle of the conservation of momentum is held to apply to the whole system of radiation and matter. It follows that the momentum which is acquired by all the absorbing electrons from the radiation, is exactly equal to the sum of the momenta, measured at the moment of disruption, of all the electrons disrupted during the same interval. But since the energy absorbed is $Nh\nu$ the value of the former amount of momentum is $\lambda Nh\nu$. If \bar{u} is the average component of velocity of the disrupted electrons, in the direction of incidence of the radiation, an alternative expression for the momentum of the N electrons is $Nm\bar{u}$. Thus:—

$$\bar{u} = \frac{\lambda h\nu}{m} = \frac{\lambda}{2} v^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if v^2 is the average value of the square of their velocity at the instant of disruption. If we take the expression for the momentum of the radiation given by the electromagnetic theory,

$$\bar{u} = \frac{h\nu}{cm} = \frac{v^2}{2c} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These relations are not sufficient to determine the distribution of the velocity among the particles. But we should expect the asymmetry to be more marked the greater the value of $\frac{\bar{u}}{v}$ and hence the greater the value of v . Thus those radiations which give rise to the emission of electrons with the greatest velocities should exhibit the greatest degree of asymmetry in this emission. This is known to be the case.

According to formula (2) the maximum value of $\frac{\bar{u}}{v}$ is $\frac{1}{2}$, and is the limit to which the fraction approaches as the velocity of the emitted electrons approaches that of light. To illustrate the possibilities it is perhaps worth while devoting a moment's consideration to this particular case.

We do not know with absolute certainty whether the fact that u is not zero is due to v being different in different directions, or to v being the same and the number different in different directions, or to both these causes. For simplicity suppose that v is the same and the number different. This supposition seems a little more probable than the first alternative and is also supported by experimental evidence, at least in the case of the Röntgen rays*. If $4\pi n$ is the total number emitted and n_θ the number per unit solid angle making the angle θ with the direction of the radiation,

$$4\pi n = \int_0^\pi n_\theta \cdot 2\pi \sin \theta d\theta \quad \dots \quad (3)$$

and since $u = v \cos \theta$,

$$\bar{u} = \frac{v}{4\pi n} \int_0^\pi n_\theta \cdot 2\pi \cos \theta \sin \theta d\theta \quad \dots \quad (4)$$

Thus if $\cos \theta = x$ and $n_\theta = n_x$

$$\bar{u} \int_{-1}^1 n_x dx = v \int_{-1}^1 x n_x dx \quad \dots \quad (5)$$

When $\frac{\bar{u}}{v} = \frac{1}{2}$, particular values of n_x which satisfy (5) are:

$$n_x = \text{const.} \times (1+x)^2, \quad -1 < x < +1, \quad \dots \quad (6)$$

and

$$n_x = 0, \quad -1 < x < 0 : \quad n_x = \text{const.} \quad 0 < x < +1. \quad \dots \quad (7)$$

* Cf. R. T. Beattie, Phil. Mag. vol. xx. p. 320 (1910).

Since the ratio of the number of ions emitted forward to the number emitted backward is

$$\psi = \int n_x dx \div \int_{-1}^0 n_x dx \quad . \quad . \quad . \quad (8)$$

we find from (6) $\psi=7$, and from (7) $\psi=\infty$.

The possibility of (6) appears to be eliminated by the results of Bragg and Madsen's * experiments on hard γ rays which, in the case of carbon, gave a ratio of about 20 to 1. Nevertheless it cannot be said to have been demonstrated that the electromagnetic theory is incapable of accounting for these effects.

In the neighbourhood of the visible spectrum, let us say when $\nu=10^{15}$ sec.⁻¹ the ratio of \bar{u} to v deduced from equation (2) is only about 1 to 500. Thus even the comparatively small differences between the emergence and incidence emission found by Stuhlmann † seem larger than would be expected. It is probable, however, that somewhat different considerations enter in these cases. The value of v is now comparable with the value which it is necessary for an electron to have in order to escape from the metal at all. A small difference in the value of v^2 in favour of the direction of emission will be equivalent, as compared with the unfavourable case, to an extension of the illumination towards the ultra-violet. The equivalent extension $\delta\nu$, of the range of frequency of the illumination, will be proportional to the difference in v^2 , and as the range of ν which is effective in causing emission is only a fraction of the total range from 0 to ν the effect will be correspondingly multiplied. A difference in the number, with v constant, will act in the same way as a difference in v , but not quite so directly. On the above view, with the same illumination, the difference will tend to be greater when the effective range of the illumination is shorter. This is the case with the more electronegative elements, as the minimum frequency and velocity required for emission are greater for them. Although, no doubt, there are other factors entering when illumination from a source like the iron arc is used, it is interesting to observe that, of the differences recorded by Stuhlmann, the greatest is in the case of the most electronegative element, platinum, and the least in the case of the most electropositive element, magnesium.

* Trans. R. S. of S. Australia, vol. xxxii. p. 1 (1908); Phil. Mag. 1909.

† Phil. Mag. vol. xxii. p. 863 (1911).

where c is the velocity of light and κ is put equal to

$$\frac{1}{\sqrt{1-v^2/c^2}}.$$

By the obvious differentiations and substitutions, Einstein has obtained the further equations:

$$\frac{dt'}{dt} = \kappa \left(1 - \frac{v\dot{x}}{c^2}\right), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\dot{x}' = \frac{\dot{x} - v}{1 - \frac{v\dot{x}}{c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\dot{y}' = \frac{\dot{y}\kappa^{-1}}{1 - \frac{v\dot{x}}{c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\dot{z}' = \frac{\dot{z}\kappa^{-1}}{1 - \frac{v\dot{x}}{c^2}}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where for simplicity we have put

$$\frac{dx}{dt} = \dot{x}, \quad \frac{dx'}{dt'} = \dot{x}', \text{ \&c.}$$

If, for an observer in system S, a point is moving with the velocity $(\dot{x}, \dot{y}, \dot{z})$ its velocity $(\dot{x}', \dot{y}', \dot{z}')$, as seen by an observer in system S', is given by equations (6), (7), and (8). It is interesting to note that if to one observer a particle appears to have a constant velocity, that is not to be acted on by any force, it appears so to any other observer who is in uniform motion.

By further differentiation and simplification it is possible to obtain from equations (6), (7), and (8) three new equations for transforming measurements of *acceleration* from system S to S', viz. :—

$$\ddot{x}' = \left(1 - \frac{v\dot{x}}{c^2}\right)^{-3} \kappa^{-3} \ddot{x}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\ddot{y}' = \left(1 - \frac{v\dot{x}}{c^2}\right)^{-2} \kappa^{-2} \ddot{y} + \dot{y} \frac{v}{c^2} \left(1 - \frac{v\dot{x}}{c^2}\right)^{-3} \kappa^{-2} \ddot{x}, \quad . \quad (10)$$

$$\ddot{z}' = \left(1 - \frac{v\dot{x}}{c^2}\right)^{-2} \kappa^{-2} \ddot{z} + \dot{z} \frac{v}{c^2} \left(1 - \frac{v\dot{x}}{c^2}\right)^{-3} \kappa^{-2} \ddot{x} \quad . \quad (11)$$

In contrast to the relation holding for the case of uniform velocity, it may be pointed out in connexion with the above

equations that, if a point has a *uniform acceleration* ($\ddot{x}, \ddot{y}, \ddot{z}$) with respect to an observer in system S, it *will not* in general have a uniform acceleration ($\ddot{x}', \ddot{y}', \ddot{z}'$) in another system S', since the acceleration in system S' depends not only on the constant acceleration but also on the velocity in system S which is necessarily varying.

We may next obtain transformation equations for a useful function of the velocity, namely, $\frac{1}{\sqrt{1-q^2/c^2}}$, where we have placed $q^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$. By substitution of equations (6), (7), and (8) and simplification we obtain

$$\frac{1}{\sqrt{1-q'^2/c^2}} = \frac{\left(1 - \frac{v\dot{x}}{c^2}\right)\kappa}{\sqrt{1-q^2/c^2}} \quad \dots \quad (12)$$

It has been shown in an earlier article* that the principles of non-Newtonian mechanics lead to the equation

$m = \frac{m_0}{\sqrt{1-q^2/c^2}}$ for the mass of a moving body, where m_0 is the mass of the body at rest and q is its velocity. By substitution of equation (12) we may obtain the following equation for transforming measurements of *mass* from one system of coordinates to the other:

$$m' = \left(1 - \frac{v\dot{x}}{c^2}\right)\kappa m, \quad \dots \quad (13)$$

where m is the mass of the body and x the X component of its velocity as measured in system S and m' its mass as measured in system S'.

By differentiation of equation (13) and simplification we may obtain the following transformation equation for *the rate at which the mass of a body is changing* owing to change in velocity :

$$\dot{m}' = \dot{m} - \frac{mv}{c^2} \ddot{x} \left(1 - \frac{v\dot{x}}{c^2}\right)^{-1} \dots \quad (14)$$

\dot{x} and \ddot{x} are the X components of the velocity and acceleration of the body in question as measured in system S.

We are now in a position to obtain transformation equations for the *force* acting on a particle. The force

* Phil. Mag. xxiii. p. 375 (1912).

acting on a body may be best defined as equal to the rate of increase of momentum *, *i. e.* by the equation

$$\mathbf{F} = \frac{d}{dt}(m\mathbf{q}) = m \frac{d\mathbf{q}}{dt} + \frac{dm}{dt}\mathbf{q},$$

$$\text{or} \quad F_x = m\ddot{x} + \dot{m}\dot{x},$$

$$F_y = m\ddot{y} + \dot{m}\dot{y},$$

$$F_z = m\ddot{z} + \dot{m}\dot{z}.$$

By the substitution of the previous equations presented in this article we obtain:

$$F_x' = \frac{F_x - \frac{mv}{c^2} \dot{v}}{1 - \frac{v\dot{x}}{c^2}} = F_x - \frac{v\dot{y}}{c^2 - v\dot{x}} F_y - \frac{v\dot{z}}{c^2 - v\dot{x}} F_z, \quad (15)$$

$$F_y' = \frac{\kappa^{-1}}{1 - \frac{v\dot{x}}{c^2}} F_y, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$F_z' = \frac{\kappa^{-1}}{1 - \frac{v\dot{x}}{c^2}} F_z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which are the desired transformation equations of force. These equations, which have here been derived from the principles of non-Newtonian mechanics, are those which were chosen by Planck to agree with electromagnetic considerations †.

Field around a Moving Charge.

As an application of these transformation equations, we may calculate the force with which a *point charge in uniform motion* acts on any other point charge, merely assuming Coulomb's

* See Phil. Mag. xxii. p. 458 (1911).

† In an article by Lewis and Tolman (*loc. cit.*) an attempt was made to deduce the transformation equation of force, which was unsuccessful, owing to the authors' assumption that the turning moment around a right-angled lever in uniform irrotational motion should be zero. This error and the interesting fact that in general, if we accept the relativity theory, the actual presence of a turning moment is necessary to produce a pure translatory motion in an elastically stressed body was pointed out by Laue, *Verh. d. Deutsch. Phys. Ges.* xiii. p. 513 (1911). For the particular case that the body on which the force is acting is stationary with respect to one of the systems, the transformation equations of force were correctly derived by the present author, Phil. Mag. xxi. p. 296 (1911).

inverse square law for the force exerted by a *stationary charge**.

Consider a set of coordinates $S(x, y, z, t)$, and let there be a charge ϵ in uniform motion along the X axis with the velocity v . We desire to know the force acting at the time t on any other charge ϵ_1 , which has any desired coordinates x, y , and z and any desired velocity $\dot{x}, \dot{y}, \dot{z}$.

Assume a system of coordinates $S'(x', y', z', t')$ moving with the same velocity as the charge ϵ which is situated at the origin. To an observer moving with the system S' , the charge always appears at rest and to be surrounded by a pure electrostatic field. Hence in system S' the force with which ϵ acts on ϵ_1 will be in accord with Coulomb's law.

$$\mathbf{F}' = \frac{\epsilon\epsilon_1\mathbf{r}'}{r'^3},$$

or

$$F_x = \frac{\epsilon\epsilon_1 x'}{(x'^2 + y'^2 + z'^2)^{3/2}}, \quad . \quad . \quad . \quad (18)$$

$$F_y = \frac{\epsilon\epsilon_1 y'}{(x'^2 + y'^2 + z'^2)^{3/2}}, \quad . \quad . \quad . \quad (19)$$

$$F_z = \frac{\epsilon\epsilon_1 z'}{(x'^2 + y'^2 + z'^2)^{3/2}}, \quad . \quad . \quad . \quad (20)$$

where x', y' , and z' are the coordinates of charge ϵ_1 , at the time t' . For simplicity let us consider the force at the time $t'=0$, then from transformation equations (1)-(3) we shall have

$$x' = \kappa^{-1}x, \quad y' = y, \quad z' = z.$$

Substituting into (18), (19), and (20) and also making use of the transformation equations of force (15), (16), and (17), we obtain the following equations for the force acting on ϵ_1 , as it appears to an observer in system S .

$$F_x = \frac{\epsilon\epsilon_1\kappa^{-1}}{(\kappa^{-2}x^2 + y^2 + z^2)^{3/2}} \left[x + \frac{v}{c^2} \kappa^2 (y\dot{y} + z\dot{z}) \right], \quad . \quad (21)$$

$$F_y = \frac{\epsilon\epsilon_1\kappa \left(1 - \frac{v\dot{x}}{c^2} \right) y}{(\kappa^{-2}x^2 + y^2 + z^2)^{3/2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$F_z = \frac{\epsilon\epsilon_1\kappa \left(1 - \frac{v\dot{x}}{c^2} \right) z}{(\kappa^{-2}x^2 + y^2 + z^2)^{3/2}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

* In its simplest form, Coulomb's law merely states the force acting between two stationary charges. It should be noted that our derivation assumes the same law for the force with which a stationary charge acts on a moving charge.

These equations give the force acting on ϵ_1 at the time t . From equation (4) we have $t = \frac{v}{c^2}x$ since $t' = 0$. At this time, the charge ϵ which is moving with the uniform velocity v along the X axis will evidently have the position

$$x_\epsilon = \frac{v^2}{c^2}x, \quad y_\epsilon = 0, \quad z_\epsilon = 0.$$

For convenience we may now refer our results to a system of coordinates whose origin coincides with the position of the charge ϵ at the instant under consideration. If X , Y , and Z are the coordinates of ϵ_1 with respect to this new system, we evidently have the relations

$$X = x - \frac{v^2}{c^2}x = \kappa^{-2}x, \quad Y = y, \quad Z = z, \quad \dot{X} = \dot{x}, \quad \dot{Y} = \dot{y}, \quad \dot{Z} = \dot{z}.$$

Substituting into (21), (22), and (23) we may obtain:—

$$F_x = \frac{\epsilon\epsilon_1}{s^3} (1 - \beta^2) \left\{ X + \frac{v}{c^2} (Y\dot{Y} + Z\dot{Z}) \right\}, \quad . \quad . \quad (24)$$

$$F_y = \frac{\epsilon\epsilon_1}{s^3} (1 - \beta^2) \left(1 - \frac{v\dot{X}}{c^2} \right) Y, \quad . \quad . \quad . \quad . \quad (25)$$

$$F_z = \frac{\epsilon\epsilon_1}{s^3} (1 - \beta^2) \left(1 - \frac{v\dot{X}}{c^2} \right) Z, \quad . \quad . \quad . \quad . \quad (26)$$

where for simplicity we have placed $\beta = \frac{v}{c}$, and

$$s = \sqrt{X^2 + (1 - \beta^2)(Y^2 + Z^2)}.$$

These same equations could also be obtained by substituting the well-known formulæ for the strength of the electric and magnetic field around a moving point charge into the fifth fundamental equation of the Maxwell-Lorentz theory $\mathbf{F} = \mathbf{E} + 1/c \mathbf{v} \times \mathbf{H}$. It is interesting to see that they can be obtained so directly, merely from Coulomb's law.

If we consider the particular case that the charge ϵ_1 is stationary (*i. e.* $\dot{X} = \dot{Y} = \dot{Z} = 0$) and equal to unity, equations (24), (25) and (26) should give us the strength of the electric field produced by the moving point charge ϵ , and in fact they do reduce as expected to the known expression

$$\mathbf{F} = \mathbf{E} = \frac{\epsilon}{s^3} (1 - \beta^2) \mathbf{r},$$

where

$$\mathbf{r} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}.$$

Gravitational Field.

This method of obtaining from Coulomb's law the expected expression for the force exerted by a *moving electric charge* is of special interest, since it suggests the possibility of obtaining from Newton's law an expression for the gravitational force exerted by a *moving mass*.

Let us assume, in accordance with Newton's law, that a stationary mass m_1 will act on any other mass m_2 with the force $\mathbf{F} = -km_1m_2\frac{\mathbf{r}}{r^3}$, where m_1 and m_2 are the masses which the particles would have if they were at rest, isolated, and at the absolute zero of temperature, and \mathbf{r} the radius vector from m_1 to m_2 . The determination of the force exerted by a mass in uniform motion may now be carried out in exactly the same manner as for the force exerted by a moving charge. In fact in analogy to equations (24), (25), and (26), we may write—

$$F_x = -k \frac{m_1 m_2}{s^3} (1 - \beta^2) \left\{ X + \frac{v}{c^2} (Y\dot{Y} + Z\dot{Z}) \right\}, \quad (27)$$

$$F_y = -k \frac{m_1 m_2}{s^3} (1 - \beta^2) \left(1 - \frac{v\dot{X}}{c^2} \right) Y, \quad (28)$$

$$F_z = -k \frac{m_1 m_2}{s^3} (1 - \beta^2) \left(1 - \frac{v\dot{X}}{c^2} \right) Z. \quad (29)$$

These are the components of the force with which a particle of "stationary" mass m_1 , in uniform motion in the X direction with the velocity v , acts on another particle of "stationary" mass m_2 . Taking m_1 as the centre of coordinates, m_2 has the coordinates X , Y , and Z and the velocity $(\dot{X}, \dot{Y}, \dot{Z})$. k is the constant of gravitation, β is placed equal to $\frac{v}{c}$, and s has been substituted for $\sqrt{X^2 + (1 - \beta^2)(Y^2 + Z^2)}$.*

It may be noted that the particle m_1 must be in uniform motion, although the particle m_2 may have any motion, its instantaneous velocity being $(\dot{X}, \dot{Y}, \dot{Z})$. It is unfortunate that the method does not also permit a determination of the force which an accelerated particle exerts. For cases, however, where the acceleration is slow enough to be neglected, it would

* These equations would accord with the electromagnetic theory of gravitation proposed by D. L. Webster, Proc. Amer. Acad. xlvii. p. 561 (1912).

be of great interest to see if these equations lead to expressions for the orbits of heavenly bodies differing appreciably from those hitherto in use.

Summary.

In this article it has been shown that the Einstein transformation equations, and the other principles of non-Newtonian mechanics, lead to a number of further transformation equations for acceleration, mass, rate of change of mass and force. The transformation equations of force are identical with those chosen by Planck. Two applications of the transformation equations have been given. By combining them with Coulomb's law, the expected equations have been derived for the force with which an electric charge in uniform motion acts on any other charge, and by combining them with Newton's law a new expression has been derived for the gravitational force with which a particle in uniform motion acts on another particle.

July 19, 1912.

XVII. *On a Certain Integral of the Problem of Three Bodies.*

By PHILIP H. LING, M.Sc.*

Introduction.

IT is well known that the motion of three particles under their mutual gravitational attractions cannot be completely determined. Certain combinations of the differential equations can be integrated, but their number is not sufficient to solve the problem, and it has been proved by Bruns and Painlevé that no other integrals can exist.

In astronomical problems it is usual to reduce the system of three bodies to the simplest possible form. One body, P, is supposed to have an infinitesimal mass, while the other two, S and J, describe circles about each other. We have then to determine the motion of P relative to the line SJ and in the plane of motion of the two finite masses. This is usually described as "the restricted problem of three bodies." Only one integral can be obtained easily, and it has been shown by Poincaré † that no others exist which are one-valued and regular.

Now, it has recently occurred to the writer to attempt to

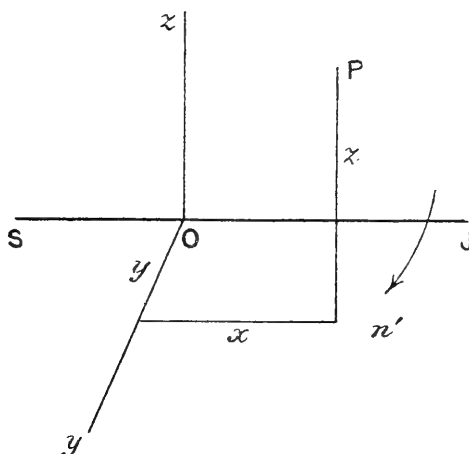
* Communicated by the Author. The first part of this paper formed a portion of a thesis accepted by the University of Bristol for the degree of M.Sc.

† An excellent account of the theorems of Bruns and Poincaré will be found in Prof. Whittaker's book on Analytical Dynamics.

repeat Poincaré's theorem, when the restriction as to motion in one plane is removed. The result seems sufficiently unexpected to be worth recording, for it appears to indicate the possibility of a second integral. The present paper also contains a number of inferences respecting this integral, which, as need hardly be said, would be of some importance in astronomy.

1. *The Equations of the System.*

Let O be the centre of gravity of S and J. Let Ox be an axis coincident with SJ, Oy a perpendicular one in the plane of motion of S and J, and Oz one perpendicular to that



plane. Let M , μ be the masses of S and J respectively, n' the angular velocity of the line SJ. Let $OS=a$, $OJ=b$, $\rho_1=SP$, $\rho_2=PJ$. U the potential at P due to S and J. Then

$$U = \frac{M}{\rho_1} + \frac{\mu}{\rho_2}.$$

Also, if SJ is taken of unit length,

$$n'^2 = M + \mu \quad \text{and} \quad Ma = \mu b.$$

Then the equations of motion are

$$\left. \begin{aligned} \ddot{x} - 2n'\dot{y} &= n'^2x + \frac{\partial U}{\partial x} = \frac{\partial \Omega}{\partial x} \\ \ddot{y} + 2n'\dot{x} &= n'^2y + \frac{\partial U}{\partial y} = \frac{\partial \Omega}{\partial y} \\ \ddot{z} &= \frac{\partial U}{\partial z} = \frac{\partial \Omega}{\partial z} \end{aligned} \right\}; \dots \dots (1)$$

where

$$2\Omega = n'^2(x^2 + y^2) + \frac{2M}{\rho_1} + \frac{2\mu}{\rho_2}.$$

The Jacobian integral of the system is obtained by multiplying the first equation of (1) by \dot{x} , the second by \dot{y} , the third by \dot{z} , adding, and integrating. This gives

$$\dot{x}^2 + \dot{y}^2 + \dot{z}^2 = 2\Omega - C \quad . \quad . \quad . \quad . \quad (2)$$

where C is a constant of integration.

Now these equations can be converted, either by a contact transformation, or by the method of variation of constants of integration, into the following Hamiltonian system :

$$\frac{dq_r}{dt} = \frac{\partial H}{\partial p_r} ; \quad \frac{dp_r}{dt} = - \frac{\partial H}{\partial q_r} \quad (r=1, 2, 3) \quad . \quad . \quad (3)$$

where $H = \text{constant}$ is the Jacobian integral, and

- $q_1 = \text{mean anomaly in the instantaneous ellipse,}$
- $q_2 = \text{angle between line of nodes and axis of } x,$
- $q_3 = \text{angle between line of nodes and line of apsides.}$
- $p_1 = \text{square root of semi-major axis,}$
- $p_2 = p_3 \cos i, \text{ where } i = \text{inclination of the orbit,}$
- $p_3 = \text{square root of semi-latus rectum.}$

If μ is not too great, H may be expanded in powers of it.

$$H = H_0 + \mu H_1 + \mu^2 H_2 + \dots \quad (4)$$

and

$$H_0 = - \frac{1}{2p_1^2} - n' p_2 \quad . \quad . \quad . \quad . \quad (5)$$

Now the Hessian

$$\begin{vmatrix} \frac{\partial^2 H_0}{\partial p_1^2} & \frac{\partial^2 H_0}{\partial p_1 \partial p_2} \\ \frac{\partial^2 H_0}{\partial p_1 \partial p_2} & \frac{\partial^2 H_0}{\partial p_2^2} \end{vmatrix} = 0.$$

This happens to be inconvenient, but the difficulty may be avoided by using H^2 in place of H , when the Hessian will not vanish.

2. *Poincaré's Theorem.*

The proof here attempted follows, in a condensed form, that given by Whittaker*.

If possible, let Φ be an integral, one-valued, regular, expandible in powers of μ , and periodic in q_1, q_2, q_3 .

Then

$$\Phi = \Phi_0 + \mu \Phi_1 + \mu^2 \Phi_2 + \dots$$

* *Op. cit.*

Now Φ_0 need not involve H_0 : for if it does, we may solve the equation connecting them for p_1 and get an identity

$$\Phi_0(q_1, q_2, q_3, p_1, p_2, p_3) = \Psi(q_1, q_2, q_3, H_0, p_2, p_3).$$

By replacing H_0 by H , we get $\Psi(H)$, an integral of the problem. Then $\Phi - \Psi(H)$ is also an integral. Call it $\mu\Psi'(H)$. Then Ψ'_0 may not involve H_0 . If it does, repeat the process. Then ultimately we arrive at a function not involving H_0 .

The condition that Φ should be an integral is that the Poisson-bracket (H, Φ) should vanish. And we have

$$(H, \Phi) = (H_0, \Phi_0) + \mu\{(H_0, \Phi_1) + (H_1, \Phi_0)\} + \dots \quad (6)$$

Since Φ is a periodic function, we may write, by Fourier's theorem,

$$\Phi_0 = \sum_{m_1, m_2, m_3} A_{m_1, m_2, m_3} e^{i(m_1 q_1 + m_2 q_2 + m_3 q_3)} \quad (i = \sqrt{-1}),$$

where the A 's are functions of the p 's only, and the summation extends over all integral values of m_1, m_2, m_3 . Then since H_0 does not involve q_1, q_2, q_3 , or p_3 ,

$$\begin{aligned} (H_0, \Phi_0) &= -i \frac{\partial H_0}{\partial p_1} \sum m_1 A \cdot e^{i(m_1 q_1 + m_2 q_2 + m_3 q_3)} \\ &\quad - i \frac{\partial H_0}{\partial p_2} \sum m_2 A e^{i(m_1 q_1 + m_2 q_2 + m_3 q_3)} \\ &= 0 \text{ (identically).} \end{aligned}$$

$$\therefore A \left(m_1 \frac{\partial H_0}{\partial p_1} + m_2 \frac{\partial H_0}{\partial p_2} \right) = 0$$

for all integral values of m_1, m_2, m_3 .

Now the quantity in the bracket cannot vanish unless the Hessian does.

Hence A_{m_1, m_2, m_3} vanishes, *except* A_{00m_2} . It follows that Φ_0 cannot involve q_1, q_2 , but may involve q_3 .

$$\text{Now let } H_1 = \sum_{m_1, m_2, m_3} B_{m_1 m_2 m_3} e^{i(m_1 q_1 + m_2 q_2 + m_3 q_3)}.$$

$$\Phi_1 = \sum_{m_1, m_2, m_3} C_{m_1 m_2 m_3} e^{i(m_1 q_1 + m_2 q_2 + m_3 q_3)}.$$

From equation (6) we have

$$(H_0, \Phi_1) + (H_1, \Phi_0) = 0;$$

i. e.:

$$\begin{aligned} \frac{\partial H_0}{\partial p_1} \cdot \frac{\partial \Phi_1}{\partial q_1} + \frac{\partial H_0}{\partial p_2} \cdot \frac{\partial \Phi_1}{\partial q_2} &= \frac{\partial H_1}{\partial q_1} \cdot \frac{\partial \Phi_0}{\partial p_1} \\ &+ \frac{\partial H_1}{\partial q_2} \cdot \frac{\partial \Phi_0}{\partial p_2} + \frac{\partial H_1}{\partial q_3} \cdot \frac{\partial \Phi_0}{\partial p_3} - \frac{\partial H_1}{\partial p_3} \cdot \frac{\partial \Phi_0}{\partial q_3}, \end{aligned}$$

whence, if Φ_0 does not involve q_3 , we get, by substituting for H_1 and Φ_1 ,

$$C \left(m_1 \frac{\partial H_0}{\partial p_1} + m_2 \frac{\partial H_0}{\partial p_2} \right) = B \left(m_1 \frac{\partial \Phi_0}{\partial p_1} + m_2 \frac{\partial \Phi_0}{\partial p_2} + m_3 \frac{\partial \Phi_0}{\partial p_3} \right).$$

Then, since this equation is true for all integral values of m_1, m_2, m_3 , we can find an infinite number of values of m_1, m_2 such that the left side vanishes. Then if B does not vanish for these values, we have the bracket on the right vanishing for all values of m_3 , and for the particular values of m_1, m_2 . Hence $\frac{\partial \Phi_0}{\partial p_3} = 0$ and we get

$$m_1 \frac{\partial H_0}{\partial p_1} + m_2 \frac{\partial H_0}{\partial p_2} = 0.$$

$$m_1 \frac{\partial \Phi_0}{\partial p_1} + m_2 \frac{\partial \Phi_0}{\partial p_2} = 0.$$

Hence the Jacobian $\frac{\partial(H_0, \Phi_0)}{\partial(p_1, p_2)} = 0$ for these values of m_1, m_2 . But there are an infinite number of such values, and the Jacobian is a continuous function. It therefore vanishes for all values. Hence Φ_0 is a function of H_0 , which we have proved not to be true: so that Φ cannot exist.

Poincaré shows that the case when $B=0$ does not affect the result.

Now we have assumed above that Φ_0 does not involve q_3 . If it does, the whole argument is upset, and we cannot say that Φ does not exist. In other words, if there are reasons for supposing the existence of such an integral, Poincaré's theorem offers no objection. There cannot be two such integrals, obtained independently, for in that case the problem could be completely integrated, and therefore the problem in one plane: which contravenes Poincaré's theorem. On the other hand, there may be two integrals, if one is the differential coefficient of the other.

3. *The Nature of the Integral.*

(i.) If the above argument is applied to the problem of attraction to two fixed centres, motion being coplanar, it will be found that a similar result is obtained. Here H_0 is a function of p_1 only, and Φ may exist, provided Φ_0 involves q_2 . But we know that an integral Φ can be obtained in this case, and consequently the presumption is that it exists in the problem of three-bodies as here considered.

(ii.) Poincaré's original proof of his theorem was on somewhat different lines*. The existence of a one-valued integral means that two out of the six characteristic exponents (which are equal and opposite in pairs) vanish. In one plane, there are four, and Poincaré shows that they cannot all vanish. But there is no argument against four of the six in our case vanishing.

(iii.) The writer has made attempts to find Φ by direct integration, but without success. It is unlikely that integration in finite terms will be effective.

(iv.) The integral obviously vanishes identically in one plane.

(v.) There is a particular solution of this problem which has been discussed by Pavanini†. Here the body P oscillates along the z axis, the two masses M and μ being equal. The integral Φ must either coincide with the Jacobian integral, or vanish identically when x, y, \dot{x}, \dot{y} vanish and $M = \mu$.

(vi.) It has been proved by Lindstedt ‡ and others that the problem may be solved by trigonometric series involving three arguments. This is not incompatible with Poincaré's theorem, since the series cannot converge in all cases. But what has been said above leads us to suppose that one particular series may do so.

Now we know, from Poincaré's paper already referred to, that the problem admits of an infinite number of periodic solutions (which reduce to circles when the disturbing mass vanishes). The Lindstedt series will then become Fourier series. Assuming the solutions to be stable, we have, in the neighbourhood of each, other solutions which may be regarded as oscillations about them, and thus a gradual transition in the nature of the curve. Now these periodic orbits must exist for all values of the inclination, and as we

* "Sur le problème de trois corps et les équations de la dynamique," *Acta Math.* xiii. (1890).

† "Sopra una nuova categoria di soluzioni periodiche nel problema dei tre corpi," *Ann. di Mat.* (1907).

‡ "Ueber die allgemeine Forme der Integrale der Dreikörperproblems," *Astr. Nachr.* cv. (1883).

pass away from them the only causes which can ultimately lead to divergence are : (a) the eccentricity may become too large ; or (b) there may be too close approach to the disturbing mass, so that the mean motion and therefore the semi-major axis must be restricted. If we consider three Lindstedt series representing the complete solution for one integration, we get p_1, p_2, p_3 in this form. Eliminate the eccentricity and the major axis. Then we get a series which does not involve these quantities, and therefore shows no tendency to diverge under any circumstances. Hence this is a true integral.

It may be added that such an integral would probably lead to interesting results in astronomical work. In particular, the fact that Φ_0 involves q_3 might enable us to examine the motion of the line of apsides in a new way.

4. *Summary.*

The restricted problem of three bodies in three dimensions probably admits of a hitherto unknown integral, which may be capable of expression as a convergent trigonometric series.

Bristol,
Oct. 29, 1912.

XVIII. *Further Experiments on the Mobility of the Positive Ion at Low Pressures.* By GEORGE W. TODD, M.Sc. (Birm.), B.A. (Cantab.), late 1851 *Exhibition Research Scholar of the University of Birmingham* *.

IN a previous paper† the author has shown that the mobility of the positive ion in gases at low pressures departs from the inverse pressure law, but at pressures much lower than is the case with negative ions. For different gases the pressures at which the mobilities begin to show abnormality appear to be approximately proportional to the normal mobilities in the gases, so that the denser the gas the lower the pressure is at which the mobility begins to increase beyond that given by the inverse pressure law. In the case of the negative ions also‡, for the same apparatus, and when certain conditions are kept constant, a similar relation is found to hold between the "critical" pressure and the normal mobility as holds for the positive ion. The curves

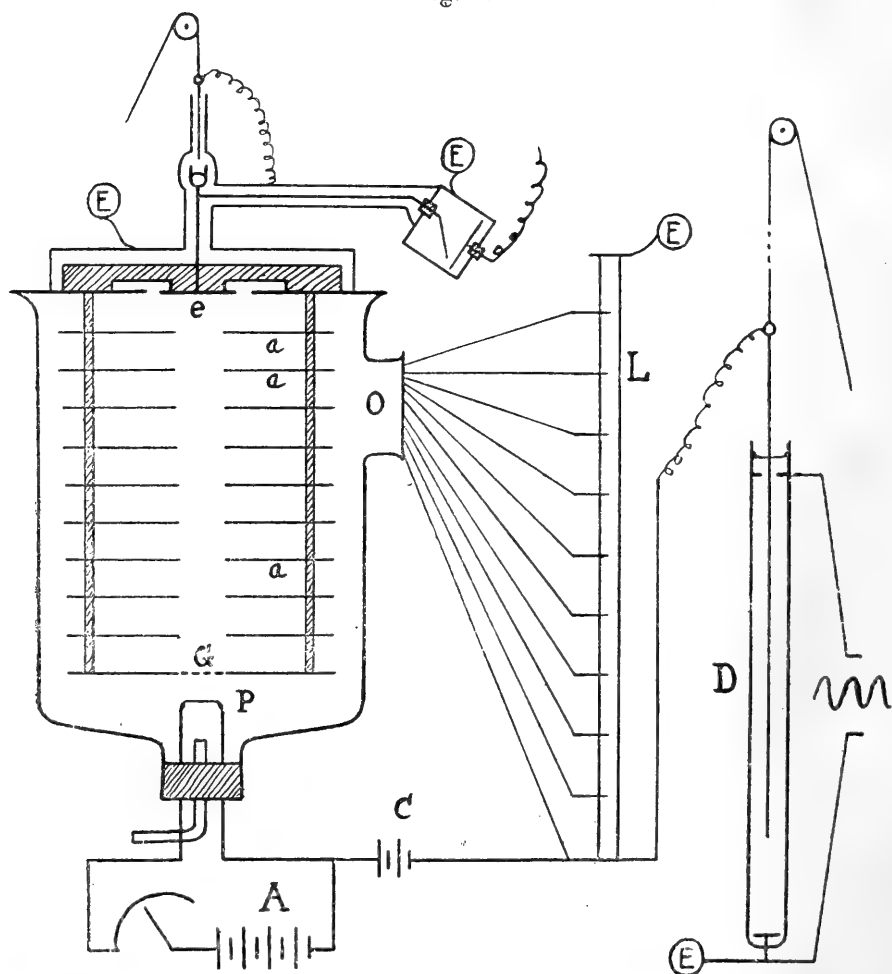
* Communicated by the Author.

† Phil. Mag. Nov. 1911, p. 791.

‡ Proc. Camb. Phil. Soc. xvi. p. 653.

in the paper quoted *, showing the relation between the product of pressure and mobility and the pressure for the positive ions, suggested that at pressures a little lower than those for which mobilities had been determined, something less than the molecule of the gas might be carrying the charge. Owing to the fact that the dimensions of the measuring apparatus became of the order of about fifty free paths of the gas molecules at these lowest pressures, it was impossible to draw definite conclusions as to the mass of the carrier from measurements of the mobility, so it was decided to construct an apparatus in which it was hoped to make the ions oscillate over a distance of 20 cm. instead of over 5 cm.

Fig. 1.



Apparatus.—An idea of the apparatus may be gathered from fig. 1. *e* was a carefully insulated metal plate surrounded by an “earthed” guard-ring, and connected to a

* Phil. Mag. Nov. 1911.

Wilson tilted electroscope. Below this electroscope plate was a tier of ten parallel circular plates, a, a, \dots , of 14 cm. diameter, insulated and equidistant from each other. In the centre of each there was a hole somewhat smaller than the diameter of the electroscope plate. The hole in the lowest plate was covered with a wire gauze G, below which, at a distance of one or two centimetres, was a platinum strip P covered with aluminium phosphate, which served as the source of positive ions. The whole of this was enclosed in a large bell-jar, which could be exhausted to the desired pressures with a mercury pump and a "liquid-air-charcoal" tube. From each plate a fine wire carefully insulated with thin glass tubes and beads passed through the opening O in the bell-jar to the potentiometer L. This was an ebonite tube three-quarters of a metre long containing water. It was divided into ten equal parts, and at each division a wire connected to its corresponding plate penetrated into the water. One end of this potentiometer was earthed, while the other was connected to a source of alternating potential. The latter was sometimes obtained from the town mains and sometimes from a specially designed commutator, described fully in the author's previous paper (*loc. cit.*) on positive ions. The maximum potential was varied by the same contrivance as before, and will be sufficiently evident from the diagram (D).

In measuring mobilities by the alternating field method it is essential that at every instant the field is uniform. The object of the parallel plates and the potentiometer L was to secure that condition. The distance between e and G was 21 cm., and there were ten plates 14 cm. in diameter with central holes less than 4 cm. diameter. With such dimensions it was reasonable to assume that the field at any instant along the path of the ions from the gauze to the electroscope plate was uniform. That it was so is supported by the fact that the mobilities measured at the higher pressures agreed with those obtained with two parallel plates near together.

The phosphate-covered strip was heated by the accumulators A, and the temperature regulated by means of a variable resistance to give a convenient number of positive ions to work with. A small potential C was maintained between P and G to direct the ions to the gauze.

The measurement of the mobility was made in the usual way by plotting the current to the electroscope for various maximum values of the alternating potential. If the latter has a period T, and the distance between the gauze and the

electroscope plate is d , then for an ion just to go the whole distance we must have

$$d = \frac{u}{d} \int_0^{\frac{T}{2}} E \cdot dt,$$

where u is the mobility and E the value of the alternating potential. The town mains gave very approximately a sine curve for the value of E , so that the mobility was given by

$$u = \frac{\pi d^2}{E_0 T}.$$

In the present apparatus $d = 21.0$ cm., $T = 1/90$ sec., and putting $E_0 = \sqrt{2} \cdot e$, where e is the "effective" value of the alternating potential, we find the mobility

$$u = \frac{88200}{e}.$$

In the case of the commutator the value of $\int_0^{\frac{T}{2}} E \cdot dt$ was

determined from the form of the curve, which was known from the construction of the commutator. Putting in this value and the proper constants, the mobility was given by

$$u = \frac{1764}{E_0} n,$$

where n is the frequency of alternation.

Experiments.—As in previous experiments, it was found that the presence of traces of water-vapour seriously affected the mobilities at low pressures. When water-vapour was present, diminution of the pressure beyond a certain point apparently depending on the amount present resulted in a diminution of the mobility. By the prolonged application of liquid air to a charcoal tube in connexion with the apparatus, and by introducing carefully dried gas, this diminution disappeared. Mobilities could easily be measured down to pressures of about $1/20$ mm. At high pressures, whether the town mains or the commutator were used as the source of alternating potential, approximately the same mobilities were obtained as those in previous experiments, but as soon as the pressure went down below a millimetre the mobilities varied with the rate of alternation of the field if this were high, and, moreover, they showed nothing like the enormous increases which were observed with the alternating chamber of small dimensions. The tables and curves below give some

results when the rate of alternation was low but constant, the source of potential being the town mains.

CO_2 .

Press. <i>p</i> .	<i>e</i> .	Mob. <i>u</i> .	<i>pu</i> .
1.47 mm.	156 v.	565 cm./sec.	83
1.13	109.5	806	91
.93	82.9	1063	99
.525	43.7	2020	103
.507	39.4	2240	113
.451	33.7	2620	118
.350	24.5	3600	126
.300	19.5	4530	136
.210	14.3	6190	130
.136	9.16	9620	131
.091	4.77	18550	169
.053	2.71	32600	173

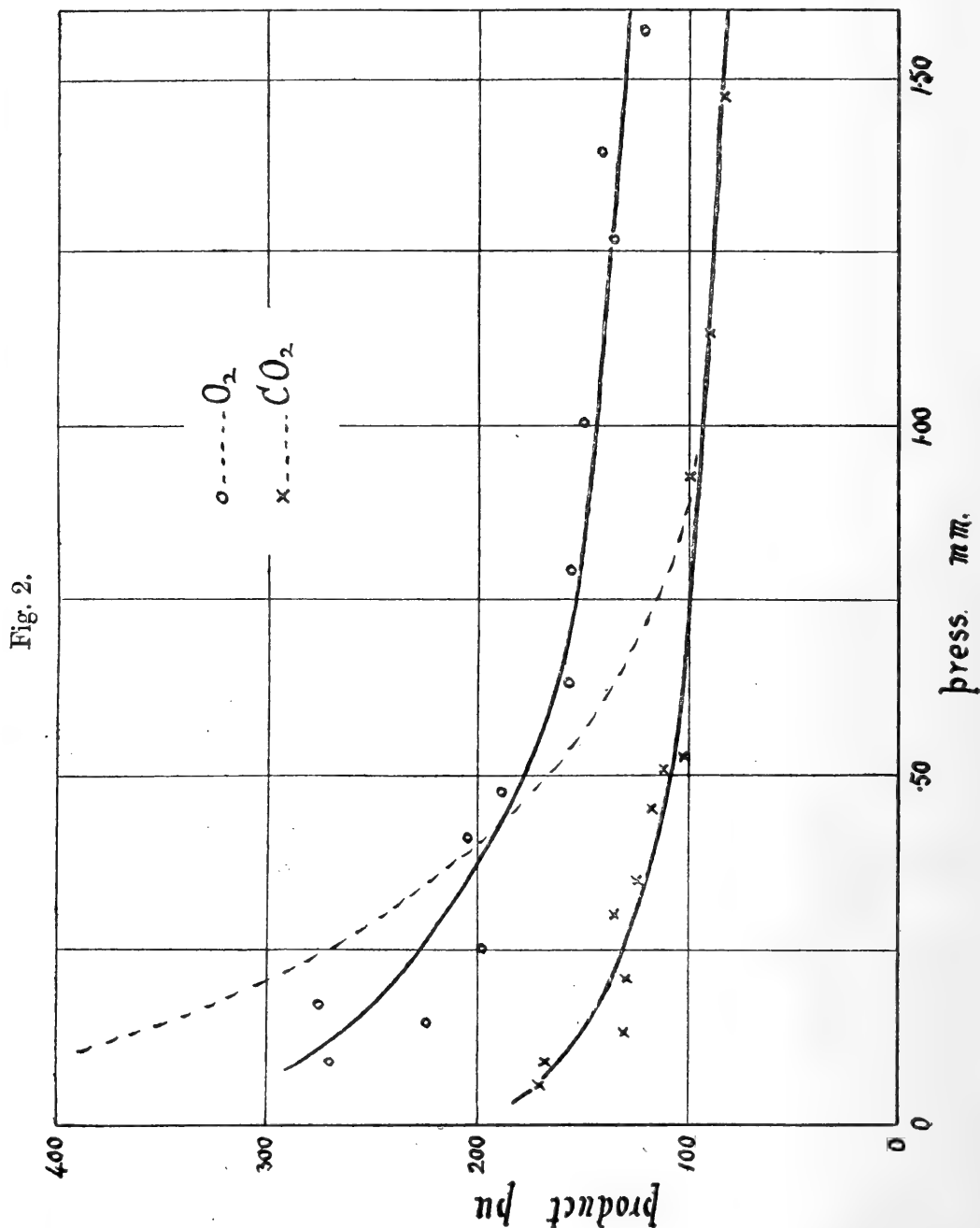
H_2 .

Press. <i>p</i> .	<i>e</i> .	Mob. <i>u</i> .	<i>pu</i> .
3.54 mm.	65.1 v.	1358 cm./sec.	481
2.68	47.1	1878	505
1.50	27.3	3240	485
1.27	20.0	4410	560
.99	14.35	6160	610
.67	9.21	9570	641
.420	5.45	16200	680
.380	4.59	19200	730

O_2 .

Press. <i>p</i> .	<i>e</i> .	Mob. <i>u</i> .	<i>pu</i> .
1.57 mm.	114 v.	771 cm./sec.	121
1.39	83.9	1015	141
1.27	83.0	1062	135
1.06	61.9	1426	151
.79	44.1	2000	158
.63	35.1	2523	159
.480	22.4	3940	189
.410	17.6	5010	206
.250	11.15	7920	198
.172	5.51	16050	276
.151	5.92	14900	225
.091	2.98	29600	270

The dotted line in the curves (fig. 2) shows the relation between the product pu and the pressure p for carbon dioxide when the plates of the alternating chamber were 5 cm. apart.



The difference between the dotted and continuous curves is remarkable, and should lead to information concerning the nature of the ions at low pressures. In a paper containing results of experiments on the mobility of negative ions at

low pressures (*loc. cit.*), the writer has suggested that corpuscles have to travel a very considerable number of molecular free paths from the source of formation before an equilibrium state of ionization exists. If the distance over which the mobility is measured is too small, and the source of formation of the corpuscles is at or near one boundary of this distance, the proportion of ions reaching the other boundary as aggregates of gas molecules will be smaller than if the distance had been sufficiently large for equilibrium to have been reached. Thus the mobility would appear to be higher than normal. Increasing the distance between the boundaries of the alternating chamber gives more time for the ions to attain equilibrium conditions, hence the mobility departs less from the normal value.

Now if the positive ion is of the same nature as the negative ion, there should also be an increase in its mobility when the pressure is sufficiently low and the distance between the plates of the measuring chamber small enough. Moreover, the mobility should approach nearer the normal value when the boundaries are much farther apart. This has been shown to be the case in the tables and curves above. The fact that abnormality sets in at much lower pressures than in the case of the negative ion, indicates that the charged nucleus of the positive ion is of much bigger dimensions than that of the negative ion.

Some measurements were made with the pressure constant and rather low, using different rates of alternation of the electric field, and it was found that after the frequency had passed a certain value the mobility began to increase. An increase in the rate of alternation means of course an increase in the electric field, if the ions are to travel the same distance. As the potential increased a stage would be reached when the violence of collision of the ions would prevent the formation of the normal clusters of molecules, and thus a different condition of equilibrium would result in which the size of the clusters on the average would be smaller than usual, and the mobility at this stage would consequently show an increase. Further, the proportion of ions present with sufficient energy to ionize the gas molecules by collision would help in the same direction.

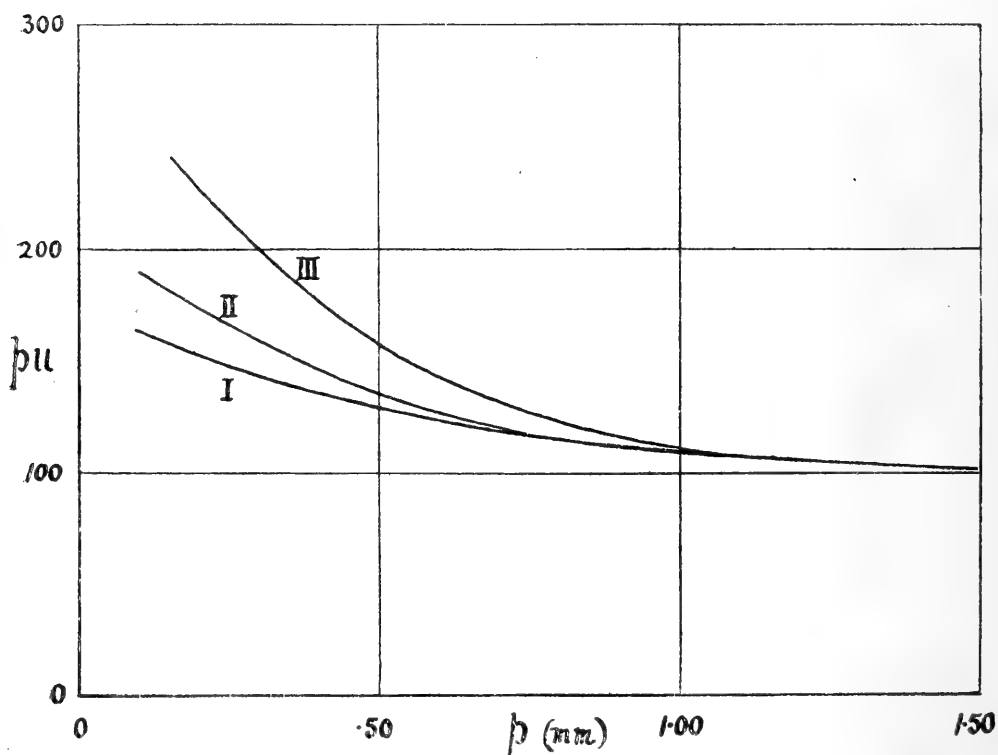
A set of readings showing the relation between the frequency of alternation and the mobility when the pressure was constant is given below (p. 170). The pressure for this particular set of readings was .365 mm., and it will be noticed that after the frequency had passed 150 per second the mobility began to increase. At lower pressures the increase began at lower

frequencies, while at high pressures it was impossible, with the limited frequencies obtainable with the apparatus used, to get any increase in the mobility. Without doubt, if the

Frequency n .	Mobility u .
55	3710
92	3750
103	3690
122	3670
178	3810
210	4010
257	4490
286	4520
318	5020

frequency could have been increased sufficiently an increase would also have been observed in these cases. From several curves showing the relation between the mobility and frequency for a number of pressures, fig. 3 was constructed.

Fig. 3.



At high pressures, whatever the rate of alternation used in the experiments, the products of pressure and mobility lie on the same curve. For frequencies of from 50 to 130 per second no differences from curve I. could be detected.

Curves II. and III. show the changes produced by frequencies of 220 and 300 respectively.

In previous work on the positive ion the author was not able to detect any certain difference in the mobility with change in the rate of alternation. This can be accounted for in two ways. It was not possible, in measuring mobilities below the "critical" pressure, to employ, with the dimensions of the apparatus, very different frequencies. The fields also were not strong enough to cause collisions sufficiently violent to prevent the formation of the normal ionic aggregates.

It has been shown* that in gases subjected to an ionizing influence at ordinary pressures, positive ions exist with mobilities corresponding to aggregates of from one up to five or six molecules of the gas. Altberg found also that a small percentage of the negative ions in a gas at ordinary pressures had a mobility giving an ionic mass of less than a single molecule, a result which one would expect if the nucleus of the negative ion were a corpuscle existing for a fraction of its life in the free state. The same experimenter found that the smaller ions had a shorter life than the larger aggregates. Now we should expect when the pressure is diminished, and consequently the mean free path increased, that the lives of all aggregates would increase in the same proportion. Hence for normal mobilities to be obtained, the measuring apparatus must also be increased in the same proportion.

It should be mentioned that the experimental results obtained in the present paper lend some support to a theoretical investigation on the nature of an ion by Kleeman†, in which he develops the idea of a continually changing aggregate to explain some properties of ions.

If the views expressed are correct, it ought to be possible to obtain abnormal mobilities at ordinary pressures by the alternating field method. The plates of the alternating chamber would have to be very near together, and the frequency of alternation very high. Some trouble would be caused by diffusion with the plates so near together.

This work was carried out at the Cavendish Laboratory, and the author, in concluding, wishes to express his many thanks to Sir J. J. Thomson for his interest in it.

Birmingham, Nov. 15, 1912.

* Altberg, *Ann. d. Phys.* p. 849 (1912).

† Proc. Camb. Phil. Soc. xvi. p. 285.

XIX. *A Study of the Ionization produced by β and γ Rays at High Pressures.* By D. C. H. FLORANCE, M.A., M.Sc.*

[Plate I.]

THE ionization produced by γ rays in a closed vessel is due partly to the β rays escaping from the walls, and partly to the β rays set up from the molecules of the gas. There is no definite proof that γ rays ionize directly. Kleeman (Proc. Roy. Soc. March 1909) has attempted to separate the wall effect from the gas effect by means of the magnetic deflexion of the β rays from the wall. He has also made a determination of the velocities and penetrating power of the "emergent" and "incident" secondary β rays produced by γ rays. Laby and Kaye (Phil. Mag. Dec. 1908), working with pressures up to 20 atmospheres, and Wilson (Phil. Mag. Jan. 1909) with pressures up to 40 atmospheres, have investigated the effect of pressure on the ionization produced by γ rays in a closed vessel.

Kovarik (Abstract Phys. Rev. Feb. 1912), by increasing the pressure of the air in his ionization-chamber to about 20 atmospheres, has found the absorption coefficient of the β rays from RaE to be 0.0149 cm.^{-1} air, and of the harder β rays from Ra D to be 0.094 cm.^{-1} air. The writer has found the absorption coefficient of the β rays from Ur X to be 0.007 cm.^{-1} air.

In the present paper a pressure of 80 atmospheres has been attained, and the apparatus has been so arranged that the β rays emitted from different metals could be examined. It was thus hoped that the absorption coefficients of the "emergent" and "incident" secondary β rays could be determined, and an estimate made of the relative number of β particles from the walls and from the gas contained in the ionization vessel. On account of the impossibility of securing a definite cone of γ rays and the incompleteness of certain experimental data, these quantities could only be approximately determined.

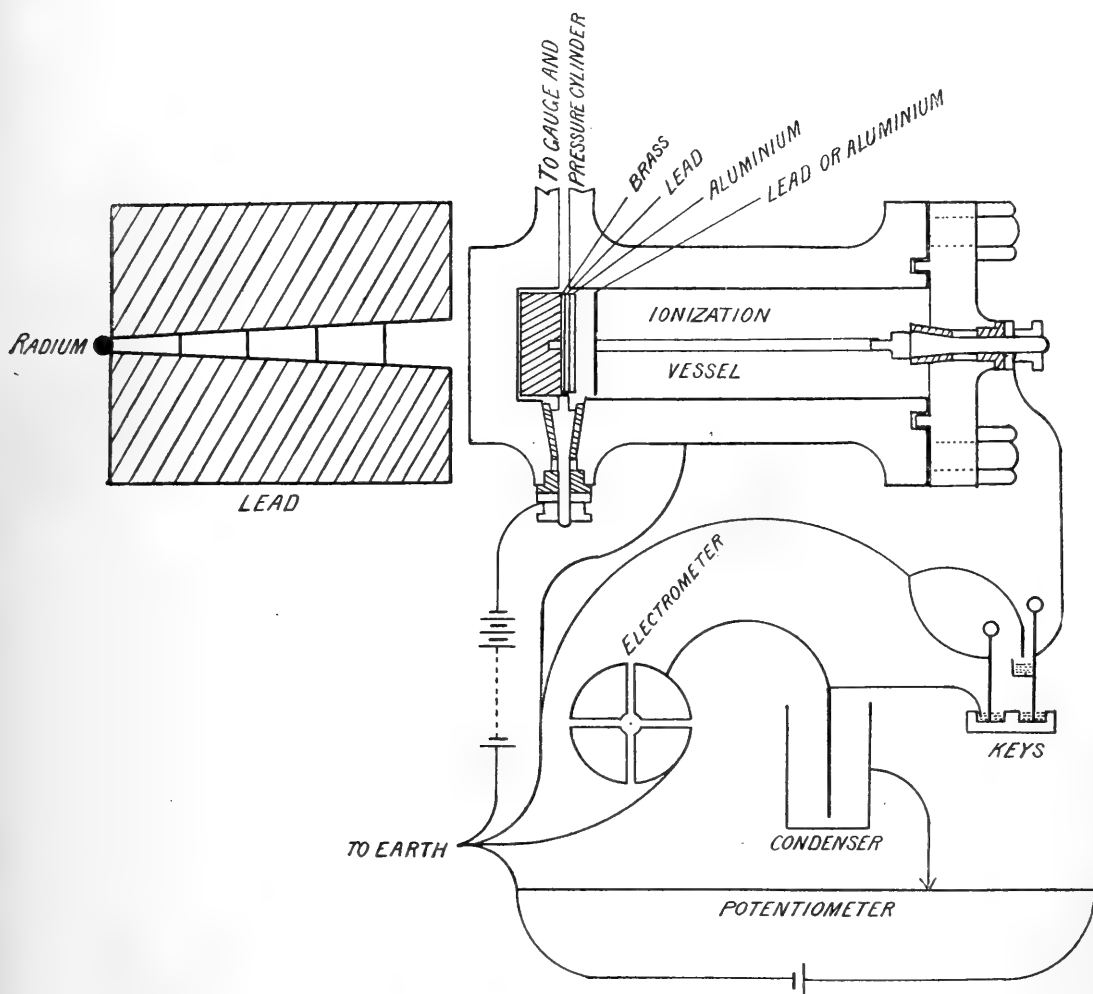
Apparatus.

The ionization vessel (fig. 1) was cylindrical, 7.4 cm. in diameter and 27.5 cm. in height. The pressure, which could be raised to 80 atmospheres, was measured by a carefully calibrated steel tube-gauge. A is a compound plate

* Communicated by Prof. E. Rutherford, F.R.S.

consisting of a bottom one of brass and two others of aluminium (3.3 mm. thick) and lead (3.2 mm. thick), the latter two being reversible. This compound plate, supported and insulated from the vessel by means of a plate of ebonite, was connected to a battery which gave a voltage of 1800.

Fig. 1.



The γ rays which pass through the bottom of the vessel and compound plate remain approximately constant. The lead absorbed some of the soft γ rays scattered by the base of the vessel. The upper plate, either of Al or Pb, was supported by means of a brass tube to an electrode at the top of the vessel. The distance apart of the two plates could be varied. For certain experiments the upper plate was thin aluminium-foil (0.00024 cm. thick) stretched over a brass ring, which was supported by knitting-needles to the electrode.

A balance method, similar to that described by Townsend (Phil. Mag. May 1903), was used in these experiments for measuring the ionization currents. This method was found to be far more accurate and certain than the ordinary rate method. A Dolazalek electrometer of sensibility about 400 mm. divisions per volt was used. The experimental arrangement is shown in fig. 1.

Variation of Current with Voltage.

It is important that at each given pressure the saturation current should be measured ; but it was found quite impossible to obtain complete saturation, even at low pressures, with a voltage of 2200. In fig. 2 (Pl. I.) the saturation curves for the ionization due to the β rays from Ur X are shown when the pressure in the ionization-chamber was raised from 5 to 70 atmospheres, and the voltage was increased from 80 to 1800 volts. Although for no pressure was complete saturation obtained, it should be noticed that all the curves are of the same character, and that there is a constant ratio between the ionization currents at any two given pressures when the voltage is constant. It would therefore appear that the true saturation current at any pressure is a definite multiple of the ionization current measured for a particular voltage. The shape of the saturation curves due to β rays at high pressures resembles those obtained for α rays at ordinary pressure. There appears to be the same difficulty in obtaining complete saturation. The saturation curves obtained when γ rays were used as the source of ionization were similar to those obtained for the β rays of Ur X.

An experiment was then carried out to see whether the saturation curves depended on the activity of the source. Two definite pressures, 5 and 25 atmospheres, were chosen. The saturation curves were plotted when the voltage was increased from 80 to 1800 volts. By a suitable adjustment of the lead screens in front of the radium, the ionization current for a given voltage and pressure was doubled. It was found that the ionization current was also doubled for all voltages at both pressures.

The numbers quoted by Laby and Kaye (Phil. Mag. Dec. 1908) seem to support the above results, except that they got complete saturation at 1500 volts for a pressure of 8 atmospheres and at 3500 volts for a pressure of 15 atmospheres. The writer had not available higher voltages than 2200, and was unable in any case to obtain evidence of complete saturation. In the experiments to be described later,

it has been assumed that no sensible error in the relative values of the ionization currents has been introduced by using a voltage of 1520 when the plates were 1 cm. apart.

Absorption by Air of the β rays from Ur X.

When γ rays pass through any material some of the γ rays are absorbed and β rays are consequently produced. "Emergent" β rays continue in the direction of the original γ rays, and "incident" β rays are returned in the opposite direction. In order to obtain some idea of what happens to the emergent and incident β rays in the ionization vessel when the pressure was increased, a comparison was made with the β rays of Ur X. This active material was chosen because a thin film could be easily prepared of any desired area, and the β rays correspond approximately in penetrating power to the β rays from Radium C.

A uniform layer of Ur X was deposited on platinum foil about 3 cm. in diameter. This was covered with aluminium 0.2 mm. thick to absorb soft β rays. This active material was fixed to the lower plate. The upper plate was aluminium foil (0.00024 cm. thick), so that reflexion in the case of the upper plate was reduced to a minimum; yet there would undoubtedly be a certain amount of reflexion from the interior of the vessel, and this it was impossible to estimate. The distance between the plates was 1 cm. The pressure in the vessel was increased, and the ionization currents were measured for the different pressures. The results are shown graphically in fig. 3 (Pl. I.). Assuming that ionization and absorption are proportional to the pressures, the saturation current at any pressure should be given by

$$i = A(1 - e^{-p\lambda d}),$$

where A = a constant ;

p = pressure in atmospheres ;

λ = coefficient of absorption at unit pressure ;

d = distance apart of the plates.

The curve, fig. 3, can be expressed approximately by an equation of this type, and the value of λ was thus found to be 0.04 cm.⁻¹. If we calculate the absorption coefficient of the β rays in air from the known absorption coefficient in aluminium, assuming the density law, $\lambda = 0.0064$ approximately. This discrepancy between the observed value and the calculated value cannot be ascribed to lack of saturation at the high pressures.

Consider the shape of the ionization-chamber and the consequent paths of the β rays. Each plate is 7 cm. in diameter, the distance apart is 1 cm., and the active material is spread over a surface 3 cm. in diameter. If the β rays pass out equally in all directions, not more than 20 per cent. of the total number of β rays emitted will traverse a distance less than 1.3 cm.; and about 30 per cent. will have a path of 3.5 cm. in air. Hence, instead of the effective distance between the plates being 1 cm., the average path between the plates, allowing for the obliquity of the rays, is roughly 2.2 cm. Allowing for this correction, the value of the absorption coefficient should be .014, instead of the calculated value .0064. The experimental value is, however, .04 cm.⁻¹.

No account has been taken of scattering and multiple reflexion, and it is obvious that these factors are of great importance in the present case. Since the upper plate is Al foil, the β rays reflected from the walls and top of the vessel will have a certain ionizing effect on the gas between the plates. It is difficult to evaluate this effect. The number of β rays striking the walls decrease as the pressure in the vessel increases; but the ionization due to these reflected β rays will rise to a maximum and then diminish. The β rays turned back by the air above the Al foil will first increase to a maximum with pressure, and then decrease on account of the absorption of the β rays between the plates. The ionization due to these β rays will increase to a maximum and finally decrease as the pressure is raised. There will also be a small effect due to the β rays finally reflected back from the plate carrying the active material. A certain number of the primary β rays that penetrated the bottom plate will be scattered back into the gas. Wilson (Proc. Roy. Soc. March 1912) has recently shown that the absorption coefficient in aluminium of reflected β particles may have average values ranging from 14 to 40.

Hence, taking into consideration scattering and multiple reflexion and the consequent variation of ionization due to increase of pressure, the discrepancy between the experimental and the calculated value of the absorption coefficient can be explained. The curve (fig. 3) can be resolved into its various components in order to allow for the separate β -ray effects, but the data at present available are too incomplete to give definite values for all the factors involved.

An experiment was made to show definitely that the high value obtained for the absorption coefficient was due mainly

to the obliquity and the scattering of the β rays. The Ur X was placed at the bottom of the ionization-chamber and covered with 0.1 mm. of aluminium. At a distance of 4.3 cm. above the active material was a lead plate, 2.3 mm. thick, with a circular opening 3 cm. in diameter. Over this opening was fastened a sheet of aluminium, 0.1 mm. thick, to absorb soft scattered radiation. The upper plate was Al foil, and the distance apart was 1.2 cm. The lead plate and aluminium covering were charged to 1520 volts.

As the pressure in the vessel was raised the ionization between the plates increased until it reached a maximum and then decreased. The distance between the active material and the bottom plate being 4.3 cm., and the circular opening in the lead and the surface of the active material being both 3 cm. in diameter, the direct distance that the β rays had to traverse was between 4.3 and 5 cm. in the lower chamber, and between 1.2 and 1.3 cm. between the plates.

The corresponding problem for α rays has been given by Rutherford in 'Radio-Activity.'

The saturation current is proportional to

$$\frac{I_0}{\lambda} (e^{-p\lambda d_1} - e^{p\lambda d_2}).$$

This is a maximum when

$$\log_e \frac{d_1}{d_2} = -p\lambda(d_2 - d_1).$$

From this expression

$$\lambda = .0076.$$

Allowing for the obliquity of the rays, λ would be about .007. It should be noticed in fig. 4 that at 80 atmospheres, when the β rays have passed through a distance equivalent to 350 cm. at normal pressure, there is a considerable ionization effect between the two plates. Substituting $\lambda = .0076$ in the expression for the saturation current and plotting the curve, there is a fair agreement between the theoretical and experimental curves.

The experiments with Ur X were in progress for over a fortnight, so that the decay of Ur X was also examined. For any definite pressure the period of Ur X was found to be about twenty-two days.

When the Ur X was covered with .4 mm. of Al the ionization-pressure curve was similar to that obtained when the material was covered with .2 mm. of Al. The absorption

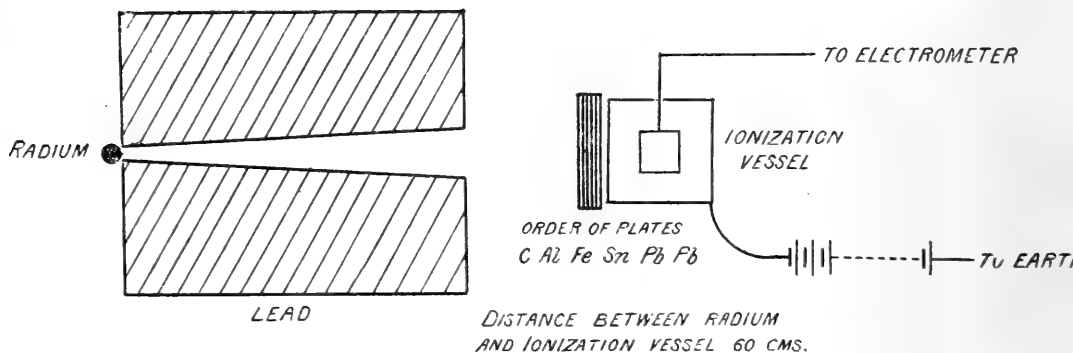
coefficient of the β rays in aluminium (between $\cdot 2$ and $\cdot 4$ mm.) for any pressure was approximately 19 cm.^{-1} , whereas in the usual experimental arrangement the value is 14.

The Effect of the Final Plate on the Amount of Emergent β Radiation.

The γ rays passing into the ionization-chamber were always approximately of the same intensity. The ionization between the plates at atmospheric pressure should be mainly dependent on the nature of the plates. Since at atmospheric pressure the ionization currents were extremely small, another experiment was performed to see how the quantity of emergent β rays depended on the material of the plates.

Fig. 5 illustrates the experimental arrangement. The ionization-chamber (kindly lent by Mr. Moseley) was constructed of Al foil supported on knitting-needles. It was

Fig. 5.



about $7\cdot 3$ cm. cube. This ionization-chamber rested on thin glass tubes. Against the side of the ionization-chamber nearest the radium was arranged the following series of plates :—

Plate ...	Carbon.	Aluminium.	Iron.	Tin.	Lead.	Lead.
Thickness in mm. }	4·9	3·4	2·1	2·0	4·3	9·2

Between the plate of lead $9\cdot 2$ mm. thick and the vessel there was just sufficient space to admit one of the other plates, the β rays of which were to be examined. The γ rays always passed through the same quantity of material; hence, in each case the effect observed was chiefly due to

the β rays emerging from the plate next to the ionization-chamber. The plate of lead 9.2 mm. thick was placed near the vessel to reduce to a minimum the effect of the scattering in the substances of smaller atomic weights. The curve (fig. 6, Pl. I.) is similar to that obtained by Bragg (Phil. Mag. Dec. 1908).

The Ionization due to the γ Rays of Radium.

The experimental arrangement is shown in fig. 1. The source of γ rays was 30 mgrs. of radium bromide. It is impossible to secure a perfect cone of γ rays on account of the scattering they undergo whenever they traverse matter. Precautions were, however, taken to obtain an approximate cone of rays. A conical opening was cut in a large block of lead, and the radium was placed in a definite position at the apex. Four lead slides, each 3 mm. thick, were placed in the positions marked in order to cut out the softer γ rays. Practically all the γ rays entering the ionization-vessel proceed from this conical opening. The space between the plates is traversed by the main cone of γ rays together with those γ rays scattered from the original cone by the plates. Besides the β rays produced by the γ rays from the two plates, there are also β rays set up in the walls of the vessel due to the scattered γ rays.

Experiments were carried out—

- (1) Keeping the bottom plate the same and varying the upper plate—Pb, Al, or Al-foil ;
- (2) Keeping the upper plate the same and reversing the bottom plate Al or Pb ;
- (3) Varying the distance between the plates in each of the two previous arrangements.

Fig. 7 (Pl. I.) shows the results obtained when the plates were kept at a constant distance of 1 cm. apart. In curve A the lower plate was aluminium and the upper plate lead, and in curve C the lower plate was lead. When the γ rays pass through 1.5 cm. of lead there are more emergent β rays from aluminium than from lead. Hence, if the curve C is subtracted from the curve A, or D from B, then the difference should give the approximate effect of the additional β rays from the aluminium plate. The difference between the curves gives an indication of what happens to a certain proportion of the corpuscular emergent radiation when the pressure is varied. Since more β rays are scattered from a

plate of lead than from a plate of aluminium, the curve (A—C) is greater than (B—D). From the curve (A—C) (fig. 8) the apparent coefficient of absorption of the β rays is observed to be approximately 0.046 cm.^{-1} ; and it has already been shown that the absorption coefficient of the β rays from Ur X determined under similar conditions was 0.04 cm.^{-1} .

There are more "incident" β rays ejected from lead than from aluminium; hence the difference between the curves A and B, or C and D, will give a general indication of the behaviour of a certain proportion of the incident β rays. The coefficient of absorption of these incident β rays = 0.056 cm.^{-1} approximately. The emergent β rays appear to be more penetrating than the incident β rays; and this is to be anticipated just as in the case of scattered β rays, which are more absorbable the greater the angle through which they have been deflected.

Beatty (Phil. Mag. August 1910) has found that the incident corpuscular radiation produced by a homogeneous beam of X rays was similar in penetrating power to the emergent corpuscular radiation.

When the upper plate was aluminium foil and the lower plate changed from lead to aluminium, the curves were similar to those in which aluminium was the upper plate. The absorption coefficient for the emergent β rays in this case was 0.04 cm.^{-1} .

In all these experiments the β radiation appears to be independent of the plates except for multiple reflexion, and the emergent radiation rather more penetrating than the incident.

The curves of fig. 7 are all concave to the pressure axis. Bragg predicted that with a light substance for the upper plate the curve should be convex to the pressure axis. An attempt was made to obtain this condition by making the upper plate of Al foil and having a column of air 24 cm. high above the plate. In order to reduce still further the scattered β rays, the top of the vessel was lined with carbon and the side of the vessel lined with ebonite coated with Al foil. Of course this has not reduced the problem to the simple one that Bragg assumes—namely, no radiation from the sides of the vessel and none from the upper plate. The result thus obtained is similar to that in which an aluminium plate was used. At lower pressures the ionization current is slightly greater for aluminium foil, and at the high pressures less than the current given when the upper plate is aluminium. Before discussing the curves further let us briefly consider the theory of the ionization by γ rays.

The theory for a large shallow ionization-chamber has been worked out by Bragg (Phil. Mag. Sept. 1910). The lower plate was supposed to be composed of some dense material, and the upper plate of some material that would reflect very few β rays. Hence, using Bragg's notation, we have:—

I. The wall effect, *i. e.*, the ionization produced in the chamber by the emergent β rays,

$$= kI(1 - e^{-\lambda'D})/\lambda;$$

where

D = depth of chamber \times density,

λ = weight absorption coefficient of β rays in the plate,

$\lambda' =$ " " " " in the gas,

$k' =$ " " " γ rays in the gas,

$k =$ " " " " in the plate.

II. The gas effect

$$= k'DI - k'I(1 - e^{-\lambda'D})/\lambda'.$$

The total ionization in the chamber

$$= I \left\{ Dk' + \left(\frac{k}{\lambda} - \frac{k'}{\lambda'} \right) (1 - e^{-\lambda'D}) \right\}.$$

In the present experiments it was found impossible to reproduce such simple conditions. A complete expression representing the action of the γ rays is very complex, and the value of the constants too uncertain to make such an expression of any value in the present case. It is necessary to take into consideration the effect of the β rays set up in the sides of the vessel due to the scattered γ rays and the effect of multiple reflexion on the resultant ionization. Again, the indirect ionization produced by the γ rays in the gas will depend, to a certain extent, on the lower and upper plates. A lead plate will always return more β rays into the ionization-chamber than will a plate of aluminium. There is in fig. 7 a slight difference in the final slope of the curves, but the pressure has not been raised sufficiently high to determine how far this is dependent on the plates.

From figs. 3 and 8 it is seen that the β ray curve due to Ur X is similar to that obtained by plotting the differences in the ionization currents when the bottom plate is changed

from Al to Pb. Hence we conclude that the β rays from the walls of the vessel are similar to the β rays from Ur X. With γ rays we have not only this "wall effect," but we have also the "gas effect"; and this shows itself in the final slope of the curve, which at 80 atmospheres is still increasing, and at a rate apparently dependent on the material of the plates.

Taking the simplest case, that of two plates of aluminium 1 cm. apart, curve B (fig. 7), between 0 and 20 atmospheres, is similar to that obtained by Laby and Kaye (Phil. Mag. Dec. 1908) when the sides of their ionization-chamber were aluminium and at a distance 1.1 cm. apart. Assume that the average coefficient of absorption of the β rays proceeding from the walls is equal to 0.04, which was the experimental value found for the β rays of Ur X. The ionization-pressure curve for these β rays reaches a maximum at about 80 atmospheres. For γ rays, when the plates are 1 cm. apart, the ionization due to the β rays set up in the gas should be small at 5 atmospheres. If we assume, then, that most of the ionization in the gas at this pressure is due to the β rays from the walls, the ionization at the other pressures can be represented by the curve x of fig. 9. The difference between the curves B and x is the curve y , which consequently represents the value of the ionization due to the γ rays in the gas at the different pressures. It seems improbable that the effect due to the γ rays in the gas is smaller than that represented by the curve y .

The "gas effect" is given by the expression

$$k'DI - k'(1 - e^{-\lambda'D})/\lambda',$$

where k' and λ' are the mass absorption coefficients for γ and β rays respectively. A correction has to be made for the ionization due to the β rays that are reflected from the Al plates. It is difficult to decide what values ought in this case to be given to the absorption coefficients of the β rays before and after reflexion, and also the value to be assigned to the constant of reflexion. By an arbitrary choice of these values the curve y can be obtained.

To determine the maximum limit of the γ ray effect, a tangent is drawn to the curve β at 80 atmospheres and the line Oz is drawn parallel to it. The straight line Oz would represent the ionization due to the γ rays in the gas if the bottom plate had been the same density as air. Since the bottom plate has cut out the β rays that would have come

from the corresponding plate of air, the true gas effect must be represented by a curve the ordinates of which are considerably less than those of Oz. When the aluminium plates are 1 cm. apart, it is probable that at 80 atmospheres not more than 25 per cent. of the total ionization is due to γ rays producing β rays in the gas, and that at atmospheric pressure the effect is negligible.

When the plates are 2 cm. apart (fig. 10), the apparent absorption coefficient of the emergent β rays is equal to 0.025 cm.^{-1} approximately, and under similar conditions the absorption coefficient of the β rays from $\text{Ur X} = 0.025 \text{ cm.}^{-1}$. Hence it would appear that the β rays produced by γ rays are similar in penetrating power to the β rays of Ur X . The high values obtained for the absorption coefficients in these experiments are due to the obliquity of the paths of the rays, and to the multiple reflexion taking place in the chamber.

Summary.

1. The apparent coefficient of absorption of the β rays from Ur X was found to be $0.04 \text{ cm.}^{-1} \text{ air}$. By a special arrangement this value could be reduced to 0.007 approximately.

2. The "emergent" β rays produced by γ rays from Ra C have an absorption coefficient $0.046 \text{ cm.}^{-1} \text{ air}$, and the incident β rays $0.056 \text{ cm.}^{-1} \text{ air}$. The emergent β rays are similar in penetrating power to the β rays of Ur X .

3. The absorption coefficient of the β rays of Ur X , and of the emergent β rays when the plates are 2 cm. apart, is 0.025 cm.^{-1} approximately.

4. The β rays appear to be independent of the material of the plates, as other investigators have also shown.

5. When the plates are 1 cm. apart the ionization due to γ rays in the gas is negligible at atmospheric pressure, and is approximately 25 per cent. of the total ionization at 80 atmospheres.

I wish to thank Prof. Rutherford for suggesting this research, and for his advice during the course of these experiments.

XX. *The Retardation of α Particles by Metals.* By
E. MARSDEN, *M.Sc., Lecturer in Physics,* and H.
RICHARDSON, *B.Sc., University of Manchester* *.

ONE of the most characteristic properties of the α particles is the existence of a definite range or distance through which they can travel in air or other material. This range differs for α particles from different radioactive products, but is characteristic of the product. Bragg and others have shown that in the case of α particles from a single product the length of the range depends not only on the density of the material penetrated but also on its chemical nature. Thus, if different gases be taken and adjusted by temperature or pressure until they are of the same density, it is found that they absorb α particles by different amounts, the absorption being apparently a function of the atomic weights only. Further, Bragg has shown that if a thin sheet of metal foil is interposed in the path of a homogeneous pencil of α particles in air, the range of each α particle is approximately reduced by the same amount, depending on the thickness and material of the foil interposed. In other words, the individual α particles are not stopped by the foil but have their velocities reduced by the same amount. In this way Bragg has determined the amounts of various substances necessary to cut down the range of α particles by one centimetre in air, and has noticed that the weights per unit area necessary for different materials are approximately proportional to the square roots of the atomic weights.

It was observed, however, that in the case of α particles from Ra C, for example, the air-equivalent of a metal foil, or the amount by which the foil cuts down the range in air at atmospheric pressure, is not quite the same when the foil is placed directly over the Ra C as when it is placed a few centimetres from the source †. Taylor ‡ has investigated this question more fully, and has shown that for layers of material of atomic weight greater than the average atomic weight of air, the air-equivalent decreases with decreasing velocity, or range, of the entering α particles, while in the case of hydrogen, whose atomic weight is less than that of air, the air-equivalent increases with decreasing velocity.

* Communicated by Prof. E. Rutherford, F.R.S.

† Bragg, *Phil. Mag.* vol. xiii. p. 511 (1907).

‡ Taylor, *Amer. Journ. Sci.* vol. xxvii. p. 357 (1909); *Phil. Mag.* vol. xviii. p. 604 (1909).

The results also showed that the rates at which the air-equivalents varied with the velocity of the α particles were functions of the atomic weight—the rate of variation for gold, for example, being greater than the variation for aluminium.

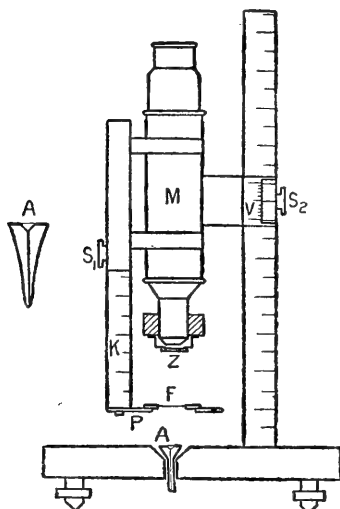
The method employed in these experiments consisted in the observation of the ionization current between two parallel sheets of gauze placed normal to a pencil of α particles and near the end of the range. It is known that the ionization changes rapidly with distance near the end of the range; and the alteration in air-equivalent of a foil when it was moved between the source and the ionization-chamber was deduced from the change in the ionization current. In these experiments, however, the amount by which the foil could be moved between the source and the end of the range was limited by mechanical difficulties, and the measurements were not made at the beginning or end of the range. In particular, they were not extended to cases where the range of the particles left after traversing the foil under investigation was greater than about 9 mm. Moreover, it is known that the velocity of an α particle falls very rapidly in the last centimetre of range, so that observations in this portion are important. Further, the ionization method of measuring ranges is somewhat affected by the scattering of α particles, which becomes very pronounced for low velocities.

It seemed to us, therefore, that the scintillation method, by which the individual α particles themselves are observed, is in some respects more direct for such measurements. Further, the scintillation method is often more convenient for determining the air-equivalents of metal foils, and it seemed of value to determine absolutely the connexion between mass per unit area and air-equivalent for different foils and different velocities of α particles.

The apparatus used is shown in fig. 1. It consisted essentially of a travelling microscope M, with a zinc-sulphide screen Z, attached rigidly to the objective, so as to be in focus. As source of α particles a conical tube A containing about 1 millicurie of radium emanation was used. The end of the tube was closed air-tight by a thin mica window fused on to the tube by AgCl. The air-equivalent of the mica was about 0.8 cm., so that a pencil of the Ra C α particles emerging from the tube had a range of about 6.3 cm. A metal foil F, whose air-equivalent was under investigation, could be placed on a

platform P and adjusted to any required distance from the zinc-sulphide screen Z by means of a ratchet-screw, S_1 .

Fig. 1.



The experiments were carried out in a dark room. The microscope, along with the zinc-sulphide screen, was raised until the screen was just outside the range of the α particles, this adjustment being made by observation of the scintillations. Only the α particles given off from the RaC deposited on the inner surface of the mica were used in this adjustment, as they have the longest range. Owing to their large number and homogeneity, however, the adjustment could be made rapidly and accurately and the position afterwards read on the vernier and scale, V. After the readings corresponding to several adjustments had been taken, the metal foil was placed in position and the end of the range again determined. The difference between the readings then gave the air-equivalent of the foil in the particular position. The position of the foil was then altered and recorded on the scale K, and the adjustment to the end of the range repeated. In this way a series of values of the air-equivalent was obtained for different positions of the foil. To obtain an average value in any position, the foil was moved in a horizontal plane and readings taken for different positions.

The following table gives an example of a set of readings:—

TABLE I.—Gold No. 5.

Weight per unit area = $\cdot 002186$ gm. per sq. cm.
Pressure 774 mm. Temp. 17° C.

Reading on scale K.	Emergent range.	Mean reading on V for end of range.	Air- equivalent.
	cm.		cm.
Zero.	...	8.845	...
0.58	0.08	8.525	.320
1.00	0.50	8.460	.385
1.50	1.00	8.422	.423
2.00	1.50	8.400	.445
3.00	2.50	8.367	.478
4.00	3.50	8.335	.510
4.74	4.24	8.326	.519

The first column gives the readings on scale K. From these readings the values of the distance between the foil F and the zinc-sulphide screen Z are deduced and entered in column 2 under the heading of emergent range. The emergent range is thus the distance through which the α particles have to travel after leaving the foil before completing their range. Column 3 gives the means of readings on vernier V for several determinations of the end of the range. From these, the values of the air-equivalents are calculated and entered in column 4. Two or three sets of observations were made for each foil, and the means obtained from a smooth curve drawn through the actual observations. In some cases a source was used consisting of RaC deposited on a small metal disk, so that the observations could be extended to higher ranges. The mean values obtained are given in the following table (p. 188) and shown diagrammatically in fig. 2 (p. 189). The results are expressed throughout in terms of the emergent range as defined above. The incident range can be obtained by adding to this the air-equivalent in the particular position. The air-equivalents and emergent ranges are reduced in all cases to 76 cm. pressure and 15° C.; for it has been well established by many observers that the range of an α particle in any gas is proportional to the density.

It will be at once seen from the curves that the variations of air-equivalent are quite considerable and specially noticeable for low ranges. In particular, the variation of air value in the cases of aluminium and mica is almost entirely confined to the last two centimetres of emergent range. It may be noted in passing, that this variation is

of great importance in many experiments in which these substances have been used in experiments on α particles. The alteration of air-equivalent tends to diminish for high ranges in all cases, although there is no indication of the values becoming constant*.

TABLE II.

Emergent Range.	Gold.			Aluminium.		
	A.	B.	C.	A.	B.	C.
0.0	.299	.750	1.310	.769	.918	1.344
0.5	.384	.895	1.487	.820	1.015	1.422
1.0	.426	.972	1.613	.851	1.051	1.473
1.5	.452	1.021	1.681	.869	1.073	1.499
2.0	.471	1.066	1.733	.880	1.086	1.514
3.0	.502	1.118	1.822	.888	1.102	1.525
4.0	.522	1.161	1.899	.892	1.110	1.528
5.0	.533	1.195895	1.116	1.530
6.0	.547

Emergent Range.	Mica.		Copper.	Silver.		Tin.	Platinum.
	A.	B.		A.	B.		
0.0	.536	.875	.668	.750	1.650	1.451	2.968
0.5	.601	.937	.787	.831	1.775	1.561	3.198
1.0	.623	.964	.860	.874	1.851	1.618	3.353
1.5	.631	.977	.896	.900	1.902	1.655	3.460
2.0	.636	.984	.916	.922	1.940	1.681	3.544
3.0	.647	.990	.939	.953	2.000	1.725	...
4.0	.655	.995	.956	.977	2.054	1.760	...
5.0	.663	1.000	.972	1.000
6.0

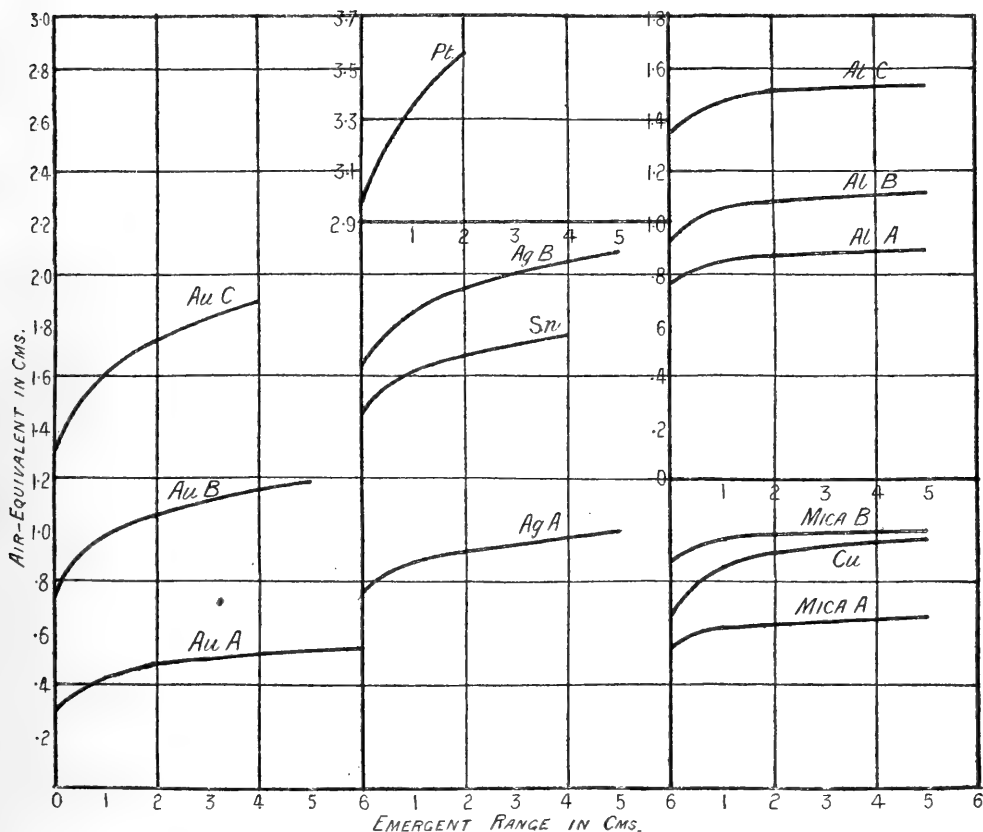
The question arises as to what is the quantity which we have called air-equivalent. As we are measuring in all cases the end of the range of the particles which have not been appreciably deflected from their path, scattering can have little influence on the results. A factor which might come in is the phenomenon which Darwin has† termed “straggling.” Darwin states, “In traversing matter some α particles encounter more atoms than others and go deeper into them. Thus after going a given distance the α particles will have straggled out and some will be moving faster than

* Cf. Bragg, ‘Studies in Radioactivity,’ p. 52.

† C. G. Darwin, Phil. Mag. vol. xxiii. p. 901 (1912).

others." Information on this point might be obtained from a consideration of the number of atoms in a particular foil which come within the sphere of influence of an α particle traversing the foil. However, no accurate data are available

Fig. 2.

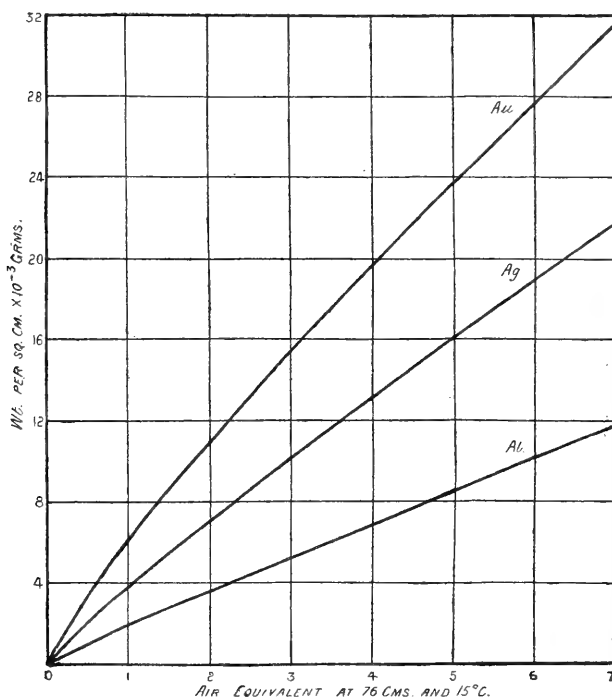


as to the atomic diameter which would of course be required for this calculation. In an experiment we made to throw light on the question, foils of aluminium and gold equivalent to about 1 cm. of air were placed at a definite distance near to the zinc sulphide screen, and their air-equivalents measured (1) when the α particles previous to traversing the foil had passed entirely through air, and (2) when they had previously traversed a gold foil equivalent to 2 cm. of air. The results for both metals agreed to within $1\frac{1}{2}$ per cent., showing that longitudinal straggling is either not very serious, or that it varies little from gold to air under the experimental conditions.

If we assume that straggling is not an important factor in the above measurements, we can deduce general expressions for the air-equivalents of any foil at any part of

the range. Starting from the end of the range, let x_1 be the air-equivalent of a foil of mass per unit area m ; then the incident range is x_1 cm. Let x_2 be the air-equivalent for emergent range x_1 , then the incident range is $x_1 + x_2$ cm., and the air-equivalent of the combined foil of mass per unit area $2m$ is also $x_1 + x_2$. Thus the air-equivalents for masses per unit area $m, 2m, 3m$, etc., are $x_1, x_1 + x_2, x_1 + x_2 + x_3$, etc. respectively. In this way by taking the values of x from the above data (fig. 2), a curve can be plotted connecting mass per unit area and air-equivalent, this being reckoned in all cases from the end of the range. Such curves are given for gold, silver, and aluminium in fig. 3. They were

Fig. 3.



determined as the means of the observations for the various foils of the same material given in Table II. The curves obtained for the different foils of the same material agreed closely, showing the approximate accuracy of the assumptions. From the mean curves given, the air-equivalents of any foil at any part of the range can be obtained. For instance, suppose it is required to find the air-equivalent of a foil of mass per unit area m for α particles of incident range R . Let M be the mass per unit area necessary to completely absorb α particles of range R , and R' the range for mass per unit area $M - m$; then $R - R'$ is the air-

equivalent required. The values of M and R' can be taken from the curve for the particular material used.

From the curves given above we have determined the mass per unit area per centimetre air-equivalent at different parts of the range. The results are given in Table III., and the values for the other materials for which we have not determined the curves sufficiently accurately are given between 5 and 6 cm. of air. The results are expressed throughout at 15°C . and 76 cm. pressure. The limits of air value are in each case reckoned from the end of the range and not from the beginning. The reason for this is that the end of the range is the only point common to α particles of different radioactive products. Moreover, there is some doubt as to the exact range of Ra C. This has generally been assumed to be 7.06 cm. at 76 cm. and 20°C . Bragg, however, has recently given the value 7.14 cm.* In our experiments the end of the range at which the zinc-sulphide screen was generally set corresponded to 7.04 cm. from the source (76 cm. and 20°C .), although an occasional scintillation could be observed up to 7.10 cm. (76 cm. and 20°C .).

TABLE III.

Material.	Atomic weight	Mass per unit area of foil equivalent to 1 cm. air at 15°C . and 76 cm. ($=m \times 10^3$ grms.).							Bragg's results.	
		0-1 cm.	1-2	2-3	3-4	4-5	5-6	6-7	Stopping power.	$m \times 10^3$.
Aluminium...	27.1	190	171	165	164	163	162	162	1.495	1.545
Copper	63.6	2.26	...	2.46	2.21
Silver	107.9	3.805	3.28	3.10	3.01	2.93	2.86	2.81	3.28	2.80
Tin	119.0	3.17	...	3.56	2.85
Platinum ...	195.2	4.4	...	4.14	4.02
Gold	197.2	6.10	4.84	4.44	4.25	4.06	3.96	3.91	4.22	3.98
Mica	1.43	...		

In column 10 of the above table we have entered Bragg's values for the stopping powers of the materials considered. They are taken from p. 44 of his book 'Studies in Radioactivity,' and Prof. Bragg has kindly informed us that they generally refer to an incident range of about 6 cm. and

* *Loc. cit.* p. 21.

emergent or residue range of about 3 cm. It will be noticed that our values are somewhat the greater. Our values are also in excess of those given by Taylor*. Further, the variations of air-equivalent for the foils given by both Bragg and Taylor are somewhat more pronounced over the range they examined than are our values. The difference is probably due to the two methods of measurement. It may be convenient here to give a few points comparing the two methods of determining air-equivalents,—ionization and scintillation. In the case of the scintillation method no trouble arises from scattering, as is possible in the ionization method. In the scintillation method a much smaller area of foil, generally only about 2 sq. mm., is used than in the ionization method, where an area ordinarily not less than 0.5 sq. cm. is employed. In the case of foils which are in any way ununiform, a better average is therefore obtained in the ionization method. This can be remedied to some extent by determining the equivalence in several places. However, difficulty arises in the scintillation method when the foils under investigation contain small holes or local irregularities, for in that case there is a tendency to measure the thinnest portion of the foil. These small local irregularities were found in all the foils examined except gold. In our experiments we avoided the error to some extent by using composite sheets of many thicknesses of foils. Any serious irregularities can be instantly noticed by the fact that they allow α particles of different velocities to fall on the screen, causing scintillations of different brightness.

The scintillation method, as used above, is convenient in that it does not involve any extensive apparatus. The observations are more direct and can be made much quicker than by the ionization method. A source such as we have used is not necessary, for instance a moderately strong preparation of polonium serves very well.

A theoretical investigation of the above results on the variation of air-equivalent is somewhat difficult in the absence of definite information of the change of velocity of the α particles in passing through the various foils. The velocity is obviously more fundamental than the range, which is of course measured in an arbitrary substance. It appears, therefore, preferable to postpone further discussion until the completion of some experiments on velocity curves in various substances now in progress by Dr. Taylor and one of us.

* *Loc. cit.*

We are indebted to Prof. Rutherford for his kind encouraging interest in these experiments, and also to the Royal Society Government Grant Committee for a grant to one of us, out of which part of the expenses have been paid.

Additional Note added Dec. 23, 1912.

It was noticed in the above experiments that when the zinc sulphide screen was moved so as to gradually approach the source of α particles, a considerable illumination of the screen appeared just prior to the point where the scintillations began to appear in large numbers on the screen. Near the end of the range the scintillations themselves consist of very faint spots of light, more localized than those due to α particles of high velocity. The illumination mentioned above appears uniform, and was specially noticeable in the experiments where adjustments of the end of the range were made with a gold or other metal foil placed within 1 mm. of the ZnS screen. The illumination appears to be connected with the α particles and not to be due to a β or γ radiation emitted from the source. The radiation producing it can penetrate about 1 mm. of air, which seems to exclude the idea of δ rays being the cause. A transverse magnetic field of 2500 gauss had no appreciable influence on the luminosity, and this, in consideration of the recent experiments by Chadwick, suggests that it may be due to γ rays excited by the α rays. Such γ rays would be of course much softer than any yet investigated by the ionization method, but might conceivably belong to a series similar to those investigated by Barkla.

Experiments with willemite and BaPtCy, which might be expected to give a larger relative illumination of γ to α rays, were somewhat unsatisfactory owing to the large illumination effect of the β and γ rays given off from the source.

XXI. *The Excitation of γ Rays by α Rays.* By J. CHADWICK, M.Sc., *Beyer Fellow of the University of Manchester**.

AT the end of a paper† published recently the writer stated that some evidence had been obtained of the excitation of γ rays when α rays impinge on matter. This has now been definitely established, and the preliminary part of the experiments will be described.

The source of α rays used in these experiments was radium emanation with its active deposit contained in a very thin

* Communicated by Prof. E. Rutherford, F.R.S.

† Chadwick, *Phil. Mag.* xxiv. p. 594 (1912).

glass tube, and consequently was also a strong source of β and γ rays. The presence of the primary γ rays renders very difficult the detection of a small amount of excited radiation, since this is observed only as an increase in the total γ radiation. Care must also be taken to eliminate the effect of any γ rays excited by the β rays.

The method finally adopted was as follows. The α ray tube was surrounded by a tube of some material of low atomic weight, say aluminium, just thick enough to stop all α rays. Then round this was placed a similar tube of a metal of high atomic weight, say gold. The ionization produced by the γ rays emitted by the emanation tube under these conditions, was measured by the balance method of Rutherford and Chadwick*. The positions of the tubes were now reversed, so that the gold tube was the inner one, and was bombarded by the α rays. The ionization was again measured.

It was found that when the face of the ionization-chamber was an aluminium plate 1 cm. thick there was no detectable difference in the ionizations in the two cases. With a plate 1 mm. thick, however, a slight difference was observed, the ionization being greater when the inner tube was of gold. The difference was about 1 part in 300.

It was evident that, to establish definitely the excitation of γ rays by α rays, some method was necessary which would increase the ionization produced by the excited γ rays relative to that produced by the primary rays. It is well known that the amount of ionization produced by X rays in a gas relative to that produced in air depends upon the penetrating power of the rays. For example, Strutt† and Eve‡ have shown that the ratio between the ionizations produced in methyl iodide and in air is 72 for soft X rays, 13·5 for hard X rays, and 5 for γ rays. As it was to be expected that γ rays excited by α rays would resemble X rays in their penetrating power, advantage could be taken of this phenomenon to increase the ionization of the excited rays relative to that of the primary rays.

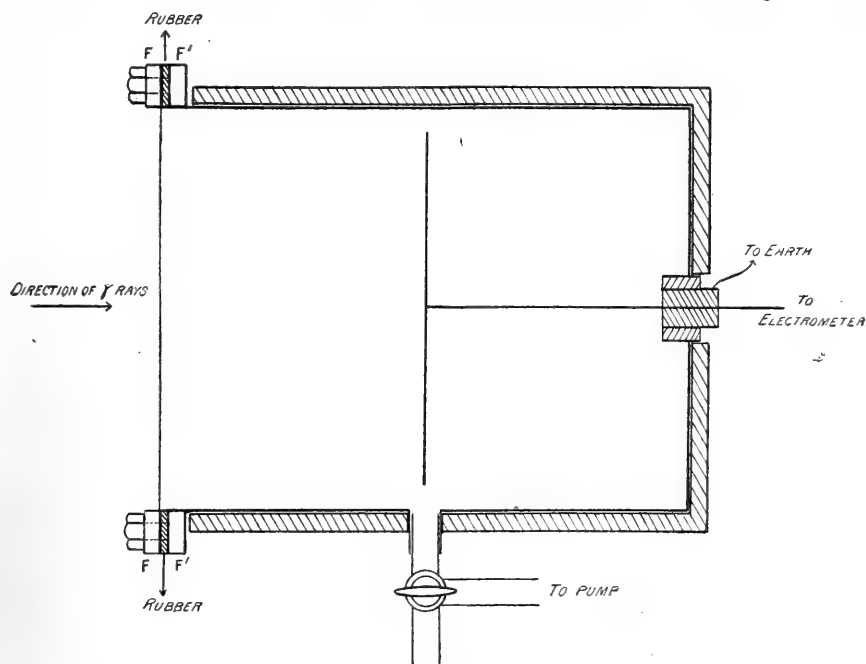
Accordingly, an airtight ionization-chamber was made, which could be quickly evacuated and filled with the vapour of methyl iodide or carbon bisulphide. The construction will be clearly seen from the figure. The ionization-chamber consisted of a brass cylinder about $8\frac{1}{2}$ cm. long and $6\frac{1}{2}$ cm. diameter. The electrode was insulated from the cylinder by

* Rutherford and Chadwick, Proc. Phys. Soc. April 1912.

† Strutt, Proc. Roy. Soc. A. vol. lxxiv. (1903).

‡ Eve, Phil. Mag. viii. p. 610 (1904).

a sulphur stopper provided with a guard-ring in the usual manner. The face of the ionization-chamber through which



the rays entered was of aluminium 0.08 mm. thick. This face was made airtight by inserting a ring of rubber between the aluminium sheet and the flange $F'F'$, and then tightly clamping the flanges FF' , $F'F'$ by means of nuts. The ionization-chamber, with the exception of the face, was enclosed in lead 3 mm. thick.

The measurements described above were now repeated when the ionization-chamber was filled with carbon bisulphide or methyl iodide at their vapour pressures. It was found that the ionization produced in the chamber when the inner tube was gold was about 5 per cent. greater than when the inner tube was aluminium. Some of the measurements obtained with carbon bisulphide are given in the table. The ionization when the inner tube was aluminium is taken as 100 in each case.

Inner tube Al.	Inner tube Au.
100	104.8
100	104.2
100	104.8
100	105.3
100	104.8
100	105.0

When the ionization-chamber was filled with methyl iodide the difference was a little greater, but the measurements could not be made with the same accuracy owing to variations in the pressure of the methyl iodide under the experimental conditions.

In order to prove that these γ rays were excited by the α rays and not by β rays, the following experiments were made:—

The emanation tube was covered with sufficient aluminium foil to stop the α rays. The measurements were then repeated, and no difference was observed when the positions of the gold and aluminium tubes were changed. This showed that the difference observed above could only be due to α rays, or to very soft β rays which were absorbed in the aluminium foil used to stop the α rays.

A simple experiment showed that the γ rays were not due to soft β rays. The emanation tube was placed in a converging magnetic field so that the soft β rays were coiled by the field into a narrow spiral round the emanation tube. In this way the slow β rays were prevented from striking the metal tubes. A difference was still observed between the two ionizations, and was of the same magnitude.

Tubes of silver, copper, and paper were also used. It was found that the ionization produced by the emanation tube was always greater when the material of the inner tube was of higher atomic weight than the material of the outer tube.

As an example, the measurements obtained when each of the other metals was combined with aluminium may be given. Taking the ionization observed when the inner tube was aluminium as 100, the ionization obtained with gold as the inner tube was 104·8, with silver 102·5, with copper 101·2, and with paper 99·7.

In order to obtain some idea of the penetrating power of the excited γ rays, a plate of aluminium 2 mm. thick was placed over the face of the ionization-chamber. The differences obtained by reversal of the tubes were now very small, but the measurements indicated that the absorption coefficient in aluminium of the excited rays was about 8 under the experimental conditions.

The detailed investigation of the γ rays excited by α rays is, for obvious reasons, only possible with a source of α rays which does not emit β rays, such as ionium or polonium. Experiments in conjunction with Mr. Russell have shown that thorium oxide, containing a quantity of ionium equal to the amount in equilibrium with 3·5 mgms. of radium, gives γ rays greatly in excess of the β rays. The amount of γ rays

is sufficient to enable a detailed study to be made of them. The further account of these investigations and their extension to other radioactive bodies is reserved for a later paper.

In conclusion I desire to express my best thanks to Prof. Rutherford for suggesting this research, and for his kind interest and advice throughout the experiments.

XXII. *Notices respecting New Books.*

Lehrbuch der Thermochimie und Thermodynamik. By Professor Dr. OTTO SACKUR. Pp. viii + 340. Berlin: Julius Springer, 1912. Price 12 M. (13 M. bound).

A VERY thoroughgoing treatise covering the whole of the subject in a very excellent manner. Although it cannot claim any originality except that of treatment, we cannot imagine a better guide to the student than what it provides. We turn naturally to the parts dealing with the newer conceptions, and find that it does not lack even these. The third law of thermodynamics of Nernst and the speculations of Einstein (based on Planck's law of radiation) are very satisfactorily put forward. We recommend the book most heartily.

XXIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxiv. p. 901.]

April 17th, 1912.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Pre-Cambrian and Cambrian Rocks of Brawdy, Hayscastle, and Brimaston (Pembrokeshire).' By Herbert Henry Thomas, M.A., B.Sc., Sec.G.S., and Prof. Owen Thomas Jones, M.A., D.Sc., F.G.S.

The district dealt with in this paper lies about 8 or 10 miles to the east of St. Davids, and consists of pre-Cambrian plutonic and volcanic rocks surrounded by, and intimately associated with, sedimentary rocks of the Cambrian System.

The pre-Cambrian igneous and pyroclastic rocks are brought to the surface along an anticlinal axis which ranges in an east-north-easterly and west-south-westerly direction: that is to say, approximately parallel to the ancient ridge of St. Davids. They are

distributed over an area measuring about 9 miles in length by 2 miles in greatest breadth.

The pre-Cambrian rocks are divisible into two classes, an older volcanic series and a newer plutonic and hypabyssal series, for which Hicks's names of Dimetian and Pebidian are respectively retained.

The authors have not attempted any detailed subdivision of the Pebidian over the whole area, but it is clear that several stages are represented. The lower exposed portion is generally andesitic in character, the upper being rhyolitic and keratophyric.

The Dimetian comprises granite, quartz-porphry, and diorite, which are intruded into the Pebidian, and present a common feature in the abundance of soda-felspar. Petrographical descriptions of the various pre-Cambrian rock-types are given.

The Cambrian has been divided into two main groups—the Welsh Hook Group below and the Ford Beds above. The Welsh Hook Group compares bed for bed with the Caerfai and Lower Solva Series of Hicks, and, like similar beds at St. Davids, consists of basal conglomerate, green sandstones, red shales, and purple sandstones.

The position of the Ford Beds, which are mostly shales, is not so certain; but the evidence is in favour of their belonging to the Upper Solva Stage, and their having transgressed lower members of the Solva Series.

The basal bed of the Cambrian apparently rests upon rocks of different ages in different parts of the district; and this fact, taken into consideration with other evidence, indicates that the Cambrian reposes unconformably on a complex series of tuffs and lavas and of plutonic rocks intruded into these volcanic rocks.

The structure of the district is that of a horst, faulted on all sides and surrounded by much younger beds. The main fractures follow an east-north-easterly to west-south-westerly direction, but frequently branch and run together, thus enclosing lenticular masses.

Much of the faulting is of pre-Carboniferous age, but that it continued into Carboniferous times is shown by the manner in which the Carboniferous rocks of the district have been affected.

2. 'The Geological Structure of Central Wales and the Adjoining Region.' By Prof. Owen Thomas Jones, M.A., D.Sc., F.G.S.

This paper deals with the structure on a large scale of an area of about 1800 square miles, comprising the western portion of Wales between the River Dovey and South Pembrokeshire.

In a historical introduction the work of earlier observers, notably Sedgwick, Ramsay, and Walter Keeping, is referred to.

The paper is accompanied by a map whereon is indicated the distribution of certain rock-groups: this map is based partly on personal observations, and partly on information gathered from various publications.

On the map the structure of the area is easily perceived. There

are two principal anticlinal axes which follow in the main the valleys of the Teifi and the Towy, and are named after these rivers; between them is an important syncline (the Central Wales Syncline) which coincides nearly with the principal watershed of Central Wales.

Both the anticlines can be traced towards Pembrokeshire, where they appear as important structures; but they cannot be distinguished beyond the northern boundary of the area. The syncline, on the other hand, becomes more important in a northerly direction, but is lost towards the south-west. These structures have a southerly pitch at the northern end of the district, and a pitch in the opposite direction at the southern end. The variation in the pitch accounts for the form of the outcrops.

The peculiar correspondence between the evenly-curved courses of these structures and the form of the coast-line of Cardigan Bay, as also the relation of the structures to the other physical features, are discussed.

May 1st, 1912.—Dr. Aubrey Strahan, F.R.S., President,
in the Chair.

The following communications were read:—

1. 'On the Geology of Mynydd Gader, Dolgelly; with an Account of the Petrology of the Area between Dolgelly and Cader Idris.' By Philip Lake, M.A., F.G.S., and Prof. Sidney Hugh Reynolds, M.A., F.G.S.

Mynydd Gader lies immediately south of the area described by the authors in a previous paper (Q. J. G. S. vol. lii. 1896, pp. 511–21). The Tremadoc Beds are here succeeded by a group of rocks which are, for the most part, of volcanic origin. These may be divided into a Rhyolitic Series below and an Ashy Series above. The Rhyolitic Series is formed chiefly of lava-flows; the Ashy Series consists mainly of volcanic ashes and slates, the ashes predominating below and the slates above. *Didymograptus bifidus* occurs near the base of the Ashy Series, *D. murchisoni* in the upper part.

There is not sufficient evidence to show whether the Rhyolitic Series is conformable or unconformable with the Tremadoc Beds; but, since it lies between the *Dictyonema* Zone and the *Didymograptus-bifidus* Zone, it belongs presumably either to the Lower or to the Middle Arenig. The Ashy Series extends from the Upper Arenig to the Llandeilo.

There are many intrusive masses of igneous rock, the largest being that which forms the greater part of Mynydd Gader itself. This intrusion is L-shaped in section—consisting of a horizontal limb which cuts across the beds, and of a descending limb which lies approximately in the bedding.

The petrology of the igneous rocks, not only of Mynydd Gader, but also of the area described in the previous paper, is dealt with.

The intrusive rocks are mostly dolerites, consisting chiefly of augite and plagioclase (labradorite-andesine), without olivine or rhombic pyroxenes. Epidote is very abundant as an alteration-product. Contemporaneous veins are met with at one locality. Small intrusions of eurite occur just beyond the limits of the map.

The rhyolites are sometimes compact, sometimes banded, and sometimes nodular. Analyses of two specimens, the one compact and the other nodular, show that the percentage of soda is high.

The tuffs or ashes vary considerably in character. Some consist of a fine matrix with numerous scattered angular fragments of all sizes up to 18 inches; the fragments are mostly rhyolitic, but pieces of slate and grit also occur. In others the fragments are smaller, and some are so finely laminated that on freshly broken surfaces the texture appears perfectly uniform, but on weathered surfaces the lamination is often quite distinct.

Andesitic lavas occur at two horizons, in the Upper *Lingula*-Flags and in the Llandeilo Series. The latter are often highly amygdaloidal.

The Rhyolitic Series appears to be older than the main mass of volcanic rocks in the Arenig area, but it may be contemporaneous with the *Calymene* Ashes of that district. It is probably of approximately the same age as the volcanic series of Skomer Island, and the fact that in both places the rhyolitic rocks are soda-rhyolites is of considerable interest.

2. 'Insect-Remains from the Midland and South-Eastern Coal-fields.' By Herbert Bolton, F.R.S.E., F.G.S., Director of the Bristol Museum.

XXIV. *Intelligence and Miscellaneous Articles.*

Trinity College,
Cambridge.
November 25th, 1912.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper, "The Relation of Airy's Integral to the Bessel Functions," published in the *Phil. Mag.* for July 1909, there is a numerical error which I wish to correct. Equation (40) on page 15 is inaccurate, so that the Table on page 16 gives the values not of $2.1123(n-z)/z^{\frac{1}{3}}$, but of $1.3447(n-z)/z^{\frac{1}{3}}$.

Yours very truly,

J. W. NICHOLSON,

FIG. 9.

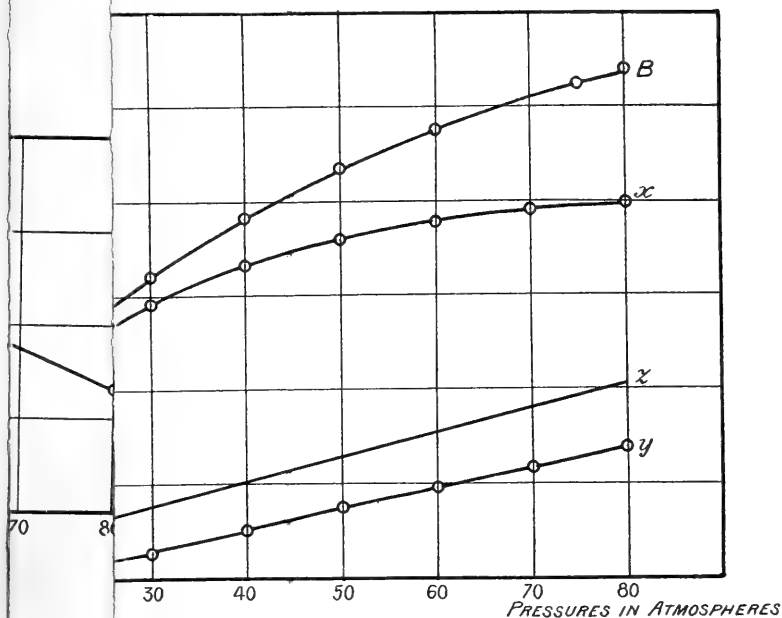


FIG. 10.

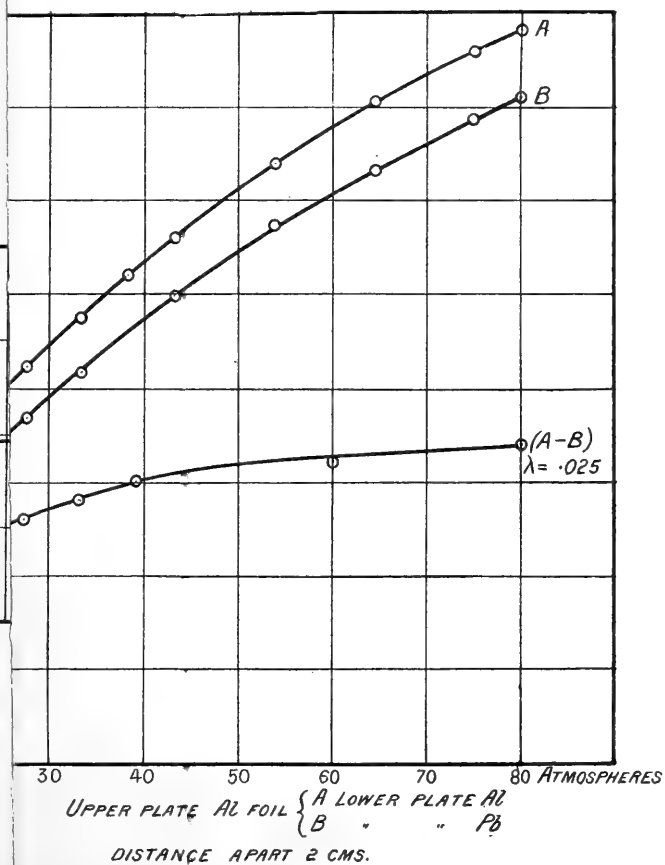


FIGURE 2.

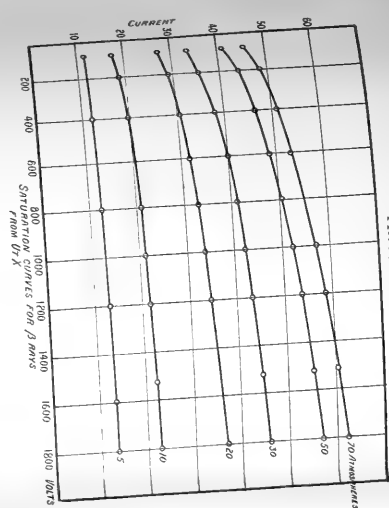


Fig. 2.

Fig. 4.

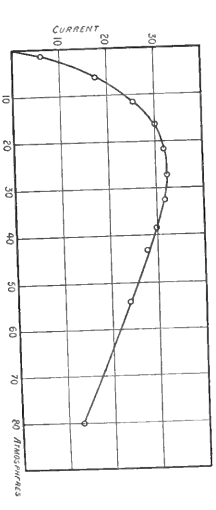


Fig. 7.

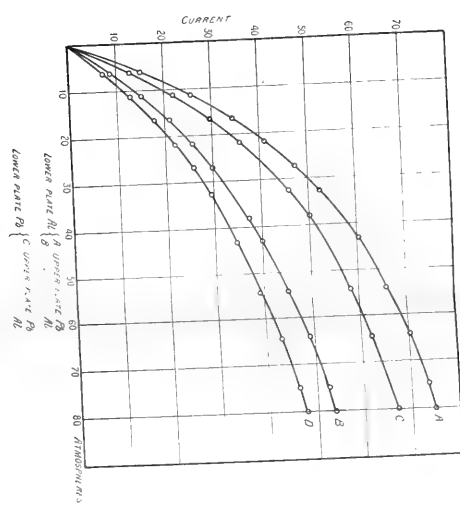


Fig. 9.

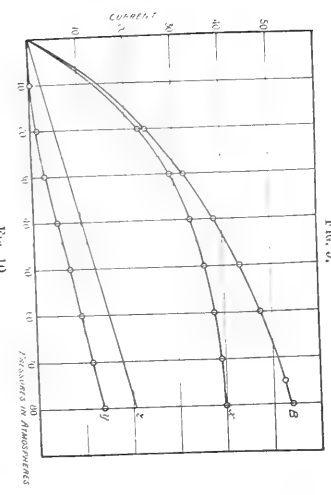


Fig. 10.

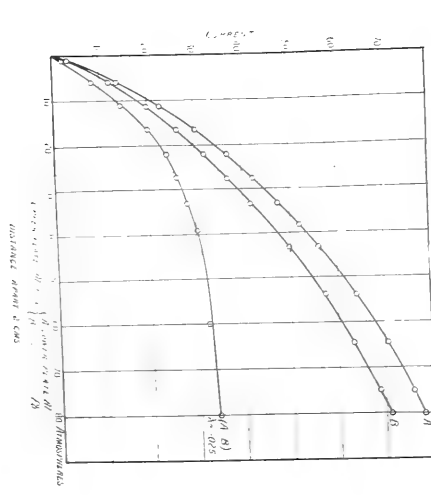


Fig. 6.

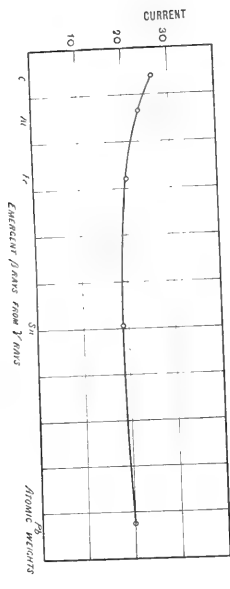
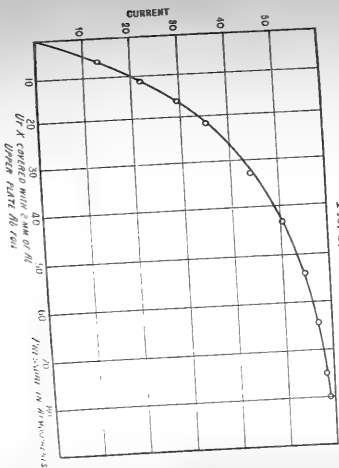


Fig. 3.



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November 28th, 1912.
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Equation (40) on
page 16 gives the
 $\alpha = 2/\beta^2$.
very truly,
J. W. NICHOLSON,
Director of the
South-Eastern Coal-

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

FEBRUARY 1913.

XXV. *On Some Orbits of an Electron.* By C. G. DARWIN,
*B.A., Lecturer in Mathematical Physics, Victoria University,
Manchester*.*

1. **I**N order to find the characteristics of such processes as the absorption by matter of β and cathode rays, it is necessary to have a knowledge of the orbits of the electrons as they pass the various charged bodies in matter. According to the theory of Rutherford†, which is strongly supported by experiments‡, an atom is composed of electrons and a nucleus of positive electricity of charge such as to neutralize them. The nucleus is seated at the centre of the atom, bears nearly the whole mass, and has its charge concentrated inside a very small region. The present paper is concerned with the orbit of a β particle as it passes such a nucleus. On account of its high velocity a β particle has apparent mass sensibly greater than that of a slow-moving electron, and during the path the attractive force of the nucleus still further increases it. The variability of mass entirely alters the character of the orbit, with the result that in certain cases it becomes a spiral, going right in to the centre. Numerical calculation shows that these cases should be of fairly frequent occurrence. The physical reason for this may be seen in the following way. On account of the increased mass the particle, when near the nucleus, will be

* Communicated by Prof. E. Rutherford, F.R.S.

† Rutherford, *Phil. Mag.* xxi. p. 669 (1911).

‡ Geiger, *Manc. Lit. & Phil. Soc.* Feb. 1911. An account of a much more complete series of experiments by Geiger and Marsden has recently been read at the Vienna Academy.

moving slower than it would if its mass were constant. This gives the attractive force more time in which to exert its effect, and analysis shows that in some cases the particle is unable to escape.

The variability of mass is of course not the only effect of rapid motion. It is observed experimentally, and is also a consequence of the general electromagnetic theory. If we proceed strictly on this theory as it stands at present there will also be a large radiation of energy due to acceleration, and in addition to this an aberration of force due to the time which is required for electromagnetic effects to be propagated from one body to the other. When the particles are very close together it is impossible to separate out all these effects and ascribe one part to variation of mass and another to radiation, but in the earlier stages it would seem justifiable to do this. If the positive nucleus has an infinite mass the aberration effect disappears. For the nucleus will remain fixed during the whole time and hence the mechanical force on the electron, no matter what its own motion, will be $-eE/r^2$ where e , E are the charges of electron and nucleus and r is the distance. Of course the force on the nucleus is not the equal and opposite of this, but as it is powerless to produce any motion it is immaterial. Although its effect is certainly not negligible the radiation will be neglected for the present, and subsequently an attempt will be made to estimate the change in the orbits. It does not appear possible that any of the neglected effects could tend to cause a separation of the particles, so that we have to conclude that in certain cases a coalescence of charges should take place, if the electromagnetic equations as given by Lorentz are universally true.

As formula for the mass we shall take that given by Lorentz for the "deformable" electron. Any of the other values which have been worked out for electrons of various characters would give a similar result, but Lorentz's formula, besides being apparently in best agreement with experiment, makes possible a complete integration of the equations of motion.

2. If c is the velocity of light, v the velocity of the electron and m its mass at low velocity, then Lorentz's values for the longitudinal and transverse mass are respectively

$$m_l = \frac{m}{\left(1 - \frac{v^2}{c^2}\right)^{3/2}}$$

$$m_t = \frac{m}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}}.$$

Since these are connected by the relation

$$m_t = m_t + v \frac{dm_t}{dv},$$

it is easy to show that the equations of motion of the electron are

$$\frac{d}{dt}(m_t \dot{x}) = -eE \frac{x}{r^3},$$

$$= \frac{d}{dt}(m_t \dot{y}) = -eE \frac{y}{r^3}.$$

Let the particle approach with initial velocity V along the negative direction of the axis of x and let the initial value of y be p . Take $V = c \sin \beta$. Then the integral of angular momentum is

$$\frac{x\dot{y} - \dot{x}y}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} = \frac{pV}{\left(1 - \frac{V^2}{c^2}\right)^{1/2}} = pc \tan \beta.$$

To find the energy integral we take

$$\dot{x} \frac{d}{dt} \frac{\dot{x}}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} + \dot{y} \frac{d}{dt} \frac{\dot{y}}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} = -\frac{eE}{m} \frac{x\dot{x} + y\dot{y}}{r^3}.$$

Now

$$\begin{aligned} \dot{x} \frac{d}{dt} \frac{\dot{x}}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} + \dot{y} \frac{d}{dt} \frac{\dot{y}}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} &= \left(1 - \frac{v^2}{c^2}\right)^{1/2} \frac{d}{dt} \frac{1}{2} \frac{\dot{x}^2 + \dot{y}^2}{1 - \frac{v^2}{c^2}} \\ &= \frac{d}{dt} c^2 \left/ \left(1 - \frac{v^2}{c^2}\right)^{1/2} \right., \end{aligned}$$

so that the integral is

$$\frac{1}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} - \sec \beta = \frac{eE}{mc^2} \frac{1}{r}.$$

Write $\frac{eE}{mc^2} = a$ an absolute constant not depending on the particular orbit. In polar coordinates we thus have

$$\frac{r^2 \dot{\theta}}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} = pc \tan \beta$$

and

$$\frac{1}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} = \sec \beta + \frac{a}{r},$$

whence

$$r^2 \dot{\theta} = \frac{pc \sin \beta}{1 + \frac{a}{r} \cos \beta}$$

and

$$v^2 = \dot{r}^2 + r^2 \dot{\theta}^2 = c^2 \left\{ 1 - \frac{\cos^2 \beta}{\left(1 + \frac{a}{r} \cos \beta\right)^2} \right\}.$$

By elimination of the time we have

$$\left\{ \left(\frac{dr}{d\theta} \right)^2 + r^2 \right\} \frac{p^2 c^2 \sin^2 \beta}{r^4} = c^2 \left\{ \sin^2 \beta + 2 \frac{a}{r} \cos \beta + \frac{a^2}{r^2} \cos^2 \beta \right\}.$$

Take $p/r = w$; then

$$w'^2 + w^2 = 1 + 2 \frac{a}{p} \cot \beta \operatorname{cosec} \beta w + \frac{a^2}{p^2} \cot^2 \beta w^2.$$

The orbit is given by

$$d\theta = \frac{dw}{\sqrt{\left\{ 1 + 2 \frac{a}{p} \cot \beta \operatorname{cosec} \beta w + \left(\frac{a^2}{p^2} \cot^2 \beta - 1 \right) w^2 \right\}}},$$

and the time by

$$c dt = p \operatorname{cosec} \beta \left(1 + \frac{a}{p} \cos \beta w \right) d\theta / w^2.$$

3. The character of the orbit depends on the sign of $\frac{a^2}{p^2} \cot^2 \beta - 1$. We distinguish three cases.

I. $p > a \cot \beta$.

The solution is best found by the use of two subsidiary angles.

Take $\cot \mu = \frac{a}{p} \cot \beta \operatorname{cosec} \beta$

and $\tan^2 \chi = \tan^2 \mu - \sin^2 \beta$,

so that $1 - \frac{a^2}{p^2} \cot^2 \beta = \cot^2 \mu \tan^2 \chi$.

When p is large $\mu = \chi = \frac{\pi}{2}$, and as it decreases they

decrease also. When $p = a \cot \beta$, $\tan \mu = \sin \beta$, and $\chi = 0$. Then

$$d\theta = \frac{dw}{\sqrt{\{1 + 2w \cot \mu - w^2 \cot^2 \mu \tan^2 \chi\}}},$$

and integration gives the orbit

$$w \cot \mu \tan \chi \sin \chi = \cos \chi - \cos (\theta \cot \mu \tan \chi + \chi).$$

This is a curve modified from one limb of an hyperbola with the nucleus in the focus, the modification consisting in increasing every element of vectorial angle in the ratio

$$\tan \mu \cot \chi : 1, \text{ that is the ratio } 1 : \sqrt{1 - \frac{a^2}{p^2} \frac{c^2 - V^2}{V^2}}.$$

The second asymptote occurs when $\theta = 2(\pi - \chi) \tan \mu \cot \chi$.

When $\frac{a}{p} \cot \beta$ is small, that is either when p is large or the velocity very high, then the orbit is nearly a true hyperbola. For smaller p or smaller velocity the curve tends to wind round the origin. When $\frac{a}{p} \cot \beta$ approaches unity the electron will describe several turns before it can escape. The time integration is perfectly simple. It gives

$$[ct] = \frac{1}{2} p \operatorname{cosec} \beta \cot \mu \tan \chi \left[-\frac{1}{\tau} - \frac{\sec^2 \chi}{\tau + \tan \chi} + 2 \cos^2 \beta \cot \chi \log \frac{\tau + \tan \chi}{\tau} \right]_{\tau = \tan (\frac{1}{2} \theta \cot \mu \tan \chi)}.$$

II. $p = a \cot \beta$.

In this critical case we have

$$d\theta = \frac{dw}{\sqrt{\{1 + 2w \operatorname{cosec} \beta\}}},$$

from which

$$w = \theta(1 + \frac{1}{2} \theta \operatorname{cosec} \beta).$$

Since $w = p/r$ the curve ultimately approaches the origin like the spiral $r = A/\theta_v^2$.

The time is given by

$$[ct] = p \operatorname{cosec} \beta \left[-\frac{1}{\theta} - \frac{1}{\theta + 2 \sin \beta} + \frac{\cos^2 \beta}{\sin \beta} \log \frac{\theta + 2 \sin \beta}{\theta} \right].$$

The time taken to arrive at the origin from any finite

distance is finite. The time taken for the circuit from $\theta = 2\pi r$ to $\theta = 2\pi(r+1)$ is approximately

$$c(t_{2\pi(r+1)} - t_{2\pi r}) = \frac{a \cos \beta}{\pi r^2}.$$

At any point of the orbit the mass of the electron is given by $m\left(\sec \beta + \frac{a}{p}w\right)$. This will increase indefinitely, but not with any extreme rapidity. Thus several rounds may be performed before it is necessary to remember that the mass of the nucleus is only finite.

III. $p < a \cot \beta$.

In this case we use as before the subsidiary angle μ where

$$\cot \mu = \frac{a}{p} \cot \beta \operatorname{cosec} \beta,$$

but we now take as second subsidiary the quantity ω where

$$\tanh^2 \omega = \sin^2 \beta - \tan^2 \mu,$$

so that

$$\cot^2 \mu \tanh^2 \omega = \frac{a^2}{p^2} \cot^2 \beta - 1.$$

When $p = a \cot \beta$, $\tan \mu = \sin \beta$ and $\omega = 0$.

As $\frac{a}{p} \cot \beta$ is increased, μ decreases and ω grows. When $p = 0$ or $\beta = 0$, we have $\mu = 0$ and $\tanh \omega = \sin \beta$, so that ω has some finite value.

Then
$$d\theta = \frac{dw}{\sqrt{\{1 + 2w \cot \mu + w^2 \cot^2 \mu \tanh^2 \omega\}}},$$

and integration gives

$$w \cot \mu \tanh \omega \sinh \omega = \cosh (\theta \cot \mu \tanh \omega + \omega) - \cosh \omega.$$

This curve ultimately approaches the origin like an equi-angular spiral of angle

$$\cot^{-1} \sqrt{\left\{ \frac{a^2}{p^2} \frac{c^2 - V^2}{V^2} - 1 \right\}}.$$

It reaches the origin in a finite time, and the time in any position is given by

$$\begin{aligned} [ct] = & \frac{1}{2} p \operatorname{cosec} \beta \cot \mu \tanh \omega \left[-\frac{1}{\tau} - \frac{\operatorname{sech}^2 \omega}{\tau + \tanh \omega} \right. \\ & \left. + 2 \cos^2 \beta \coth \omega \log \frac{\tau + \tanh \omega}{\tau} \right]_{\tau = \tanh (\frac{1}{2} \theta \cot \mu \tanh \omega)}. \end{aligned}$$

The mass of the β particle increases exponentially, but

several rounds may be made before it approaches that of the nucleus, unless p or the velocity are very small.

When the force between the particles is repulsive the integration of the equations is very similar, but now in all cases there are of course two asymptotes, and the only effect is that the particle is not so much deflected as it would be if its mass were constant. These orbits do not seem to be of any great interest.

4. We must now consider the numerical values for the various orbits. In the first place $a = eE/mc^2$. Let $E = ne$ so that n is the number of electrons in the atom. Then $a = n \times 2.8 \times 10^{-13}$. Take $n = 100$, which is probably roughly the value it would have for a heavy element, say lead. We shall take $a = 2.8 \times 10^{-11}$ throughout. A simple proportional reduction will give it in other cases. To show the general behaviour of the orbits I take four values of the velocity, $0.01c$, $0.1c$, $0.9c$, and $0.99c$ and find in each case the value of p which gives the critical orbit. This determines what particles cannot escape. Speaking loosely, it may be sup-

posed that the spiral part of the orbit begins when $\theta = \frac{\pi}{2}$; to find the shape of the spiral I therefore find r for $\theta = \frac{\pi}{2}, \frac{5\pi}{2}, \frac{9\pi}{2}$. I also find $c(t_{\frac{5\pi}{2}} - t_{\frac{\pi}{2}})$ and $c(t_{\frac{9\pi}{2}} - t_{\frac{5\pi}{2}})$, as these are roughly the first two wave-lengths of the emitted radiation, provided that this radiation does not itself entirely modify the orbits. It will be seen that when the velocity is small the critical value of p increases in inverse proportion to it and is of a size quite comparable to that of an atom. All the quantities are, of course, measured in centimetres.

TABLE I. The Critical Orbits.

V/c01	.1	.9	.99
p^{crit}	2.8×10^{-9}	2.8×10^{-10}	1.35×10^{-11}	4.0×10^{-12}
$r_{\frac{\pi}{2}}$	2.2×10^{-11}	2.0×10^{-11}	4.6×10^{-12}	1.4×10^{-12}
$r_{\frac{5\pi}{2}}$	9.1×10^{-13}	8.9×10^{-13}	3.2×10^{-13}	1.0×10^{-13}
$r_{\frac{9\pi}{2}}$	2.8×10^{-13}	2.8×10^{-13}	1.1×10^{-13}	3.5×10^{-14}
$c(t_{\frac{5\pi}{2}} - t_{\frac{\pi}{2}})$	3.8×10^{-11}	3.4×10^{-11}	8.8×10^{-12}	2.7×10^{-12}
$c(t_{\frac{9\pi}{2}} - t_{\frac{5\pi}{2}})$	3.2×10^{-12}	3.2×10^{-12}	1.2×10^{-12}	3.8×10^{-13}

To show the character of the orbits which are not spirals, I shall find those for which the β particle describes exactly one and exactly two rounds and returns towards the direction from which it came. The p 's for these cases will be denoted by p_1 and p_2 .

TABLE II. The External Orbits.

$V/c \dots$	$\cdot 01$	$\cdot 1$	$\cdot 9$	$\cdot 99$
$p_1/p_{\text{crit.}} \dots$	5.5	2.6	1.5	1.5
$p_1 \dots\dots\dots$	1.5×10^{-8}	7.2×10^{-10}	2.0×10^{-11}	6.0×10^{-12}
$p_2/p_{\text{crit.}} \dots$	1.16	1.15	1.11	1.11
$p_2 \dots\dots\dots$	3.3×10^{-9}	3.2×10^{-10}	1.5×10^{-11}	4.4×10^{-12}

5. These orbits have been calculated with a complete neglect of radiation. There are, of course, very definite indications that the mechanism of radiation is in some way different from that given in the electromagnetic equations, and our incomplete theory is certainly most at fault in the parts which concern the emission of energy in radiation. But in spite of this it is almost impossible that this emission should help the escape of the electron. For the radiation corresponds to a loss of energy, and this means a reduction of velocity; and we have seen that a reduction of velocity makes escape harder. Nor can the aberration of forces help escape; for when two oppositely charged particles A and B *both* revolve fast round their common centre, there will still be this radiation of energy and a consequent reduction of velocity. This is quite independent of the direction of the force of each on the other; but as a matter of fact it is easy to show that for very high velocities the force of B on A produces a direct retardation quite apart from the reaction of A's own acceleration on itself.

An estimate of the influence which the radiation may have can be made in the following way. Constrain the electron to follow with the proper velocity the path it would take if radiation were neglected. It is then possible to calculate the radiation emitted under these circumstances. If this amounts to any considerable fraction of the whole initial energy of the electron, we may expect that it will be caught.

To make the estimate I have used Abraham's formula for the radiation*. Since this is calculated for a rigid spherical

* M. Abraham, *Theorie der Elektrizität*, vol. ii. p. 122.

electron, it is not strictly comparable with the formula for the mass, but it suffices for a rough estimate. The particular character of the orbits gives rise to a great simplification in the integrand of Abraham's expression, but the final integration is laborious. If W is the whole energy radiated and ϵ is the whole energy of the electron $\left(\epsilon = mc^2 \left\{ \frac{1}{\sqrt{1 - \frac{V^2}{c^2}}} - 1 \right\}\right)$,

then we find that W/ϵ , for a given value of the velocity V , increases very rapidly with decreasing p . It is about 2 or 3 per cent. when $p = \pm p_{\text{crit.}}$ for velocities $\cdot 9c$ and $\cdot 1c$. For both the high and low velocities $\cdot 99c$ and $\cdot 01c$ it is about 4 per cent. when $p = 9p_{\text{crit.}}$ In all these cases quite a small decrease in p will very much increase W/ϵ . Thus if radiation is emitted according to the ordinary electromagnetic equations, we may suppose that the critical p is about three or four times as large as it would be if there were no radiation.

6. The experiments of Geiger and Marsden* show that the nucleus can be regarded as a point charge down to distances of about 10^{-12} cm. Beyond this we cannot go, as no α particle can explore any closer. But this distance is quite sufficient to allow for a considerable part of our orbits, and to bring out their spiral character. That an actual coalescence between two point charges should take place seems very improbable; the charge of the nucleus is characteristic of the substance and a coalescence would change its value and cause a transmutation of elements. There must therefore be some way by which the electron can escape from the extreme neighbourhood of the nucleus. This is contrary to the ordinary electromagnetic theory, which therefore requires some modification; and this modification extends to parts of the theory not simply concerned with the emission of radiation. Hitherto the emission and absorption of radiation have been almost the only points of definite disagreement between theory and experiment.

7. We may suppose that the earlier parts of the orbits are of the form calculated, and that the later processes, though quite different, do not give back its velocity to a particle. Thus the function of the nucleus is simply that in certain cases it destroys the velocity of a β particle. In this way, using the numbers found above, values for the absorption coefficient can be deduced which are surprisingly close to those observed. We proceed neglecting all scattering and merely counting those β particles whose velocity is

* *Loc. cit.*

destroyed. This procedure gives an exponential law of absorption for homogeneous rays; but in experiments this law should certainly be regarded not as the result of homogeneity but of extreme heterogeneity and of scattering.

If p is the greatest distance from the nucleus for which a β particle is caught and if N is the number of atoms in a c.c., the mean free path of a particle is $1/N\pi p^2$, and the absorption coefficient λ is $N\pi p^2$. For lead $N=4 \times 10^{22}$, and for rays of velocity $\cdot 9 c$ (that is fairly hard β rays), $p_{\text{crit.}} = 1.35 \times 10^{-11}$. This gives $\lambda = 20 \text{ cm.}^{-1}$. If the effect of radiation is to be included, p should be taken about three times as great, and this multiplies λ by about 10. This calculation neglects all scattering by the nuclei of those particles which are not absorbed, and also the effect of the electrons in the atoms. These should still further increase the coefficient. For rays of this type the experimental value is somewhere between 100 cm.^{-1} and 500 cm.^{-1} .

When caught the β particle emits a stream of radiation. This may be supposed to be the secondary X ray. Our calculation suggests that this will be on the scale of 10^{-11} cm. , a value very much smaller than is indicated by other methods.

My thanks are due to Sir J. J. Thomson and to Professor Rutherford for the interest they have taken in this work and for their advice.

Dec. 4, 1912.

XXVI. *Some Properties of Red Vulcanized Fibre.*

By F. H. PARKER, B.Sc., Woolwich Polytechnic.*

THE attention of the author was drawn to the fact that vulcanized fibre is one of the few materials, if not the only material suitable for the pistons of compressing engines in the plant for the liquefaction of air, and as, in order to prevent jamming, allowance has to be made for the expansion of the fibre, it seemed desirable to make some measurements on the change of volume due to absorption of water, as no data appeared to be available.

The results were rather of an unexpected character and seem of some interest.

The specimens examined were cut from two sheets, 1.9 cm. and 1.35 cm. thick respectively.

* Communicated by the Author.

They were made into approximately rectangular prisms and the lengths of the three edges measured with a metal millimetre scale, the fractions of a millimetre being estimated by eye. They were next weighed on a delicate balance. They were now placed in a beaker of water and allowed to remain in for one or more days, when they were taken out, and after wiping with a cloth, re-measured and weighed. It was soon seen, however, that the specimens swelled most near the edges, making the measurement of their three dimensions of little value for the purpose of calculating the volume, and consequently these measurements were given up and the volume deduced by weighing in water as well as in air. The results obtained for some of the specimens are given in the following tables and diagrams. It will be seen that the two dimensions in the plane of the sheets, called the length and breadth, have only altered slightly, while the third dimension at right angles to the plane of the sheet has increased by about 30 per cent.

Further, the final volume of the specimens was considerably less than the initial volume plus the volume of the water absorbed. [It was assumed in the calculations that the water was at the temperature of maximum density, the correction for the actual temperature, approximately 16°C. , being quite immaterial as far as the nature of the results go.]

In order to ascertain if temperature had any influence on the amount of water absorbed or on the change of volume, a bath was maintained at a temperature of approximately 60°C. , and two specimens were placed in it and readings taken in a similar way to those for the specimens in the water at room temperature. The effect of the higher temperature was clearly to cause both the water to be absorbed more rapidly and the final volume to be attained more rapidly, the maximum amount of water absorbed as well as the change of volume both being smaller.

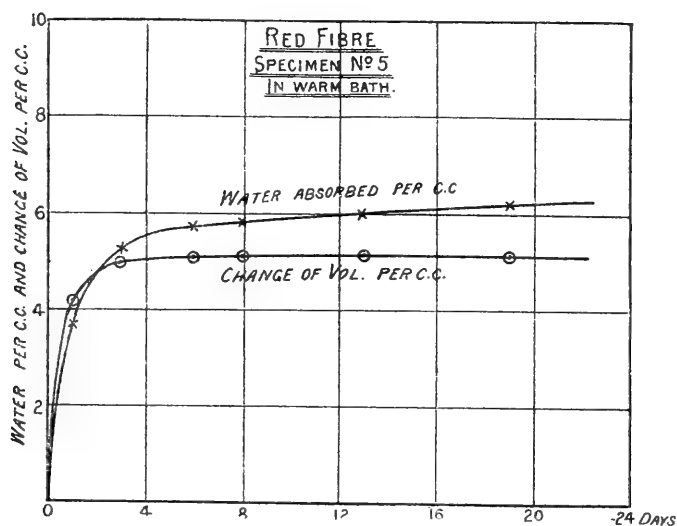
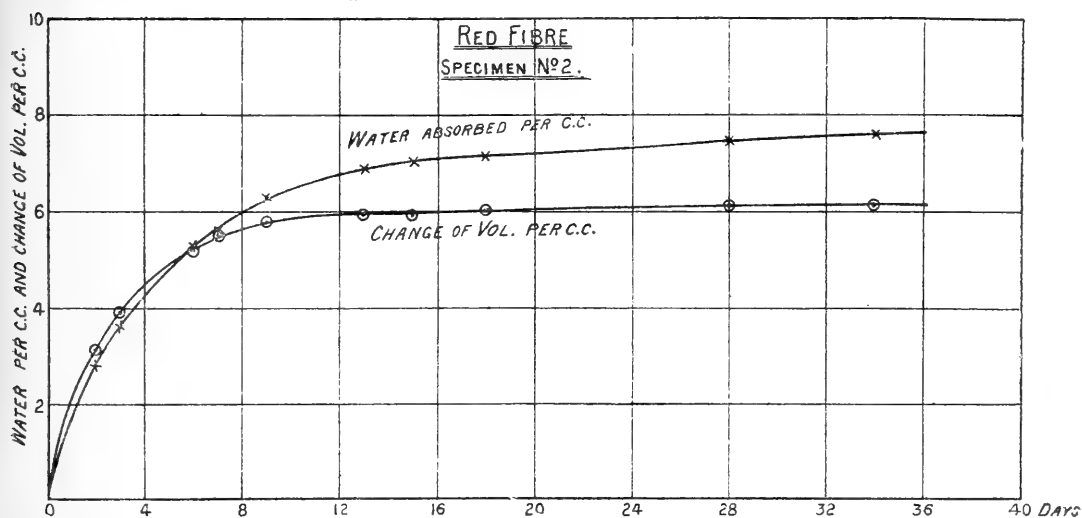
For the sake of comparison, observations were made at room temperature on two specimens of wood, one American bass and the other white deal. Here the changes of dimensions were all small and, as far as the measurements show, approximately of the same order as that for the two dimensions in the plane of the fibre, while the volume of the water absorbed was at least as large as in the case of the fibre, but did not appear to have reached its maximum amount when the observations were discontinued.

Specimen No. 2.

	Weight (1).	Weight in water (2).	Volume from (1) & (2).	Volume by measurement from (3), (4), (5).	Weight of water absorbed.	Length (3).	Breadth (4).	Thickness (5).	Change of volume per c.c.	Water absorbed per c.c.
June 4th	16.98	13.986	...	5.6	1.85	1.35
June 6th	20.95	18.41	3.97	5.7	1.9	1.7	.31	.28 gr.
June 7th	22.105	19.49	5.12	5.7	1.9	1.8	.39	.36
June 10th	24.37	21.3	7.39	5.75	1.95	1.9	.52	.53
June 11th	24.86	...	21.68	21.39	7.88	5.77	1.95	1.9	.53	.56
June 13th	25.85	3.18	22.08	21.37	8.87	5.77	1.95	1.9	.53	.58
June 17th	26.61	4.34	22.27	22.50	9.73	5.8	1.97	1.92	.59	.63
June 19th	26.84	4.53	22.31	22.29	9.86	5.8	1.97	1.95	.59	.70
June 22nd	27.06	4.69	22.37	22.01	10.08	5.82	1.91	1.98	.60	.71
July 2nd	27.50	4.98	22.52	22.27	10.52	5.8	1.97	1.95	.61	.75
July 8th	27.70	5.15	22.55	21.45	10.72	5.79	1.94	1.91	.61	.76

Specimen No. 5.

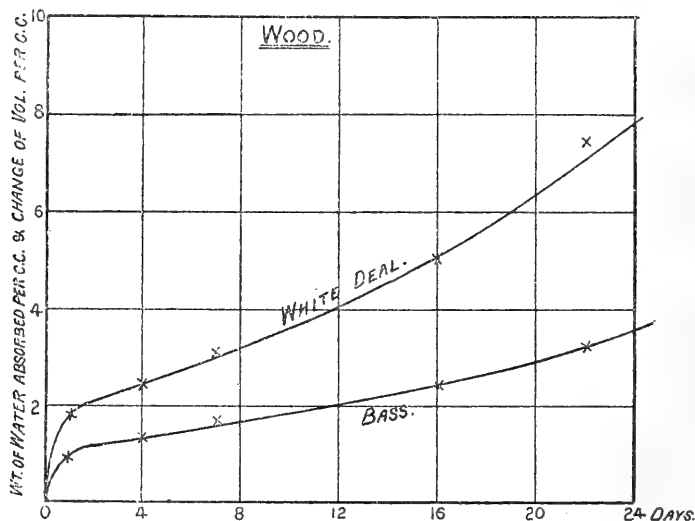
	Weight (1).	Weight in water (2).	Volume from (1) & (2).	Volume by measurement from (3), (4), (5).	Weight of water absorbed.	Length (3).	Breadth (4).	Thickness (5).	Change of volume per c.c.	Water absorbed per c.c.
June 19th	17.32	4.16	13.16	13.07	...	4.0	1.72	1.9
June 20th	22.23	3.45	18.78	18.82	4.91	4.12	1.85	2.47	.42	.37
June 22nd	24.37	4.63	19.74	18.82	7.05	4.1	1.8	2.55	.50	.53
June 25th	24.88	5.06	19.82	20.28	7.56	4.17	1.87	2.60	.51	.57
June 27th	24.92	5.03	19.89	19.58	7.60	4.12	1.85	2.57	.51	.58
July 2nd	25.25	5.31	19.94	20.07	7.93	4.15	1.86	2.60	.51	.60
July 8th	25.57	5.67	19.90	19.91	8.25	4.14	1.85	2.60	.51	.62
			In	warm	bath.					



Bass wood.	Weight (1).	Weight of water absorbed.	Length (3).	Breadth (4).	Thickness (5).	Water absorbed per c c
June 6th	3.735	...	4.05	2.0	1.25	...
June 7th	4.70	0.96	4.10	2.0	1.30	.095
June 10th	5.15	1.39	4.0	2.0	1.32	.13
June 13th	5.53	1.77	4.05	2.0	1.3	.17
June 22nd ...	6.25	2.49	4.1	1.97	1.3	.24
July 8th	6.95	3.19	4.05	1.97	1.3	.31
White deal.						
June 6th	3.79	...	2.85	1.85	1.9	...
June 7th	4.93	1.14	2.87	1.90	1.92	.18
June 10th	5.31	1.52	2.90	1.90	1.92	.24
June 13th	5.78	1.99	2.90	1.92	1.90	.31
June 22nd ...	6.92	3.13	2.90	1.95	1.94	.50
July 8th	8.45	4.66	2.90	1.95	1.92	.74

The first specimen of fibre immersed, after being in for 9 days, was taken out and found at the end of 9 days to have yielded up 90 per cent. of its absorbed water.

The explanation of the enormous change in one dimension did not perhaps appear clear. In order to account for this thin sections were examined under the microscope, when it was seen that the structure was very heterogeneous. When



we attempt to split the fibre it yields easily in the plane of the sheet with a more or less flaky appearance, but it is very difficult to split in a direction perpendicular to the sheet. This agrees with the character of the sections in the plane of the sheet and perpendicular to it as seen in the microscope. The sections in the plane of the sheet showed a mass of long fibres or cells separated by a considerable amount of matrix or intercellular space, while the sections perpendicular to the sheet were of a very much denser character and showed only a few fibres longitudinally. (The sections perpendicular to the plane of the sheet were also much harder to cut than those in the plane of the sheet.) In the manufacture of the sheets great pressure is applied when the walls of the fibres or cells are in a partly gelatinous state, and hence the number of fibres or cells per centimetre perpendicular to the plane of the sheet is immensely greater than the number in the plane of the sheet, and consequently when water is absorbed the amount of swelling perpendicular to the plane of the sheet is much greater than in the plane of the sheet.

XXVII. *On a Relation between Ionization by Cathode Rays and certain Chemical Effects.* By E. JACOT, B.A. (Univ. of Cape of Good Hope), B.A. (Cantab.), 1851 Exhibition Research Scholar of the South African College, Cape Town; Emmanuel College, Cambridge*.

PART I.

AS is well known, cathode rays have certain well-marked chemical effects. Up to the present time, however, little work has been done on the subject; and this has been for the most part of a purely qualitative kind. Goldstein† first found that certain salts suffered discoloration by the action of cathode rays. Wiedemann and G. C. Schmidt‡ found that salts under the influence of cathode rays show alkaline characteristics; while according to Elster and Geitel§ such salts exhibit marked photo-electric phenomena. Villard|| has observed further well-marked reducing effects of the rays, cupric silicate being reduced to cuprous silicate, cupric oxide to metallic copper, &c. Lenard, too, has shown that the passage of cathode rays through air is accompanied by the formation of ozone. More recently, G. C. Schmidt¶ has advanced the theory that in certain instances of metal salts the positive valency of the metal is directly satisfied by the negatively charged corpuscles of the rays. This would leave the acid radicle unattached, and chemical dissociation of some kind would follow.

This theory cannot apply generally. In the general case it is important to enquire more carefully into three points: (1), what proportion of the so-called chemical effect of cathode rays is a direct effect such as, for example, Schmidt presumes; (2), what proportion is a secondary chemical effect arising from purely thermal effects of the rays; and (3), what proportion is a secondary effect following from a primary chemical effect on the gas or gases in the discharge-tube? Villard** insists that such residual gases in no way enter into the question; but this only refers to the case of the reduction of CuO by the rays, and generalization is not justified.

The case of phosphorus is one in which the statement clearly fails to apply.

* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

† Goldstein, *Wied. Ann.* vol. liv. p. 371 (1895); vol. lx. p. 491 (1897).

‡ Wiedemann & Schmidt, *Wied. Ann.* vol. liv. p. 262 (1895); vol. lxiv. p. 78 (1898).

§ Elster & Geitel, *Wied. Ann.* vol. lix. p. 487 (1896).

|| Villard, *Journ. de Phys.* 3^e série, vol. viii. p. 140 (1899).

¶ G. C. Schmidt, *Ann. der Phys.* vol. vii. p. 321 (1902).

** Villard, *Journ. de Phys.* 3^e série, vol. viii. p. 140 (1899).

The writer examined the effect of a direct beam of cathode rays on white phosphorus. Rapid transformation of the phosphorus (apparently to the red modification) occurred, and this was attended by rapid exhaustion of the gas in the tube. Now direct chemical effects of cathode rays are, in the particular case of phosphorus, not necessarily to be expected. The better known effects of the rays are reducing effects as they appear in the cases of various salts. Any observed chemical effects of the rays on phosphorus could therefore reasonably be accepted as secondary effects following on the direct thermal effects of the rays; and the observed modification of the phosphorus to the red variety, when viewed in this light, would seem to be a very natural effect. But quantitative experiments showed that, even on making the extreme assumption that all the kinetic energy of the rays could be converted into available heat energy, and calculating the mass of phosphorus so modifiable, the mass actually modified was yet in excess of the calculated value.

A definite mass of white phosphorus was subjected to a direct stream of cathode rays for a definite interval of time, a part being so transformed apparently to the red modification. The remaining white modification was separated by solution in carbon bisulphide, and an estimate obtained of the mass modified by the rays. From a knowledge of the order of the kinetic energy of the rays used, and on the hypothesis that all the energy of the rays was reducible to heat, a comparison could be made between a maximum value of the heat supplied by the rays and the heat actually required for the observed transformation. In every case the mass of phosphorus actually modified proved excessive.

The rays, then, had two distinct effects at least on white phosphorus. There was a purely thermal effect; and there was a more directly chemical effect. The latter might be due either, (1) to a direct effect of the corpuscles on the phosphorus; or (2), to an effect of the corpuscles on the gas in the tube (ionizing or otherwise) followed by a reaction between the modified gas and the phosphorus.

Experiments were made with various modified forms of discharge-tubes in which the phosphorus was carefully kept out of the direct path of the rays, screened from any ultra-violet light from the discharge, &c. These experiments made it evident that a large part of the original effect must be due to a reaction between the phosphorus and the gas in the tube, modified in some way by the passage of the rays through it. The passage of the discharge continued to be attended by a certain exhaustion of the gas in the tube and a similar simultaneous slow modification of the phosphorus.

As the phosphorus was contained in a chamber separated from the actual discharge-tube by a U-tube immersed in liquid air, it is impossible to argue that the observed effects might be due to a direct action of the rays on any phosphorus vapour that might have made its way into the actual path of the rays. Clearly the rays so modified the gas through which they passed as to render it chemically active towards the phosphorus.

As the gas in these experiments was necessarily—with the exception of traces of the rarer gases of the atmosphere—exclusively nitrogen, these results bear interestingly on certain results of R. J. Strutt, who finds that nitrogen, when subjected to an energetic electric discharge, assumes a certain chemical activity which enables it to react with various substances in a manner and according to a mechanism as yet not fully determined*.

A special study was made of this effect of cathode rays on nitrogen and its relation to the attendant chemical effects between the gas and phosphorus.

Fig. 1.

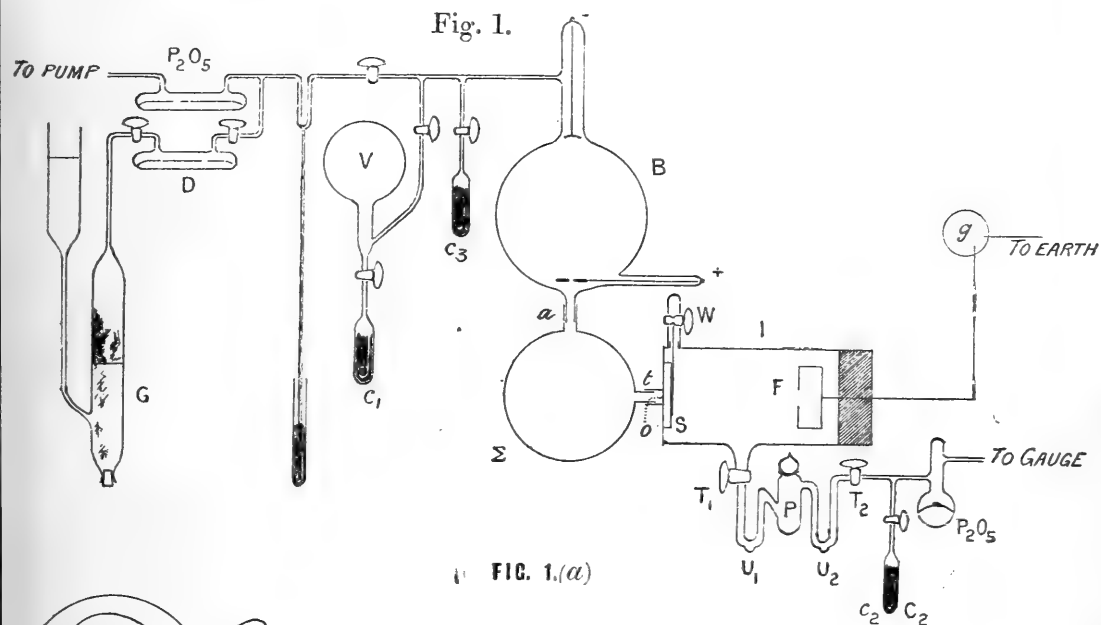


FIG. 1.(a)

(b)

The apparatus shown in fig. 1 (a and b) was set up for the purpose of working with definite measurable quantities of gas, homogeneous rays, &c.

* "An active modification of Nitrogen," Proc. Roy. Soc. March 1911, *et seq.*

B is the cathode-ray bulb. For the production of the discharge a Cox coil was used and proved very satisfactory, the discharge being perfectly unidirectional at the low pressures under which all the work was carried out. A rectifier was at one time included in the circuit. It had the effect of inconveniently reducing the density of the cathode stream and proved unnecessary. The rays on passing through the anticathode entered the solenoid Σ (shown in section) to which the bulb was waxed at a . They could here be subjected to a very uniform magnetic field of measurable intensity and deflected in a magnetic spectrum*. The solenoid, 13 cm. long, was wound in 3 layers, of 77 turns each, on a tube of external diameter 3.70 cm. The external diameter of the windings was 4.65 cm. The calculated field at the centre gave a value of $H=21$ gauss per ampere. On entering the solenoid, deflexion of the rays through a right-angle brought a pencil of any required velocity opposite the orifice o , through which it emerged from the solenoid and entered the ionization-chamber I. The radius of the circle into which the rays are bent to enter o is equal to the internal radius of the casing of the solenoid, which was

1.77 cm. From the formula $\rho = \frac{mv}{eH}$ we find the velocity of these rays is $6.8 \times 10^8 \times C$ cm. per sec., where C is the current passing through the solenoid, in amperes; from which the velocity of the rays which enter the chamber corresponding to any desired current may easily be calculated.

After resolution into the magnetic spectrum, a small pencil of rays of very nearly uniform velocity entered the ionization-chamber through o , where, provided any external field due to the solenoid had been duly balanced out, the pencil travelled without further deflexion to the Faraday cylinder F. This, as also the ionization-chamber and the casing of the solenoid, was of brass. There was of course scattering of the rays by the gas in the chamber; but this was very small in practice, and was allowed for by suitably choosing the dimensions of the Faraday cylinder. The Faraday cylinder was connected to a sensitive galvanometer of the Nalder type (sensitiveness: 8.7×10^{-10} ampere per scale-division, at 1 metre). The other terminal of the galvanometer was earthed, as were also the ionization-chamber and the casing of the solenoid. It was the gas in I that was eventually brought into contact with phosphorus. The phosphorus was contained in the tube P and separated from the remainder of the apparatus by wide U-tubes, U_1 and U_2 , maintained at the

* Whiddington, Proc. Roy. Soc. July 1911.

temperature of liquid air during the experiments; this prevented the diffusion of phosphorus vapour into other parts of the apparatus. (To prevent diffusion of the vapour while no experiments were being made the taps T_1 and T_2 could be kept closed.)

The orifice o was a small slit parallel to the axis of the solenoid, .7 mm. broad and 2 mm. long. Such a slit ensured the admittance into I of a maximum density of the cathode-ray stream without sacrificing homogeneity of velocity. o could be closed by a shutter S , shown in detail in fig. 1 *b*. Several attempts were made to adapt an ordinary tap to this purpose, the tap being placed at t . As this tap must necessarily be earthed it was essential that a metal one be used. With a view to preventing any heating of the tap grease by the cathode rays in their passage through the bore, the taps tried were grooved immediately above and immediately below the bore and left ungreased between these grooves. The experiment proved fairly satisfactory; but no tap was entirely reliable, and unless repeatedly greased soon failed to hold a vacuum. The idea was abandoned and a shutter system substituted. S is a heavy brass slab shaped as in fig. 1 *b*, as perfectly plain as possible and polished to a mirror surface with emery and rouge. It was completely in contact with the wall of I at the centre of which is o . Its normal position was such as to cover o completely. W is a tap deeply grooved at the centre so as to allow of its taking a few turns of thread. It operated as a windlass and allowed of S being manipulated from outside the apparatus. S rotated about the peg p and, by shortening or lengthening the thread, o could be exposed or covered at will. Although this system did not, of course, prevent diffusion of gas through o when dealing with ordinary pressures, it was entirely efficient at the low pressures required for cathode-ray work (.050 mm. of mercury). Knudsen* has shown that for such an orifice and at such pressures as we are here concerned with, the ordinary laws of diffusion do not apply. The mean free path of the gas molecule becomes the important factor in the problem, and any diffusion through the orifice is determined only by the chance of its lying directly in the path of any gas molecules. Diffusion, then, becomes very much reduced; being, as a matter of fact, only proportional to the first power of the pressure difference between the gases on the two sides of the orifice. The experimental application of this principle proved perfectly satisfactory.

* Knudsen, *Ann. der Phys.* vol. xxviii. p. 75 *et seq.*

The gauge used was a McLeod gauge with a bulb of large capacity. The gauge had been carefully calibrated before setting up, observations being made directly in mm. In the course of the work the readings were of course comparative, and were accepted as correct to two parts in ten thousand.

The gas used throughout the work was specially prepared and carefully dried nitrogen. In practice the preparation of the pure gas involves considerable difficulty, chiefly in the removal of the nitric oxide, which is produced in small quantities by most of the reactions in which nitrogen is the chief product. Nitric oxide is an extremely stable compound, and can only be eliminated with great difficulty. Hempel first showed that copper gauze in contact with a solution containing equal parts of ammonia solution ($\cdot 880$) and water saturated with ammonium carbonate absorbs oxygen absolutely and with great rapidity. This was made the basis of a method for preparing nitrogen. The gauze was packed in rolls into a gas pipette G, which was then filled with the solution. Air, duly freed of CO_2 , was forced into the pipette, and total absorption of oxygen followed. The residual nitrogen, with possible traces of argon and free ammonia, was admitted into the apparatus through the drying-chamber D, where it was left for some time in contact with P_2O_5 . Here the gas was thoroughly dried and any traces of ammonia eliminated*.

Sir J. J. Thomson has also made use of this method of preparing nitrogen in his more recent work on positive rays†.

The method of experiment was as follows :

Let V_1 = volume of the apparatus included by the bulb and the solenoid.

V_2 = volume of the ionization-chamber I.

V_3 = volume of the apparatus contributed by P, U_1 , U_2 , the gauge, and any connecting tubes.

V_2 , then, was separated from V_1 at o ; and V_3 from V_2 by the tap T_1 . A large flask V of known volume could be very thoroughly exhausted by the use of the coconut-charcoal tube C_1 maintained at the temperature of liquid air. It

* Ammonium metaphosphate, in the presence of moisture, being formed at once :



† *E. g.*, Phil. Mag. vol. xxi. no. 122, Feb. 1911.

served as a volumenometer, and by its means V_1 , V_2 , and V_3 were determined. With the apparatus used V_2 was 90.12 c.c. and V_3 , 343.78 c.c.

At the beginning of any one experiment, nitrogen, under any required pressure p , occupied $V_1 + V_2 + V_3$, the orifice o and the tap T_1 being open.

T_1 was then closed and V_3 very thoroughly exhausted by means of the charcoal tube C_2 to a small residual pressure p' . (In all the experiments this was of the order of .0001 mm. of mercury.)

Cathode rays, of known velocity v , were then passed through I and the galvanometer deflexion θ noted; this deflexion being proportional to the number of corpuscles passing through the chamber per second. (By suitably regulating the current through B it was found possible to ensure very constant and steady galvanometer deflexions, even when working with rays of a velocity approaching 10^{10} cm. per sec.)

After 90 seconds S was dropped, o closed and the rays cut off. T_1 was immediately opened and the nitrogen in I allowed to distribute itself between the volumes V_2 and V_3 , a certain proportion "reacting" with the phosphorus in P—which was of course always present in excess. This "action" was rapid. The resultant pressure in $V_2 + V_3$ was observed after an interval of one minute; this pressure Π being the pressure under which that proportion of the nitrogen from V which was "inactive" occupied the volume $V_2 + V_3$.

If ϕ is the pressure under which the "active" proportion of nitrogen would have occupied the volume $V_2 + V_3$,

we have
$$pV_2 + p'V_3 = (\Pi + \phi)(V_2 + V_3),$$

and can deduce $\phi = \frac{pV_2 + p'V_3}{V_2 + V_3} - \Pi$ from the experiment;

and hence, if necessary, the actual mass of nitrogen rendered "active."

For all purposes of discussion, we need only concern ourselves with the quantity ϕ . ϕ is the pressure under which a mass m of "active" gas occupies the volume $V_2 + V_3$. The volume $V_2 + V_3$ is a constant quantity; and provided the gas undergoes no important changes of temperature in the course of the experiments, ϕ is proportional to m .

Results.

The results obtained are tabulated in Table I. The pressures at the beginning of each experiment are given in column 1. The currents passing through the solenoid, proportional to the ray velocities, are arranged in column 2. The galvanometer deflexions in the third column are a measure of the number of corpuscles n passing through the ionization-chamber per second during successive experiments. Values of ϕ as calculated from the results of each experiment appear in column 4.

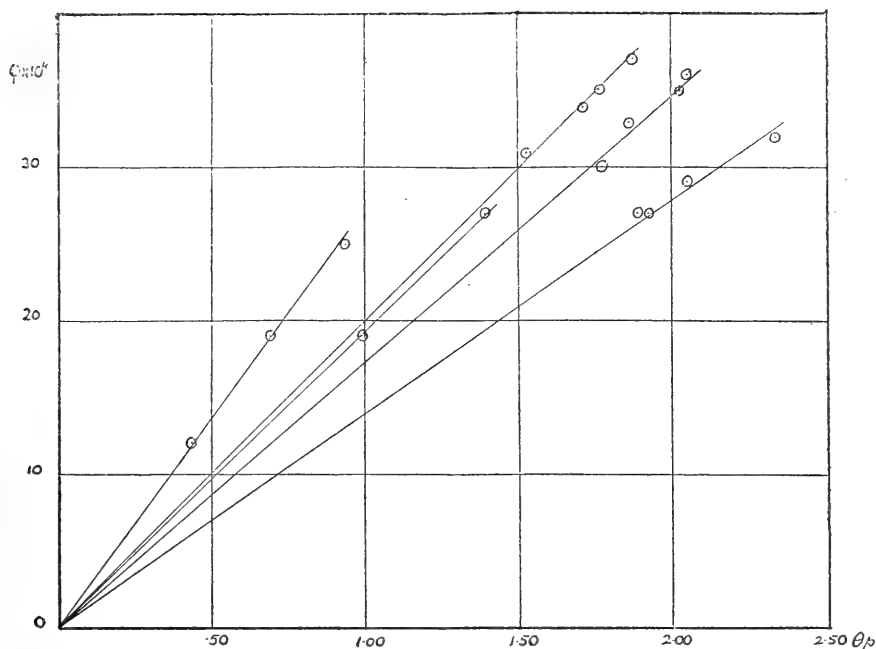
TABLE I.

1	2	3	4	5	6	7
Pressure p , mm. of Hg.	Solenoid current, amps.	Galvano. deflexion. θ .	$\phi \times 10^4$.	$\theta \times p$ prop. to np .	$\frac{\phi}{\theta p} \times 10^4$.	R.
·080	4·3	2·5	6	·20	30	·04
	4·7	5·5	12	·44	27	·08
·066	4·3	7·5	15	·49	30	·13
	4·7	10·5	19	·69	27	·14
	5·1	15	19	·99	20	·14
·052	4·7	18	25	·94	27	·21
	5·1	19	19	·99	20	·18
	5·5	29	31	1·51	20	·27
·041	5·1	34	27	1·39	20	·32
	5·5	43	35	1·76	20	·41
	6·0	50	36	2·05	17	·41
·036	5·5	52	37	1·87	20	·49
	6·0	56	35	2·02	17	·47
	6·5	57	28	2·05	14	·37
·030	5·5	57	34	1·71	20	·53
	6·0	62	33	1·86	18	·52
	6·5	63	26	1·89	14	·32
·025	6·0	71	30	1·78	17	·56
	6·5	77	26	1·93	14	·50
	7·0	101	25	2·52	10	·48
·021	6·5	111	32	2·33	14	·73
	7·0	126	26	2·65	10	·59

In fig. 2 the values of ϕ have been plotted against the products θp for various velocities of the rays. The curves are straight lines passing when produced through the origin

of coordinates ; and show a very fair proportionality between ϕ and θp over the range considered.

Fig. 2.



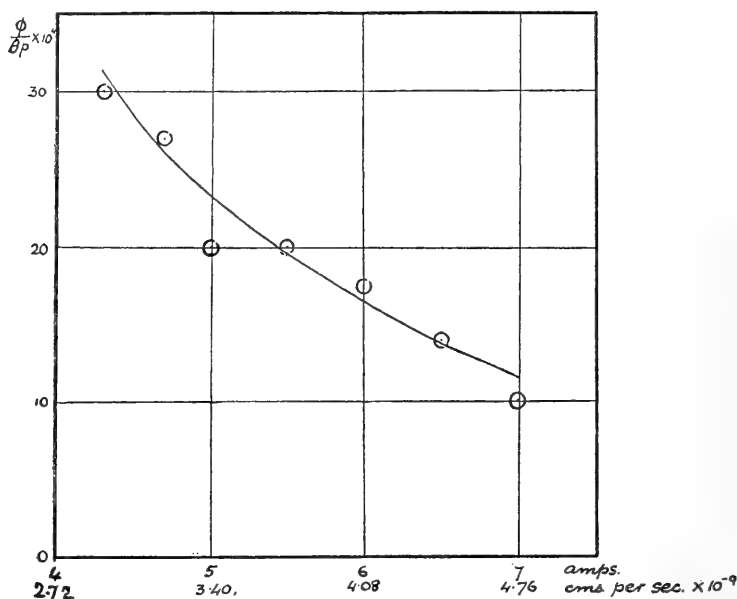
To plot the variation of ϕ with ray velocity the values of ϕ as they appear in Table I. have been reduced to a common value of θp and entered in column 6 of the same table. In Table II. these values of $\frac{\phi}{\theta p}$ are collected and entered against the values of the corresponding ray velocities, the mean for any one ray velocity being taken.

TABLE II.

1	2	3
Cathode-ray velocity in terms of solenoid current.	Cathode-ray velocity, cm. $\times 10^{-9}$.	$\frac{\phi}{\theta p} \times 10^4$.
4.3 amps.	2.92	30.0
4.7	3.20	27.0
5.1	3.47	20.0
5.5	3.74	20.0
6.0	4.08	17.3
6.5	4.42	14.0
7.0	4.76	10.0

In fig. 3 the values of $\frac{\phi}{\theta p}$ have been plotted against the velocities of the rays. The curve shown is the curve obtained on the hypothesis that $\frac{\phi}{\theta p}$ varies inversely as the second power of the velocity of the rays. The points plotted are the experimental points.

Fig. 3.



We may take it, then, that the variation of ϕ specifically with the velocity of the cathode rays is given by an inverse square law.

Its variation with θp and hence with np has been shown to be linear. ϕ then, is proportional to $\frac{np}{v^2}$; and hence the total mass of nitrogen which enters into combination with the phosphorus is proportional to $\frac{np}{v^2}$.

PART II.

The ionization in the chamber V_2 immediately before the gas is admitted to the phosphorus in P, is the equilibrium ionization due to cathode rays when a steady state has been attained.

In the general case, this steady state is reached when the gain in the ions made per second by the rays is exactly balanced by the loss through recombination and diffusion.

Consider the ionization by a cathode ray per c.c. of gas.

In the special case that follows on the hypothesis that the only source of loss of ions is recombination, the total number of ions is *

$$2l \sqrt{n/a},$$

where l is the diameter of the chamber, n is the number of ions produced per c.c. per second, and a is the coefficient of recombination.

In the special case that follows on the hypothesis that the loss is entirely due to diffusion, the total number of ions is †

$$\frac{2}{3} \frac{n}{D} l^3,$$

where D is the coefficient of diffusion.

Hence, if $\frac{2}{3} \frac{n}{D} l^3$ is small compared with $2l \sqrt{n/a}$, the loss of ions from diffusion becomes large in comparison with the loss due to recombination, and the latter justifiably negligible.

For pressures of the order of those involved in the present work this condition becomes

$$9n < 3 \times 10^3 \sqrt{n},$$

$$\text{or} \quad n < 10^5,$$

and is amply satisfied.

While cathode rays cross the ionization-chamber,

$$\alpha p \text{ ions are made per second,}$$

where α is a constant.

There is a loss $\frac{\beta}{p} N$ due to diffusion to the walls of the chamber; where β is a constant and N is the finite number of ions in the interior of the chamber.

When the steady state is attained, we have

$$\alpha p = \frac{\beta}{p} N,$$

or

$$N = \frac{\alpha}{\beta} p^2;$$

N , then, the equilibrium ionization, is proportional to p^2 when diffusion through ions to the walls of the ionization-chamber is considered.

If, however, the radius of the chamber is comparable with

* J. J. Thomson, 'Conduction of Electricity through Gases,' p. 16 (second edit.).

† *Ibid.* p. 31.

the mean free path of the ions, the only loss is that due to a direct impact of the ions on the walls of the chamber ; and this is proportional to N .

Hence, in the steady state,

$$\alpha p = \gamma n,$$

or N , the equilibrium ionization, becomes proportional to p , the pressure.

From a consideration of Townsend's work *, this mean free path for pressures of the order of those involved here is about 1 cm. The radius of the ionization-chamber $I = 1.5$ cm. ; a value of the same order as the mean free path of the ions considered ; and N , the equilibrium ionization, is therefore proportional to p , the pressure.

The total mass of nitrogen which enters into combination with phosphorus under circumstances treated of in Part I., has been shown to be proportional to the pressure immediately before the gas is admitted to the phosphorus in P. It is therefore also proportional to the equilibrium ionization in the gas.

Glasson † has experimentally investigated the variation of specific ionization with velocity of cathode rays for a particular case, and has found that, in air, the ionization due to cathode rays per unit length of path of the rays varies nearly as the inverse square of the velocity of the rays and directly as the pressure.

If this applies to other gases, and more particularly for present consideration to nitrogen, the specific ionization due to cathode rays is proportional to the pressure, and hence the equilibrium ionization is proportional to the specific ionization.

We therefore arrive at the result that the total mass of nitrogen which enters into combination with phosphorus under the circumstances treated of, is directly proportional to the specific ionization of the nitrogen immediately before combination occurs.

The writer has extended Glasson's experiments, working with pure nitrogen where Glasson worked with air. The range of cathode-ray velocities examined was of course the same as entered into the work described in Part I. above ; and this constituted a range of lower values than those examined by Glasson. Glasson's work extended over the range 4.08×10^9 to 6.12×10^9 cm. per sec. The work here described covered the range 2.92×10^9 to 4.76×10^9 cm. per sec.

* Townsend, Phil. Mag. ser. 6, vol. i. p. 198.

† Glasson, Phil. Mag. Oct. 1911, p. 647.

The arrangement of the apparatus was in its essentials the same as that described by Glasson. The apparatus used in the previous work (fig. 1*a*) comprised it in part. The discharge-tube B, the solenoid, and the ionization-chamber I were the same; the outlet from the ionization-chamber to P being now closed. The casing of the solenoid and the ionization-chamber were earthed as before, while the Faraday cylinder was raised to a potential sufficient to saturate the gas by a battery of a few storage-cells, whose other terminal was connected through the galvanometer to earth. In these experiments a potential of 10 volts was applied to the cylinder. Experiments, as before, were made at various pressures, rays of known velocity being made to cross the ionization-chamber I.

The effective length of path of the rays in the chamber was the distance between the entrance *o* to the chamber and the entrance to the Faraday cylinder F. It was the ionization in this length of path that was examined.

The current through the chamber, as measured by the galvanometer during any one experiment, was evidently made up of

- (1) the current carried by the rays themselves,
and (2) the ionization current.

The direction of the former was independent of the sign of the potential applied to the Faraday cylinder, while the latter could be changed in direction if the imposed field was reversed. By such a reversal of the potential of the Faraday cylinder the sum and the difference of the effects (1) and (2) were obtained.

If, in any one instance, *n* is the number of cathode rays crossing the chamber per second; and *α* the number of pairs of ions made by one corpuscle in travelling 1 cm. in nitrogen at a pressure of 1 mm. of mercury; and *l* is the length of path of the rays in the chamber, we have as follows:

The current carried by the rays = ne .

The saturation current carried by the ions = $\alpha lpne$.

When the Faraday cylinder is positively charged the current is given by

$$c_1 = ne + \alpha lpne,$$

and when the cylinder is negatively charged

$$c_2 = ne - \alpha lpne.$$

Thus

$$\frac{c_1 - c_2}{c_1 + c_2} = \alpha lp.$$

This ratio, which we will call N , is the number of pairs of ions made by a ray in crossing the chamber. Knowing l and p we derive α , the specific ionization produced by one corpuscle travelling 1 cm. in nitrogen at a pressure of 1 mm. of mercury.

Results.

The results of the experiments are shown in Table III. Column 1 gives the pressure throughout the apparatus in mm. of mercury ; column 2 the current passing through the solenoid during each successive experiment ; column 3 mean values of the ratio $\frac{c_1 - c_2}{c_1 + c_2} = N$, the number of pairs of ions made by a corpuscle in crossing the chamber.

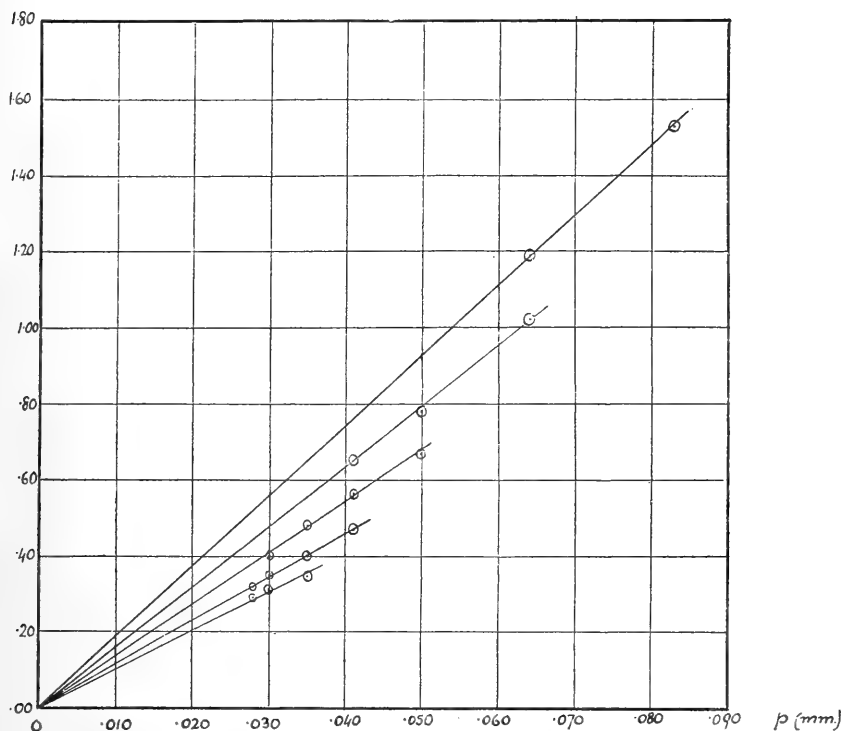
TABLE III.

1. Pressure p , mm. of Hg.	2. Solenoid current, amps.	3. N .	4. $\frac{N}{p}$.
·083	4·3	1·83	22·1
	4·7	1·53	18·4
·064	4·3	1·41	22·1
	4·7	1·19	18·6
	5·1	1·02	15·9
·050	4·7	·92	18·4
	5·1	·78	15·7
	5·5	·67	13·4
·041	5·1	·65	15·9
	5·5	·56	13·6
	6·0	·47	11·4
·035	5·5	·48	13·8
	6·0	·40	11·4
	6·5	·35	10·0
·030	5·5	·40	13·4
	6·0	·35	11·5
	6·5	·31	10·2
·028	6·0	·32	11·6
	6·5	·29	10·4
	7·0	·25	9·0
·025	6·5	·25	10·0
	7·0	·23	9·2

In fig. 4 the values of N have been plotted against the values of p for various velocities of the rays. The curves

are straight lines passing when produced through the origin of coordinates—showing a very fair proportionality between N and p over the range of values examined.

N Fig. 4.



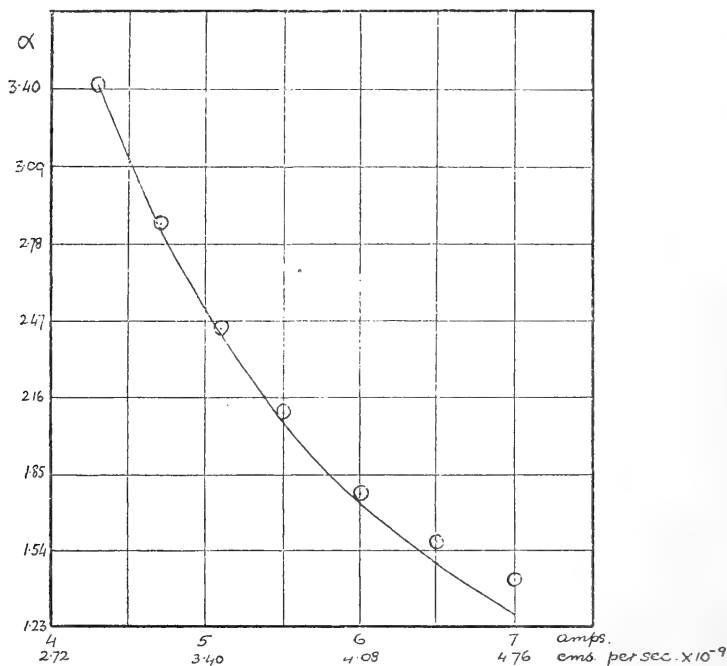
To plot the variation of N with ray velocity the values of N as they appear in Table III. have been reduced to a common pressure and entered in column 4 of the same table. In Table IV. these values of $\frac{N}{p}$ are collected and entered against the values of the corresponding ray velocities, the means for the various ray velocities being taken.

TABLE IV.

1. Ray velocities in terms of solenoid current.	2. Ray velocities, cm. $\times 10^{-9}$.	3. $\frac{N}{p}$.	4. α .
4.3 amps.....	2.92	22.1	3.4
4.7	3.20	18.5	2.8
5.1	3.47	15.8	2.4
5.5	3.74	13.6	2.1
6.0	4.08	11.5	1.8
6.5	4.42	10.2	1.6
7.0	4.76	9.2	1.4

In fig. 5 the values of α have been plotted against the velocities of the rays. The curve drawn is the curve obtained on the hypothesis that α varies inversely as the second power of the ray velocity. The points plotted are the experimental points.

Fig. 5.



We may take it, then, that the variation of the specific ionization in nitrogen by cathode rays with the velocity of the rays is given by an inverse square law.

From the results of the work described in Part I., considered in the light of this conclusion, it becomes established that the total mass of nitrogen which enters into combination with phosphorus under the conditions treated of is directly proportional to the equilibrium ionization of the nitrogen.

Discussion.

- (1) Calculation of the specific ionization in nitrogen by a cathode-ray corpuscle of known velocity.

We proceed to a numerical estimate of the specific ionization in nitrogen by a cathode-ray corpuscle of known velocity. This is given by the value of α .

From columns 3 and 1 of Table IV. we have as follows:—

For a current of 5.5 amps. through the solenoid, *i. e.* a ray velocity of 3.7×10^9 cm. per sec.

$$\frac{N}{p} = 13.6.$$

α , as defined, is $\frac{N}{pl}$; and in these experiments l was 6.5 cm.,

whence α , for a velocity of 3.7×10^9 cm. per sec., = 2.1. That is, 1 cathode-ray corpuscle moving with a velocity of 3.7×10^9 cm. per sec. through nitrogen under a pressure of 1 mm. of mercury involves the absolute formation of 2.1 pairs of ions.

Other values of α , corresponding to other velocities of rays, are collected in column 4 of Table IV.

Conformity with theory of results.

Sir J. J. Thomson * has recently considered from a theoretical point of view the problem of ionization in gases by moving particles.

Working on the assumptions:—

(1) That the corpuscles in the gas atom are attracted or repelled by cathode rays as these pass through the atom and so acquire kinetic energy ;

and (2) that if in any one instance this energy exceeds a certain value—the value necessary to ionize the atom—a corpuscle escapes, leaving us with a positively charged atom and a free corpuscle ;

and considering the special case of one cathode-ray corpuscle approaching an atom, he arrives at the relation

$$d^2 = \left(\frac{T}{Q} - 1 \right) \frac{e^4}{T^2},$$

where d is the perpendicular distance from a corpuscle—relatively at rest in the atom—on the direction of propagation of the first corpuscle.

T is the kinetic energy of the first corpuscle, and Q is the energy transferred to the second. Hence, if a corpuscle requires an energy W to escape from the atom, then, for ionization to occur,

$$d \text{ must be } > \sqrt{\left(\frac{T}{W} - 1 \right) \frac{e^4}{T^2}}.$$

If n is the number of corpuscles in the atoms in unit volume of gas, the number of collisions for which d is not greater

* "Ionization by moving particles," *Phil. Mag.* April 1912.

than this expression that are made per cm. by a corpuscle moving through the gas is

$$n\pi d^2$$

or

$$\frac{n\pi e^4 \left(\frac{T}{W} - 1 \right)}{T^2}.$$

This is a maximum when $T=2W$.

In the case of cathode particles T is large compared with W and the expression becomes

$$\frac{n\pi e^4}{WT}.$$

Hence the number of ions produced per cm. by cathode particles varies as $\frac{1}{T}$; that is, inversely as their kinetic energy.

The results of the work described in Part II. above are in agreement with the theory.

- (2) Calculation of the proportion of nitrogen, ionized by rays of known velocity, that enters into combination with phosphorus.

The following will serve as an example :—

At the beginning of an experiment,

- (1) The ionization-chamber (volume $V_2=90.12$ c.c.) contained nitrogen under a pressure .041 mm.
- (2) The volume $V_3=343.78$ c.c. was thoroughly exhausted, the pressure as recorded by the gauge being of the order of .0001 mm.

After the passage through V_2 of rays of velocity 3.7×10^9 cm. per sec., the gas in V_2 was shared between V_2 and V_3 and the resultant pressure recorded : .0085 mm. nitrogen, then ("active" and "inactive"), occupied a total volume $V_2 + V_3 = 433.90$ c.c. under a pressure .0085 mm. Of this, a volume 433.90 c.c. under .0035 mm. press. was "active"; and a volume 433.90 c.c. under .0050 mm. press. was "inactive." A ratio $R=.41$ of the total gas was therefore "active."

The values of R for the series of experiments are collected in column 7 of Table I.

Numerical estimates of the number of ions in any given mass of "active" nitrogen after admission to the phosphorus

chamber P cannot be made with any accuracy. Recombination and diffusion of ions are factors that enter into any calculation of this kind. At the low pressures at which the work was necessarily carried out, these are factors that cannot be neglected; and we have as yet no working data to allow of any calculation of these factors. From a general consideration of our results, however, it is evident that, in any one experiment, the proportion of ions in the "active" portion of nitrogen concerned is small; and hence that the observed combination between nitrogen and phosphorus is not in the main a combination between ions and the phosphorus. The combination is a well-defined function of the equilibrium ionization of the nitrogen. But the function of the ions in P need be no more than that of assisting a combination which could not otherwise effect itself.

On the other hand, the observed activity of the nitrogen may be due to some effect of the cathode rays on the gas quite apart from the ionizing effect. The corpuscles in the gas molecule are attracted or repelled by cathode rays as they pass through or near the molecule and so acquire kinetic energy. If this energy does not exceed a certain value—the value necessary for ionization—the effect on the gas molecule may yet be such as to effect its stability. The molecule may break up with the formation of two free atoms. This monatomic nitrogen would constitute the active gas; and the results described above would show that this atomizing of the gas by cathode rays is proportional to the ionization by the rays.

Summary.

I. The action of cathode rays on white phosphorus has been made a special study. The action is at least twofold:

- (1) There is a purely thermal effect of the rays, resulting in the formation of red phosphorus;
- (2) There is a more directly chemical effect due to an effect of the corpuscles on the nitrogen in the tube, followed by a reaction between the modified gas and the phosphorus.

The latter effect is proportional to the equilibrium ionization of the nitrogen; but the total number of active atoms or molecules in the gas is of a much higher order than the number of ions present in the gas at the instant of combination. The function of the ions may be that of assisting a combination which does not otherwise effect itself. More probably, the activity of the gas is not directly

due to its ionization, but rather to an atomizing effect of the cathode rays on the gas—the active product being monatomic nitrogen, and the total number of modified gas molecules showing an exact proportionality to the ionization in the gas by the rays.

II. The ionization in nitrogen by cathode rays has been shown to vary inversely as the kinetic energy of the rays, for rays of velocities ranging from 2.92×10^9 cm. per sec. to 4.76×10^9 cm. per sec.

The ionization also varies linearly with the pressure over the range .083 mm. to .025 mm. of mercury.

My best thanks are due to Prof. Sir J. J. Thomson for his kind interest in this research.

Cambridge,
Dec. 1912.

XXVIII. *The Theory of the Scattering of Röntgen Radiation.*
By D. L. WEBSTER*.

IN a recent paper by Mr. J. A. Crowther †, are described some experiments on the scattering of Röntgen rays by disks of aluminium or paraffin paper, made to test the formula that gives the intensity of the rays scattered to an angle θ as proportional to $(1 + \cos^2 \theta)$. This formula may readily be obtained from the expressions for the radiated electric and magnetic vectors given by Prof. Sir J. J. Thomson in his book, 'The Conduction of Electricity through Gases,' with the assumption that each electron in the radiator scatters the same amount of energy that it would scatter if it were alone.

The observed radiation is found to fit the formula well at angles greater than about 60° , but to be much in excess of the calculated value at small angles. The properties of this excess radiation are summarized in a second paper by Mr. Crowther ‡, as follows:—

"(1) For a given radiator and for primary rays of given hardness the excess radiation in any direction is directly proportional to the thickness of the radiator.

"(2) The total excess radiation round the radiator decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator.

"(3) Within the limits of experimental error the hardness

* Communicated by Dr. Theodore Lyman.

† Proc. Roy. Soc. A. lxxxvi. pp. 472-494.

‡ Proc. Camb. Phil. Soc. xvi. 6, pp. 534-539.

of the excess radiation is the same as that of the primary from which it is produced.

“(4) If $E_{\theta}\delta\theta$ is the intensity of the excess radiation between the angles θ and $\theta + \delta\theta$ with the primary beam

$$E_{\theta}\delta\theta = \frac{2}{b} E e^{-\theta^2/b} \delta\theta,$$

where E is the whole intensity of the excess radiation round the radiator, and b is a constant depending only on the quality of the primary beam and the substance of the radiator.

“(5) The value of b decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator. It is independent of the thickness of the radiator.”

In Mr. Crowther's first paper these effects were explained by the hypothesis that each molecule refracted part of the rays falling on it through a certain small angle, and the distribution of the excess radiation was shown to agree with the distribution calculated on this hypothesis by Prof. Thomson. But in the second paper another explanation, on the basis of radiation from the stoppage of secondary cathode particles, was put forward.

The purpose of the present paper is to revise the original formula without the hypothesis that each electron scatters energy exactly as if it were alone, and to show how the re-enforcement of the radiation from one electron by that from another may produce the “excess radiation” that Mr. Crowther has observed.

For this purpose, we may first consider a single, polarized, primary pulse, specified by the formula

$$E_z = E_x = 0, \quad E_y = E_0 f\left(\frac{t-x}{T}\right), \quad . \quad . \quad . \quad (1)$$

where t is the time, considered equal to the distance light has gone since the time $t=0$. Let $f(s)$ be zero except in the interval $-\frac{1}{2} < s < +\frac{1}{2}$, over which the average value of its square is 1, so that E_0 is the square root of the mean square of E_y . Let there be n electrons per unit volume in the radiator, each with a charge e and mass m^* ; and let the origin of coordinates be the position of one of the electrons at the time $t=0$.

At the point $r, \theta, \frac{\pi}{2}$, in the x, z plane, where r is very large compared with the distance of any electron in the radiator

* It must be noticed here that with the time unit used in this paper, to make force equal to mass times acceleration, the mass of any body must be c^2 times the mass in units in which the velocity of light is c .

from the origin, and $z > 0$, the electric vector radiated from an electron at x, y, z , is in the $-y$ direction, of intensity,

$$\frac{\epsilon^2 E_0}{4\pi m r'} f\left(\frac{t - r' - x}{T}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r' is the distance from the electron to the point x, y, z .

For the electron at the origin, letting $E_1 = \epsilon^2 E_0 / 4\pi m r$, this reduces to

$$E_1 f\left(\frac{t - r}{T}\right). \quad . \quad . \quad . \quad . \quad . \quad (2')$$

Neglecting small quantities of the second order, (2) becomes

$$E_1 f\left(\frac{t - r - x(1 - \cos \theta) + z \sin \theta}{T}\right). \quad . \quad . \quad . \quad (3)$$

If now the electron at the origin is to be re-enforced by the one at x, y, z , the times of arrival at $r, \theta, \frac{\pi}{2}$ of their scattered radiations must differ by less than T , so that the point x, y, z must at least lie between the planes,

$$\text{and} \quad \left. \begin{aligned} x(1 - \cos \theta) - z \sin \theta &= -\frac{1}{2}T, \\ x(1 - \cos \theta) - z \sin \theta &= +\frac{1}{2}T, \end{aligned} \right\}, \quad . \quad . \quad . \quad (4)$$

the distance between these planes being $T/2 \sin \frac{\theta}{2}$, and their direction being parallel to the y axis and to the bisector of the angle between the x axis and the radius vector r .

This, however, is not the only limitation on the space available for re-enforcing electrons, for there is also the limitation due to the second order terms, neglected in (3). But since the limits thereby imposed may be widened indefinitely by making r large enough, we shall disregard this limitation.

But another limitation, that cannot be disregarded, is imposed by the irregularities of the primary pulse, due to the disturbing effects of electrons near the $-x$ direction from the region considered. To determine the shape of the space to which we are limited by this effect, we have no data except the fact that each electron disturbs the primary pulse only throughout a very sharp cone with its apex at the electron and its axis in the x direction from it. For a rough approximation we may assume the region to be a sphere with a number of these practically cylindrical pieces cut out of it; and for purposes of computation the result may be assumed to be a spheroid, flattened in the x direction, with its centre at the origin.

If we knew the equation of this spheroid, we might now calculate the volume, V , that lies at the same time within the spheroid and between the planes of equations (4). But any accuracy in such a calculation would be worthless when combined with the approximations already made, and a qualitative analysis of the behaviour of V as a function of θ is more useful.

As the thickness, T , of the primary pulse may be supposed fairly small compared with any radius of the spheroid, at least if the material is not too dense and n not too large, V may be considered as the product of the distance $T/2 \sin \frac{\theta}{2}$, between the planes by the mean area of the sections of the spheroid parallel to the planes and included between them. Since the inclination of the planes to the x axis is $\frac{\theta}{2}$, this mean area will be a maximum when θ is 180° , and will decrease, slowly at first, then more rapidly, as θ decreases. But since the thickness of the segment increases, slowly at first, and then more rapidly, V may change very slowly until θ is fairly small. At this stage of the process the rate of change of the mean area will diminish, while the thickness continues to increase faster than before. The volume will now begin to increase and continue to do so until the whole spheroid is included between the planes, and no further increase is possible.

From the experimental fact that the scattered radiations are about as hard as the primary, we may be sure that, when θ is large, V must be small enough to contain rarely more than one electron, or cluster of electrons, if they are in compact clusters; for if there were many electrons, or clusters, radiating only slightly out of phase, the resultant radiation would appear as a pulse thicker than the primary. If there are such clusters, the charge, e , and mass, m , must be the charge and mass of the whole cluster.

In either case, if one such charge is known to be in the volume V , the probability of there being no other there is e^{-nV} ; so that of all the secondary pulses scattered per unit volume of the radiator, ne^{-nV} may be supposed to have electric vectors specified by expression (2), and to scatter energy per unit area at the distance r equal to

$$E_1^2 ne^{-nV} \int_{-\infty}^{+\infty} \left[f\left(\frac{t-r}{T}\right) \right]^2 dt = E_1^2 T ne^{-nV}. \quad (5)$$

Of the $n(1-e^{-nV})$ charges per unit volume not radiating alone, to which expression (5) cannot be applied, a fraction e^{-nV} may be supposed to radiate in pairs only, each pair giving an electric vector in the $-y$ direction, of intensity,

$$E_1 \left[f\left(\frac{t-r}{T}\right) + f\left(\frac{t-r'-x}{T}\right) \right], \quad . \quad . \quad . \quad . \quad (6)$$

where the origin is on one of the electrons of the pair. Squaring and integrating with respect to t , we find for the energy scattered per unit area from each pair

$$2E_1^2 T(1+F), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where F is the mean product of the functions f for pairs of which one electron is at the origin, while the other may be in any part of the volume V with no preference for any part over any other. Evidently F is constant for large values of θ , but variable, increasing as θ decreases, at smaller angles, but always remaining less than (1).

The case of three electrons in the volume V presents no additional difficulties, except the introduction of the mean product F' of the functions f for pairs of which both members are scattered indiscriminately over the volume.

We may now discard the assumption of a single, polarized, primary pulse, and assume that there are N primary pulses per unit time, and that the mean square of the z component of the primary electric vector is the same as that of the y component, where the mean is over a long time, rather than over a single pulse. This change in our assumptions must, of course, result in the introduction of a factor $N(1+\cos^2\theta)$ into the expression for the scattered radiation, to obtain the total energy scattered per unit time, per unit area of the receiving screen at a distance r , and per unit volume of the radiator. The resulting quantity, which takes account of all re-enforcements of radiations, is

$$E_1^2 T N (1 + \cos^2 \theta) n e^{-nV} [1 + (1 + F)(1 - e^{-nV}) + (1 + F + F')(1 - e^{-nV})^2 + (1 + F + 2F')(1 - e^{-nV})^3 + \dots]. \quad (8)$$

To obtain what Mr. Crowther terms the "excess radiation," we may subtract from expression (8) the value, $E_1^2 T n N (1 + \cos^2 \theta)$, of the same quantity calculated without reference to re-enforcements of the radiations. And since, for large values of θ , nV is very small, and the excess radiation extremely small, the total excess radiation between the angles θ and $\theta + d\theta$ may be obtained by multiplying this

result by $2\pi r^2 \theta d\theta$, so that the final value of the excess radiation becomes

$$\left. \begin{aligned} 2\pi r^2 E_0^2 T N n (1 + \cos^2 \theta) e^{-nV} [F(1 - e^{-nV}) + (F + F')(1 - e^{-nV})^2 \\ + (F + 2F')(1 - e^{-nV})^3 + \dots] \theta d\theta \end{aligned} \right\} \quad (9)$$

$$= \frac{\epsilon^4 E_0^2 T N n}{8\pi m^2} (1 + \cos^2 \theta) (1 - e^{-nV}) [F + (e^{nV} - 1)F'] \theta d\theta, *$$

where by excess radiation we must mean the energy scattered per unit volume of the radiator per unit time in the whole solid angle between θ and $\theta + d\theta$, in excess of the value for the same quantity calculated from the simpler formula.

On account of our lack of knowledge of the values of many of the quantities occurring in this expression, it is impossible to compute the amount of this radiation. To test the theory, let us therefore compare the changes of this quantity with those found experimentally by Mr. Crowther for the real excess radiation.

The first of his statements, of proportionality of the excess radiation to the thickness of the radiator, is obviously true of the calculated value, which is a certain quantity per unit volume of the radiator.

By making the primary beam harder, keeping $E_0^2 T N$ constant, the volume V is diminished at any given angle, so that the excess radiation, which increases with V , is thereby diminished. On the other hand, an increase of atomic weight, if it means an increase of n , must increase the excess radiation. The second condition is therefore satisfied.

The agreement of the formula with Mr. Crowther's third statement is apparently not so good, as it seems as if, when the pulses from two neighbouring electrons arrived at the observing point at times differing by some fraction of T , the resulting radiation might not be quite so hard as the primary. But it may be that this effect would be too small to be detected experimentally.

The agreement of the expression (9) with Mr. Crowther's formula for the scattered radiation depends of course on the way in which V , F , and F' vary with θ ; but on careful

* Note that

$$e^{+nV} = \frac{1}{e^{-nV}} = \frac{1}{1 - (1 - e^{-nV})} = 1 + (1 - e^{-nV}) + (1 - e^{-nV})^2 + (1 - e^{-nV})^3 + \dots,$$

and that

$$e^{+2nV} = \frac{1}{(e^{-nV})^2} = \frac{1}{[1 - (1 - e^{-nV})]^2} = \frac{d}{d(1 - e^{-nV})} \left(\frac{1}{1 - (1 - e^{-nV})} \right)$$

$$= 1 + 2(1 - e^{-nV}) + 3(1 - e^{-nV})^2 + 4(1 - e^{-nV})^3 + \dots$$

examination it may be seen that some variations of the sort specified above will suffice.

The fifth statement, about the changes of b , is equivalent to a statement that as the primary beam becomes harder, the excess radiation will be confined more and more to the smaller angles. This is obviously equally true of the calculated value, as an increase of hardness, and consequent decrease of T , makes V begin to decrease sooner with increase of θ , and confines the re-enforced radiations to smaller angles.

While it seems probable from these considerations that no further assumptions than the existence of electrons and the truth of the electromagnetic equations as applied to them are necessary to explain most of the effects observed by Mr. Crowther, it is by no means certain that the secondary cathode particles of which he speaks in his second paper do not have an important effect upon the phenomena. But as his hypothesis is based partly on the assumption that a cathode particle radiates only when being stopped, and then only in the direction of its motion just before stoppage, the accuracy of his conclusions must depend partly on the accuracy of this assumption. On this the equations of the electromagnetic field lead to some interesting suggestions.

For if an electron already in rapid motion is accelerated in any direction, and the retarded potentials due to it are computed for any point in the radiated pulse, they will both contain the factor $(1 - \beta_r)^{-1}$, where β_r is the component of the velocity of the electron in the direction of the point considered, the time units being the same as above. Therefore, as a brief calculation would show, the radiated vectors would differ from the values for the case of an electron momentarily at rest by the same factor, and the radiated energy per unit volume of the pulse by the square of this factor. But the thickness of the pulse varies directly as $(1 - \beta_r)$. Hence the radiation per unit area of the pulse will be stronger in the ratio

$$\left(\frac{1 + \beta_r}{1 - \beta_r}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in this direction than in the opposite. To the extent indicated by this ratio, and only to this extent, may we therefore say that the Röntgen pulse follows the direction of the cathode ray from which it is produced.

The results of the experiments by Mr. Kaye *, quoted by Mr. Crowther as a confirmation of his hypothesis, are easily explained by expression (10). For in these experiments it

* G. W. C. Kaye, *Proc. Camb. Phil. Soc.* xv. p. 269 (1909).

was found that if cathode rays were allowed to strike a very thin metallic anticathode, the intensity of the Röntgen radiation in a direction near that of the cathode beam was much greater than in the opposite direction, the ratio in the case of an aluminium anticathode being sometimes as great as 3·2, indicating a mean velocity of the radiating electrons of nearly ·5. As Mr. Kaye does not say what the velocity of his rays was, a direct comparison with the calculated velocity is impossible ; but indeed it would be a very poor check on the accuracy of the assumptions, for the opposing influences of the retardations and deflexions of the cathode particle, that diminish the effect, and the increase of its velocity on close approach to a positive electron (the only kind that can cause appreciable radiation), may produce great changes in the velocity of an electron before it radiates. But the order of magnitude of the effect, as well as an observed difference in hardness of the rays, to be accounted for by the well-known Doppler effect, does much to confirm this hypothesis.

From these results it appears that the secondary cathode particles, while they must produce some radiation, possibly a part of Barkla's homogeneous secondary radiation, cannot produce any distributed like the secondary radiation on which Mr. Crowther's experiments were performed. And since the results of his experiments, as well as those of Mr. Kaye, are well accounted for by the theory of Röntgen rays as electromagnetic pulses, and are necessary consequences of this theory, they are also important confirmations of its fundamental assumptions.

Jefferson Physical Laboratory,
Harvard University.
Nov. 2, 1912.

XXIX. *On the Charged Surface Layers in Contact Potential Phenomena between Metals.* By A. NORMAN SHAW, M.Sc., 1851 Exhibition Scholar of McGill University, Montreal ; Research Student of Gonville and Caius College, Cambridge*.

THE presence of charged surface layers has been assumed by many investigators on contact electromotive forces, not only by those supporting the "chemical theory" of its nature, but also by some of those who believe that the phenomenon is an intrinsic property of the metals. The following experiments were performed with the idea of obtaining some

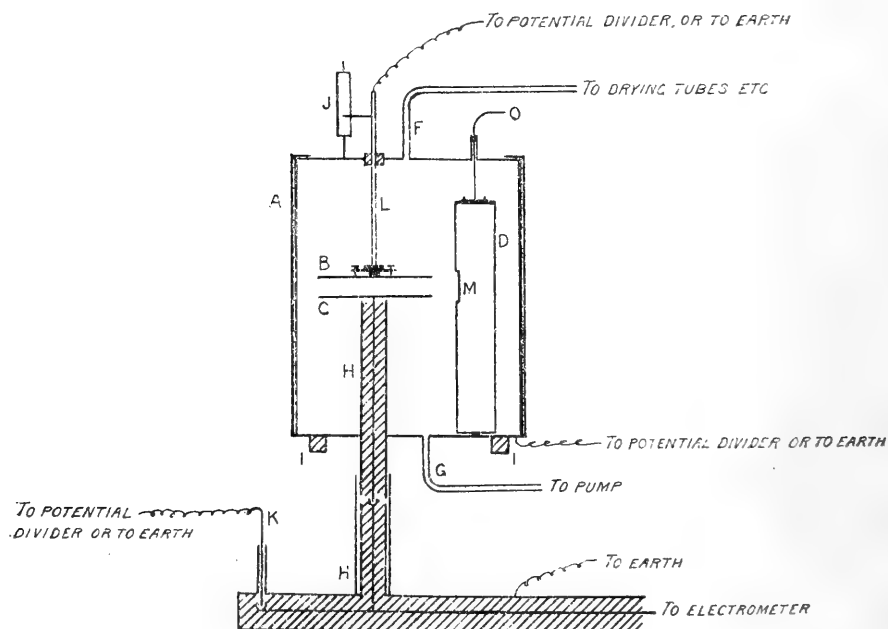
* Communicated by Sir J. J. Thomson, O.M., F.R.S.

method of detecting these layers in a direct manner, and of getting further information concerning their nature. Erskine-Murray*, Greinacher†, and Anderson and Bowen‡ have shown experiments in which an insulated plate placed near another plate which is earthed assumes, whenever the intervening gas is ionized, a difference of potential equal to the contact potential between the two plates. This effect is analogous to that obtained by connecting two different metals with a drop of an electrolyte, and it was thought that a further study of the rate at which this potential was assumed might be profitable.

§ 1. *Apparatus.*

After several preliminary experiments had been performed, the apparatus shown in fig. 1 was constructed for the investigation.

Fig. 1.



A is a brass cylindrical vessel (12 cm. \times 10 cm.) resting on insulating supports, II. Its side can be removed by sliding vertically, and the top of the vessel is supported on

* Erskine-Murray, Proc. Roy. Soc. vol. lix. p. 333 (1896).

† Greinacher, *Ann. de Phys.* vol. xvi. p. 708 (1905).

‡ Anderson and Bowen, Proc. Phys. Soc. Lond. vol. xxiii. p. 346 (1911).

rods erected from the base, which are represented in the figure by the vertical lines immediately beside the sides. B and C represent plates (5 cm. in diameter) which may be tightly screwed on to the connexions L and H respectively. L may be raised or lowered, and its position indicated on a scale J. D is a double cylindrical shell of lead 1 cm. in thickness, containing a small square window M, inside which is enclosed a glass tube containing radioactive material. By means of the handle O, D may be rotated and M closed. The surface of D is covered by a layer of polished brass foil. F and G are openings by means of which gases may be introduced or removed. HH represents an insulated wire which is contained in an earthed brass covering filled with sulphur, and leads to the insulated quadrants of the electrometer. (In this arrangement C is thus the only part of its particular section of the circuit which is exposed to ionized gas.) K is a key by means of which C may be connected to earth or to the potential divider. If the ionizing source is removed, the apparatus is at once available for measuring contact potential differences by the usual Kelvin electrostatic method.

A Dolezalek electrometer with suitable telescope and scale (giving 2000 small divisions per volt), potential divider, batteries, pump, drying-flasks, and apparatus for generating hydrogen either chemically or electrolytically comprised the remainder of the apparatus.

It is important to note that the plate B and all the exposed interior surfaces of the vessel A were of brass, excepting the plate C to be examined. This was necessary because the ionization was not completely confined to the volume of gas between the plates. For example, if the lead cylinder D was left uncovered with brass, the plate C when insulated would assume a difference in potential which lay intermediate between the values of its contact potential with brass and lead respectively. If, however, D was covered with brass, and if all the various exposed internal brass surfaces were polished to a similar condition to the surface of B, then the change in potential of C upon insulating was always exactly equal to the contact difference between the plates as obtained independently by the Kelvin electrostatic method—providing that the distance between B and C was not less than a millimetre.

The use of the sulphur insulation in HH is another essential feature eliminating an ionization current leak which tended to reduce the apparent contact potential as measured by the ionization method.

§ 2. *Measurement of Contact Potential between the Plates.*

The contact potential between a given plate C and the brass plate B could be measured with this apparatus in the following ways:—

(1) The Kelvin method:—The ionizing source is removed, all parts of the apparatus are earthed, and B and C are placed a few millimetres apart. L is then connected to a potential divider, and B is charged to such a potential that, if C be insulated after this charging of B, it will be impossible to alter the electrometer reading by raising or lowering B, providing that metallic contact is not made with C. The applied potential necessary to produce this condition is equal to the contact potential difference between the plates.

(2) Ionization Method, No. 1 :—All parts are earthed at first, then C is disconnected from earth by raising the key, K. If the gas between the plates is ionized, then the electrometer reading will immediately change, and after a short interval become steady at a new position. C is then connected to the potential divider, and it is found that the potential necessary to maintain the second reading is equal to the required contact potential difference.

(3) Ionization Method, No. 2 :—The plate B and the vessel A are both connected to the potential divider. If A and B are charged so that the electrometer reading remains unchanged when C is disconnected from earth, then this charging potential is also equal to the contact potential difference between the metal, C, and brass.

Aluminium, zinc, lead, iron, copper, and brass plates were tested in this way, and in every case there was complete agreement between the three methods*. The two ionization methods were, however, about five times as sensitive as the electrostatic method, and gave results agreeing with each other to within two-thousandths of a volt.

§ 3. *The Direct Electrical Detection of Charged Surface Layers.*

This section presents an account of some experiments which were performed with the object of obtaining direct evidence of charged surface layers by determining whether there was any appreciable time lag between the ordinary charging of a metal and the formation of the charged layers. It is

* An exposure of only a few millimetres of the wire in HH to the effects of ionization will vitiate this agreement. Especial care must be taken in the preparation of the insulating sulphur.

necessary in this case that the movement of the electrometer needle for the actual changes examined should be non-oscillatory in character. This condition can be obtained in the usual way by the introduction of suitable capacity.

In an attempt of this kind it must first be decided whether an effect attributed to the surface of the metal can be distinguished from effects due to defective or charged insulation material. It was found possible to do this by a series of insulation tests.

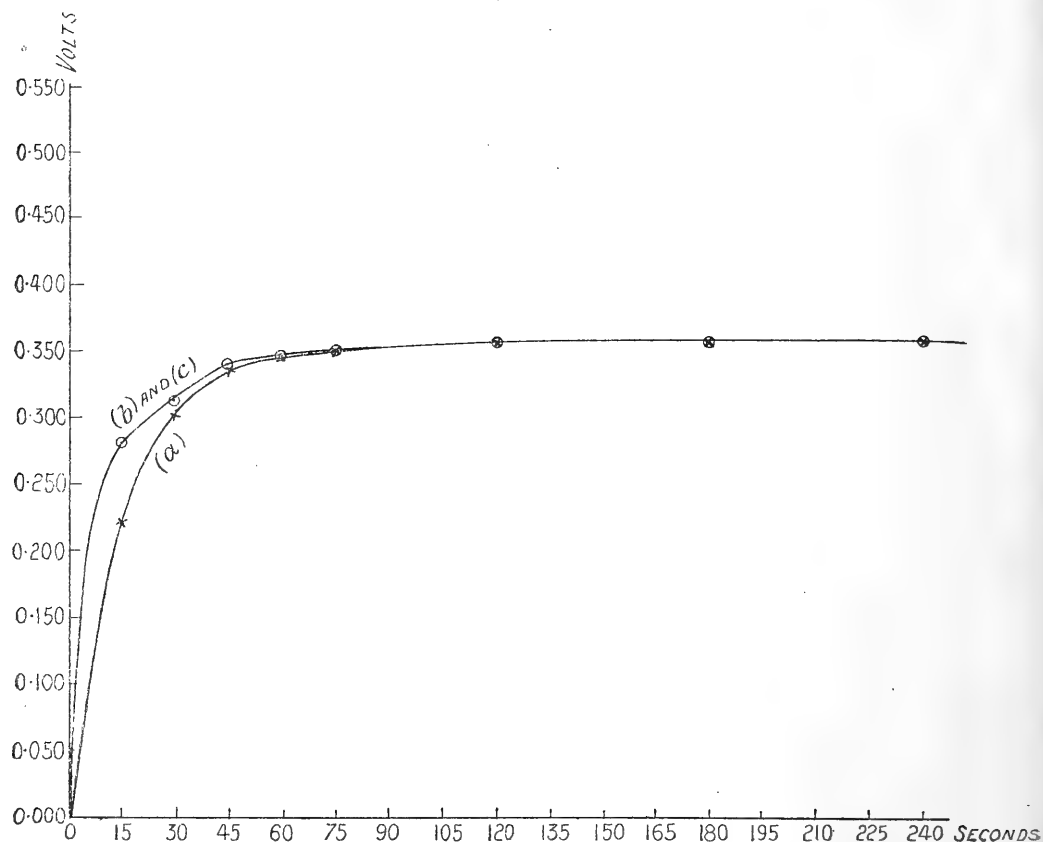
Summary of insulation tests :—The three different methods of measuring contact potential with the apparatus were repeated from time to time as outlined in § 2. There was always the same agreement between these methods, and, as indicated above, it may be affirmed (1) that there was no direct leak across the insulation; (2) that the sulphur coating on the connexions leading to the plate C eliminated the possibility of any reaction between surface layers on the connecting wires and the ionized gas; (3) that all the internal surfaces of the vessel A remained at approximately the same potential as the surface of the brass plate B. These conditions alone, however, do not preclude the possibility of charges on the insulation which might be supposed to produce such effects as those outlined below. It was necessary to ascertain whether a residual charge could be produced in the insulation of sufficient magnitude to affect the electrometer reading. The cylinder D was removed, and attempts were made to charge the sulphur with voltages of the same order of magnitude as those existing across it during the experiments. Neither permanent nor temporary effects could be detected with voltages up to five or six times the contact potential. If the ionizing source was present there was no perceptible tendency for the insulation resistance to alter owing to any action of the γ rays on the sulphur. It should be noted also that, when the surrounding gas is ionized, the ratio of the equivalent resistance between the plates to the insulation resistance is so much decreased that an effect due to the insulation must necessarily be diminished also.

The construction of the key, K, was also important in this connexion, as it was necessary to eliminate any perceptible kick in the electrometer reading when K was raised or lowered. A key was constructed which produced no detectable movement, either temporary or permanent, in the electrometer when contact at K was made or broken.

The detection of the layers :—Dry air was found to be more suitable than the moist laboratory air, because it reduced the small daily decrease in the contact potential between

plates which had been polished. A lead plate was placed in the apparatus as the plate C; dry air was passed through for some hours; and the vessel A was then sealed. Three sets of special observations, (a), (b), and (c), were taken as outlined below, with the plates at a distance of 8 millimetres.

Fig. 2.



The conditions of ionization in the vessel A were constant, and throughout the set there was no change in the circuit which could involve a change in capacity as ordinarily produced.

(a) The plates and vessel A were earthed for some time; then the lead plate C, together with the quadrants to which it was connected, were insulated, and found to assume gradually a difference in potential from the brass equal to the contact difference, at a rate given by the curve (a) in fig. 2. The constancy with which these figures could be repeated is shown in Table I.

(b) After the electrometer reading had become steady the brass plate B and also the vessel A were charged to a potential equal and opposite to the contact potential between brass and the plate C. The reading then returned to zero, as

shown by curve (b) and Table I., and it remained stationary as long as the brass was charged.

(c) The brass plate and vessel A were earthed quickly, and the reading returned again to that representing the contact potential difference, and the figures and curve for this return were found to be the same as those for (b).

Similar tests were made with different plates and similar results obtained. Each set of three could be repeated as often as desired when the contact potential remained constant. In Table I. the results for lead-brass and zinc-brass are given. (In fig 3 the curves for zinc-brass are shown.) The electrometer readings are reduced to volts, and in the case of the lead-brass two series are inserted in order to demonstrate the accuracy of repetition.

TABLE I.

Lead-brass.							Zinc-brass.	
Time after start.	(a).	(a).	(b)*.	(b)*.	(c).	(c).	(a).	(b)* and (c).
0 sec.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
15 "	0.223	0.222	0.284	0.282	0.284	0.282	0.186	0.215
30 "	0.303	0.303	0.313	0.314	0.313	0.313	0.317	0.341
45 "	0.339	0.341	0.343	0.343	0.346	...	0.402	0.422
1 min. 0 sec.	0.345	0.346	0.346	0.346	0.347	...	0.454	0.465
" 15 "	0.350	0.351	0.352	0.350	0.352	...	0.485	0.490
" 30 "	0.356	...	0.356	...	0.501	0.505
" 45 "	0.511	0.513
2 " 0 "	0.356	0.358	0.356	...	0.356	...	0.518	0.518
3 " 0 "	0.360	0.360	0.358	0.360	0.358	0.360	0.522	0.522
4 " 0 "	0.360	0.361	0.360	0.361	0.359	0.360	0.523	0.523

* The values given in the columns for (b) represent the results obtained by subtracting each of the readings from 0.360 in the case of the lead-brass and from 0.523 in the case of the zinc-brass, in order to express the creep in the same direction, and thus facilitate comparison.

(The slower initial rate of increase in the case of the zinc-brass readings was due to the use of a lower charging potential for the electrometer.)

The complete agreement of curves (b) and (c) with each other and their disagreement with curve (a), considered in conjunction with the results of the insulation tests, cannot be attributed to effects due to electric absorption in the sulphur. These curves can, however, be explained on the assumption of definite charged layers, and lead to a simple means of tracing electrically the actual formation of the layers. Suppose that the vessel A and both plates are earthed, and that the air is not ionized, then, calling the potential of the brass V_1 , and the potential of the plate C, V_2 , we have on the brass a layer at a potential $V_1 + a_1$, and

on C we have one at $V_2 + a_2$, where $(V_2 + a_2) - (V_1 + a_1) = P$, the contact potential as defined in the usual way. The states of the metals, and their layers before and after each of the three cases, are expressed with this notation in Table II.

Fig. 3.

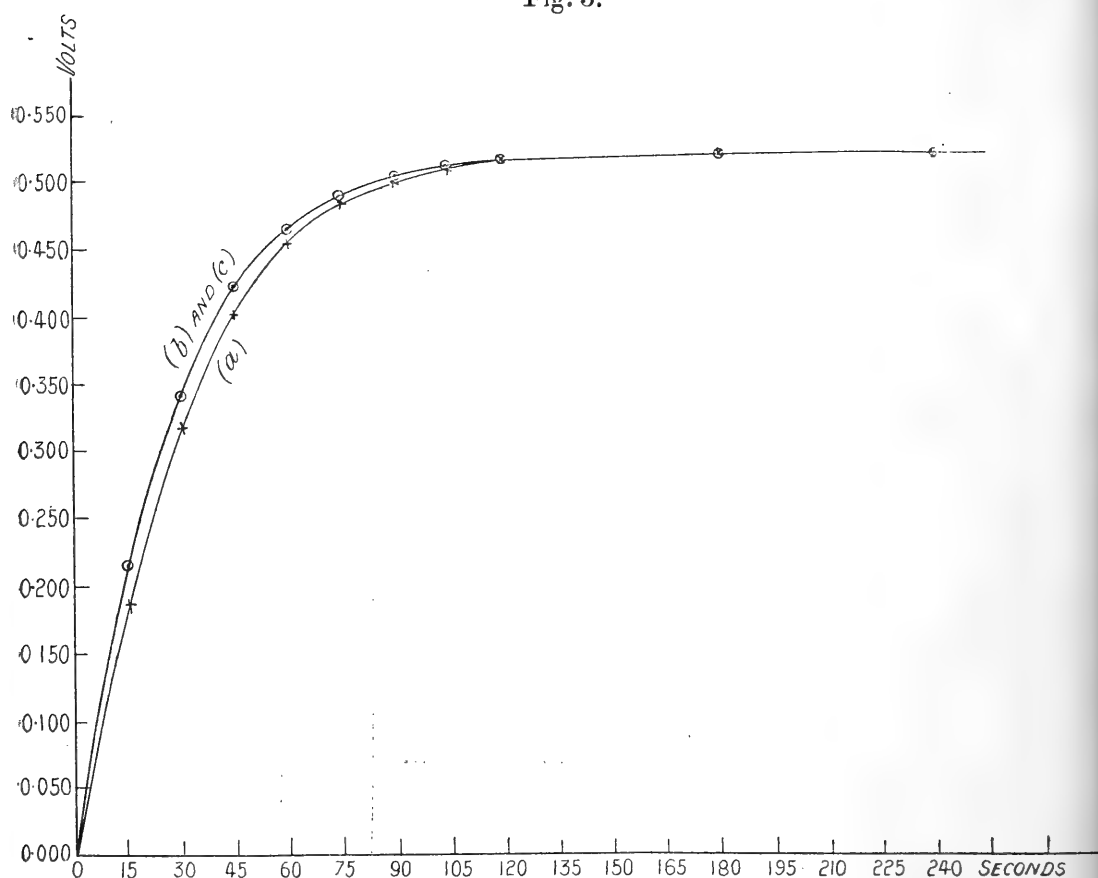


TABLE II.

	Potential at start of (a).	Potential at end of (a).	Potential at start of (b).	Potential at end of (b).	Potential at start of (c).	Potential at end of (c).
Brass ...	V_1	V_1	$V_1 + P$	$V_1 + P$	V_1	V_1
Layer on brass.	$V_1 + a_1$	$V_1 + a_1$	$V_1 + a_1$	$V_1 + a_1 + P$	$V_1 + a_1 + P$	$V_1 + a_1$
Layer on Plate C.	$V_1 + a_1 + P$ ($= V_2 + a_2$)	$V_1 + a_1$ ($= V_2 + a_2 - P$)	$V_1 + a_1$ ($= V_2 + a_2 - P$)	$V_1 + a_1 + P$ ($= V_2 + a_2$)	$V_1 + a_1 + P$ ($= V_2 + a_2$)	$V_1 + a_1$ ($= V_2 + a_2 - P$)
Plate C.	$V_1 + a_1 - a_2 + P$ ($= V_2$)	$V_1 + a_1 - a_2$ ($= V_2 - P$)	$V_1 + a_1 - a_2$ ($= V_2 - P$)	$V_1 + a_1 - a_2 + P$ ($= V_2$)	$V_1 + a_1 - a_2 + P$ ($= V_2$)	$V_1 + a_1 - a_2$ ($= V_2 - P$)

It can now be seen at once why the curves (a) will differ from the curves (b) and (c). During (a) there is no permanent change in the layer on the brass, while in (b) and (c) this layer does change, and as the passage of electrons would be retarded with the formation of the surface layers, it is apparent in the case of (a) that with one layer already in its final state, there will be a slower transfer than in the case of (b) and (c), where both layers change. A perceptible time factor in the formation of the layer is thus definitely indicated, and some capacity due to the layers should be detectable. This conclusion was verified by another test as follows:—

All parts of the apparatus were earthed for more than five minutes, then the brass plate and brass vessel were suddenly charged to the contact potential, P, and the plate C was disconnected from earth immediately after. The time of charging the brass itself was, however, negligible in comparison with the time necessary for completing the subsequent disconnexion of the plate C from earth. In ordinary circumstances the electrometer would remain stationary, but in this experiment we should expect a temporary change in the potential of the plate C, while the layer on the brass was assuming its new potential. The plate C should first assume a slightly lower potential (*i. e.* if $V_2 + a_2 > V_1 + a_1$) and then return to V_2 . Observations showed that this was actually the case; the electrometer needle moved rapidly in the right direction, and then slowly returned to the zero value. An enumeration is given in Table III. of the various changes that take place in the metals and in their layers.

TABLE III.

	Potential immediately after connecting brass to potential divider.	Potential a short time after C is insulated.	Final potential.
Brass	$V_1 + P$	$V_1 + P$	$V_1 + P$
Layer on Brass.....	$V_1 + a_1$	$V_1 + a_1 + P - E_1$	$V_1 + a_1 + P$
Layer on Plate C...	$V_1 + a_1 + P$	$V_1 + a_1 + P - E_2$	$V_1 + a_1 + P$
Plate C	$V_1 + a_1 - a_2$	$V_1 + a_1 - a_2 - E_3$	$V_1 + a_1 - a_2$

E_1, E_2, E_3 represent the effects due to the fact that it takes over a minute for the surface layers of the brass to follow the change of the brass itself. E_1 alters steadily in value from P to zero, and E_2, E_3 first grow from zero to a small value and then return to zero. The magnitude of the effect

depends on the speed with which C is insulated after the brass has been charged. It ranged from 0.030 to 0.040 volt for lead-brass. The effect usually lasted as long as 66 seconds, but was almost completed in about 40.

These variations could be greatly increased or altered in direction by charging up the brass and its layer to several volts immediately before bringing it to the potential P. In this case changes as large as 0.100 volt could be produced, growing rapidly and then slowly vanishing as before, but if voltages over three volts were used disturbances due to the insulation were obtained which slightly altered the variation. By keeping both plates earthed for several hours (either in normal or ionized air) it is possible to make the first few creeps slower than the normal ones of type (a). This appears merely to indicate that the layers become more compact or thicker if held for a considerable time. It requires at least an hour to produce a perceptible difference of this kind, but two or three minutes is sufficient to bring it back to the normal state. The layers themselves probably do not reach the same potential in ionized air as under ordinary conditions. It is also possible temporarily to alter the final value or contact potential by bringing the plates into close proximity without contact. If the plate C is left insulated in ionized air at a distance from the plate B greater than 1 mm., this preliminary retardation is not produced. If left for several days, however, there may occur small permanent changes in any circumstances due to the slow oxidation or deterioration of the polished surface. It is, indeed, usually necessary to wait several days before a polished surface is sufficiently constant in contact potential to render such comparative experiments as those mentioned above possible.

§ 4. *Some Experiments on the Influence of the Gaseous Medium and of the State of the Metals on the Formation of the Layers.*

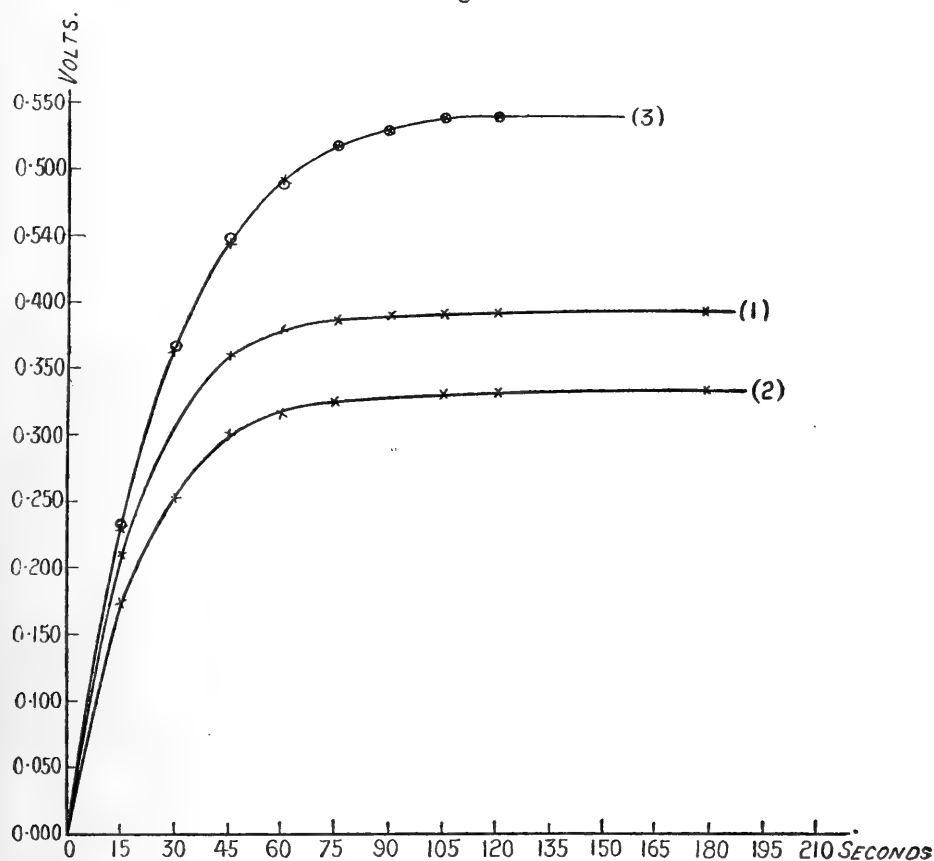
(1) The well-known effects of polishing the plates discussed in detail by Kelvin*, Erskine-Murray†, and others were repeated and examined by these ionization methods. Results similar to those obtained by the electrostatic methods were presented, and no new point was apparent. [The type of the curves for the various chargings varied proportionally with the magnitude of the contact potential

* Kelvin, *Phil. Mag.* vol. lvi. p. 82 (1898).

† Erskine-Murray, *Proc. Roy. Soc.* vol. lxiii. p. 113 (1898).

as measured from time to time after polishing. Curves (1) and (2) in fig. 4 illustrate this point in the case of lead-brass. Curve (1) was taken several weeks after polishing the lead plate, and curve (2) was taken eleven days later.

Fig. 4.



The following figures represent the type of decrease in the total contact potential obtained after freshly polishing with sandpaper in the case of zinc-brass, which is much more constant.

1 hour after polishing	0.596 volt.
2 hours " "	0.583 "
3 hours " "	0.575 "
1 day " "	0.561 "
2 days " "	0.550 "
3 days " "	0.546 "
1 week " "	0.543 "

A repetition of such an experiment will involve variations in the above values up to 0.02 volt, but the rate of change remains approximately the same. As the surface of a metal

becomes tarnished or dirty it always assumes a potential nearer that of its surroundings.]

(2) It was found that for different metals tested the charging curves appeared to differ merely in proportion to the contact potential. Thus the curve obtained by first charging up the plate C to some potential $P_1 + X$ where P_1 is the contact potential between the plate C and the brass, and then insulating, was similar to that obtained when another plate was substituted for C, charged up to $P_2 + X$ and insulated, P_2 being the contact potential between the second plate used as C and the brass. In Table IV. a comparison is shown between curves of the same type for zinc-brass and brass-brass, in which the plate C in the latter case has been charged to a potential $P_1 - P_2$, where P_1 is the contact potential between the two brass plates and P_2 that between the zinc and brass. In the case of the experiment recorded, $P_1 = 0.060$ volt and $P_2 = 0.546$ volt.

TABLE IV.

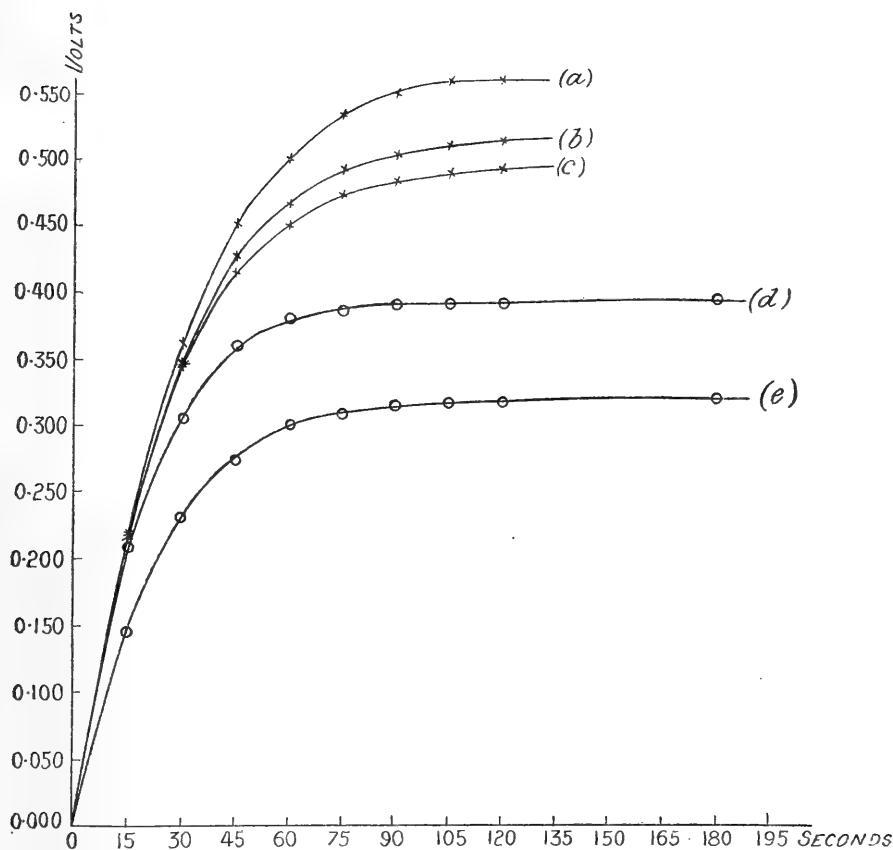
Time.	Zinc-Brass.	Brass-Brass.
0 sec.	0.000	0.000—0.486
15	0.229	0.231— „
30	0.363	0.366— „
45	0.448	0.444— „
1 m. 0	0.491	0.489— „
15	0.519	0.518— „
30	0.530	0.530— „
45	0.540	0.541— „
2 m. 0	0.541	0.542— „

In fig. 4, curve (3) represents these sets; the zinc-brass points are represented by crosses, and the brass-brass points by small circles, the value $P_1 - P_2$ (-0.486 in this case) being omitted in the plotting in order to facilitate comparison. It will thus be observed that the rate of charging (or removal) of layers is independent of the metal and the manner in which the layers are produced. The general behaviour is the same whether the layers are produced by the phenomenon of contact potential or by external means, and the behaviour of the layers on one metal can be made similar to those on another by supplying the difference in surface charge by external means. This similarity in all metals appears to be further evidence in favour of the idea that contact potential phenomena are due to some intrinsic property of metals in which the boundary conditions vary for different metals, such as, for example, in the conception that it depends upon

the different amounts of work to take an electron across the surfaces of different metals.

(3) The influence of the dryness of the air on the charging curve is shown in fig. 5 for zinc-brass.

Fig. 5.



Curve (a) is taken with laboratory air in the vessel A (contact potential 0.564 volt).

(b) is taken after passing dry air through the apparatus for four hours (contact potential 0.518 volt).

(c) is taken after passing dry air through for three days (contact potential 0.495 volt).

Upon allowing ordinary air to enter the apparatus at the end of this time the contact potential returned to 0.545 volt, hence showing that part of this decrease is due to the usual slow change in contact potential when using polished plates. It will be seen that this latter change is in agreement with the magnitude of change recorded in (1).

After this preliminary decrease was obtained it was found that the contact potential became far more constant and

steady in the presence of dry air than in moist air. If the presence of water-vapour was an essential factor in the phenomena of contact potential it would have been expected that the continued presence of dry ionized air would lower the value of the contact potential by a much larger amount, and that it would at least render it uncertain.

(4) When pure dry hydrogen was used as the gaseous medium it was possible to produce changes such as those shown by curves (d) and (e) in fig. 5 for lead-brass, and curves (1) and (2) in fig. 6 for zinc-brass. Curve (d) in

Fig. 6.

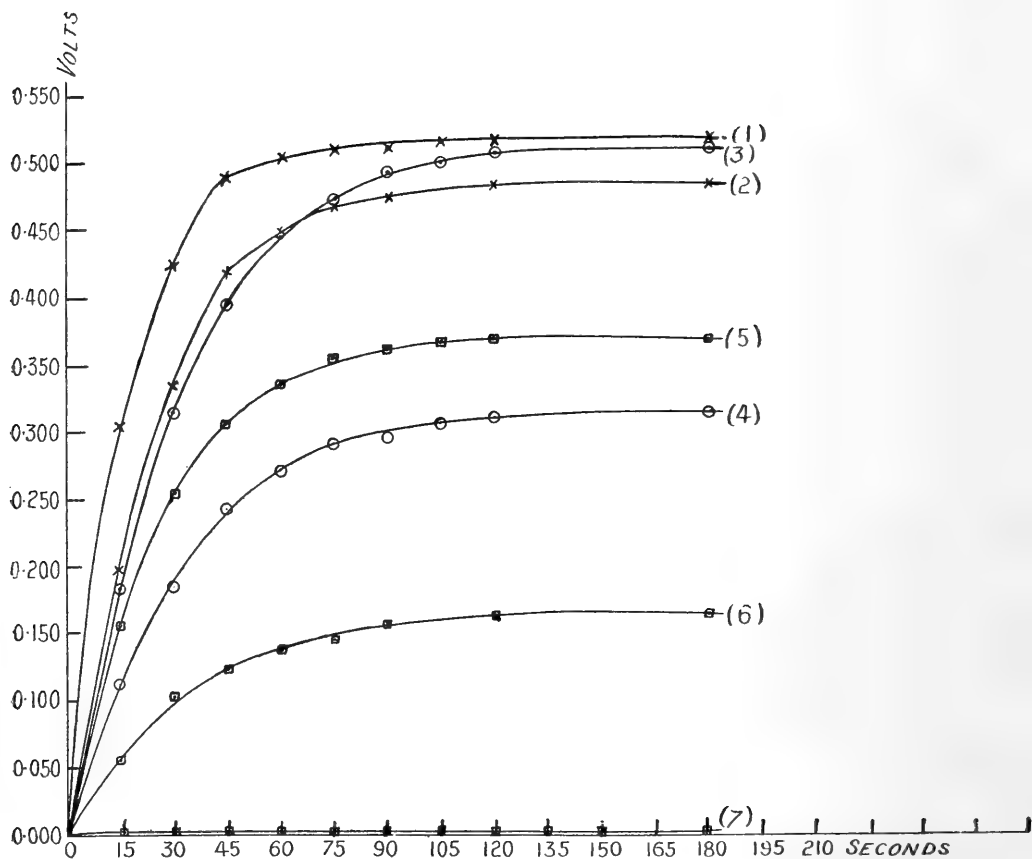


fig. 5 is for lead-brass taken in dry air, while curve (e) shows the effect after passing pure dry hydrogen through the apparatus for several days. In this case the hydrogen was prepared electrolytically, and passed through an alkaline pyrogallic solution and the usual drying-flasks. Curves (1) and (2) in fig. 6 represent the change from dry air to hydrogen in the case of zinc-brass. It will be seen that under the influence of pure dry hydrogen it was not possible

to produce any large change. Those recorded were the largest obtained; an exposure of a week, in the case of an experiment with copper-brass, produced no change in the final value of the contact potential. The difference in mobility of the hydrogen ions is partly responsible for the difference in shapes of the curves.

An interesting result was, however, obtained if the hydrogen was prepared from chemically pure zinc and dilute sulphuric acid. Curves (3)* and (4) in fig. 6 show the largest effect obtained for zinc-brass in changing from dry air to this preparation of hydrogen. Curves (5), (6), and (7) in fig. 6 show the exceptional effect in the case of lead. Curve (5) is for lead-brass in dry air. In (6) the impure hydrogen has been passed through for one hour, and in (7) for one day. The effect sometimes became negative, and could always be made as small as shown in (7) for lead only. In the case of pure hydrogen the values were constant and could be repeated, but in this case they were uncertain and variable, suggesting chemical action. The presence of H_2S and SO_2 in small quantities is probably responsible for these changes. It has been shown by Spiers†, "that even in a high vacuum of pure dry hydrogen at a pressure of 0.0001 mm. of mercury, and after four washings in the gas, there is still a large contact effect," which he attributes to the fact that there is still enough oxygen present to "completely oxidize the surface." He endeavours to show that the large diminution in the contact potential due to his "heating method" is due to the final removal of this small amount of oxygen. The behaviour of the surface layers in our experiments strongly supports the idea that in cases where the contact potential is diminished we have merely the formation of extra layers which hold back sufficient electrons to minimize the normal contact effects. This would support the opinions expressed by Richardson in a recent paper on the Electron Theory of Contact Electromotive Force‡, concerning the experiments of Spiers§, Brown||, Greinacher¶, and Majorana**, which have formerly been interpreted as strong support for the chemical theory.

* The change in the shape of curve (3) from curve (1) is due to a change in the charging potential used for the electrometer needle.

† Spiers, Phil. Mag. vol. xlix. p. 70 (1900).

‡ Richardson, Phil. Mag. [6] vol. xxiii. p. 263 (1912).

§ *Loc. cit.*

|| Brown, Phil. Mag. [6] vol. v. p. 591 (1903).

¶ *Loc. cit.*

** Majorana, *Atti de Lincei*, vol. ix. p. 162 (1900).

Summary.

Ionization methods for measuring contact potential are described and found to be exceptionally efficient.

A study of the rate of charging due to contact potential in the case of an insulated plate in ionized gas leads to new direct evidence of the presence of charged surface layers. The time necessary for their formation and change is found to be observable, and effects due to their capacity are shown to be detectable. Their behaviour agrees with the conception that contact potential phenomena can be explained by the different amounts of work done by electrons in escaping from different metals.

The rate of charging or removal of the layers responsible for contact potential is shown to be apparently independent of the metal and identical with the behaviour of ordinary charges imparted by external means.

The influence of the dryness of the gaseous medium and the nature of the gas is examined, and it would appear that although chemical action may cause large contact effects, it is not usually responsible for more than a small part of the phenomenon.

My best thanks are due to Professor Sir J. J. Thomson for his suggestion of the research and kind interest in the experiments.

The Cavendish Laboratory,
November 1, 1912.

XXX. *Thermal Radiation from Hot Gases.*

By W. T. DAVID, B.A., B.Sc., *Trinity College, Cambridge* *.

THE radiation emitted by a substance constitutes in general either a continuous spectrum or a line or band spectrum.

Continuous spectra are generally emitted by solid bodies when heated. It seems probable that these continuous spectra are emitted, not by the intra-atomic corpuscles or electrons, but by the free corpuscles which determine the conductivity of metals. These corpuscles possess high velocities, and during collision with an atom at the end of their free flight, pulses are emitted along the Faraday tubes attached to them. This is also the theory of the origin of Röntgen rays. In this case, however, the velocity of the corpuscles (cathode rays) before striking the molecules is enormously

* Communicated by the Author.

great, and the pulses emitted during collision are very "thin" because the duration of collision is very short. When the velocity is much less the duration of collision is greater and the pulses emitted are broader, giving rise to ultra-violet, luminous, or infra-red radiation, according to the magnitude of the velocity in the free-path. If the law of equipartition of energy applies approximately to systems consisting of atoms and free corpuscles, this theory accounts very well for the known laws of radiation. It accounts, for instance, for the shift of the maximum point in the continuous spectrum energy curves towards the shorter wave-lengths with rise in temperature.

Line and band spectra in the visible part of the spectrum are not emitted as the result of heat alone. It seems probable that an element can only emit its characteristic spectrum when it is in the state of a gas, and its molecules more or less free from the influence of their neighbours. The spectrum of an element which is solid at ordinary temperatures is observed by placing it in a non-luminous flame, or by examining the light from an electric spark or arc between terminals made of that element. It was at one time thought that the emission of the spectrum was caused by the high temperature to which the element was raised by these means, but it seems probable that the only influence of temperature is to vaporize the element. Whenever a gas is emitting its characteristic spectrum it is ionized, and it seems fairly certain that the emission of the spectrum is in some way dependent upon ionization. It is, however, possible that a gas would emit its characteristic spectrum in virtue of its temperature alone, if it were possible to heat it to a temperature much higher than that which can be commanded in a laboratory *. When an atom loses a corpuscle (in other words, when it is being ionized) the remaining corpuscles vibrate about new positions of equilibrium, and again when the atom is restored to electrical neutrality, the corpuscles vibrate about their old positions of equilibrium. These corpuscles grip the æther in virtue of their electrical charge, and when vibrating they send out trains of waves which travel through the æther with the velocity of light. The corpuscles in an atom of a particular element have certain definite periods of vibration which correspond to the wave-lengths of the lines in its characteristic spectrum. The corpuscles in an atom may also be set in vibration if the atom is bombarded by the free corpuscles which move with high velocities in the heated ionized gas. The collisions

* See p. 258.

between molecules in a gas are apparently too soft to set the intra-atomic corpuscles into vibration, even though the gas be heated to the highest temperature we can command. According to Mr. Jeans, the intra-molecular vibrations are not appreciably excited if the duration of molecular collision (*i. e.*, the time during which two molecules remain in contact or within each other's sphere of influence during collision) is long in comparison with the periods of the intra-molecular vibrations, though if the duration of collision is comparable with the periods of these vibrations the intra-atomic corpuscles will be set into vibration by these molecular collisions*. The duration of molecular collisions is dependent upon the velocity with which the molecules approach one another; the higher the velocity the less time they remain in contact during collision. The mean velocity of the molecules is approximately proportional to the square root of the absolute temperature, and the duration of molecular collisions therefore decreases as the temperature of the gas is increased. Therefore, according to this theory, at extremely high temperatures the duration of molecular collisions may be short enough to excite the intra-molecular vibrations which give rise to the characteristic spectrum, and the emission of the characteristic spectrum would then be thermal in origin. In the case of an ionized gas, however, the free corpuscles, which possess a very small mass, would have a much higher velocity than the heavier molecules, and the duration of collision between a molecule and free corpuscle seems to be short enough to shake the intra-atomic corpuscles into vibration, at any rate when the gas temperature is in the neighbourhood of 1000°C .

The Emission of Infra-red Radiation by Gases.

The molecules of some gases possess vibrations of much lower frequencies than those corresponding to luminous radiation (which is of wave-length from 0.3μ to 0.7μ). Carbonic acid gas and steam emit radiation of much greater wave-length than that of luminous radiation. Carbonic acid gas has emission and absorption bands whose maxima are at 2.8μ , 4.4μ , and 14.1μ approximately, and water-vapour has a series of bands throughout the whole of the infra-red region, the first band (and the one possessing most energy) being in the neighbourhood of 2.8μ . Paschen † in 1894

* Jeans, 'Dynamical Theory of Gases,' Camb. Univ. Press, chapt. ix.

† 'Die Emission der Gase,' Wied. Ann. l. p. 409 (1893); li. p. 1 (1894); and lii. p. 209 (1894).

investigated the infra-red emission spectrum of CO_2 and water-vapour. He heated CO_2 in a metal tube with open ends and found that between 150° and 500° C. the intensity of the emitted radiation of wave-length 4.4μ from a 7 cm. thickness of gas is only a little below that of a black body at the same temperature. He concludes from his experiments that CO_2 and water-vapour have a true temperature emission. These experiments will be criticized later. But if, for the moment, we assume that Paschen's experiments do conclusively prove that these gases have a true temperature emission, the theory sketched above leads us to assume that the duration of molecular collisions when these gases are at 150° C. is short enough for the intra-molecular vibrations giving rise to infra-red radiation to be excited during molecular collisions, though the collisions are too soft at this temperature to excite the higher-frequency vibrations which give rise to luminous and ultra-violet radiation.

When a gas is heated infra-red radiation is first emitted (provided, of course, the internal parts of its molecules are capable of executing low-frequency vibrations like those of CO_2 and water-vapour *) and, according to the above theory, if the gas could be raised to a sufficiently high temperature (which would probably have to be much greater than that which we can command in a laboratory) luminous and ultra-violet radiation would be emitted. This is exactly what happens in the case of a solid body when it is heated : at low temperatures only infra-red radiation is emitted, but when the temperature is raised the solid body begins to glow.

In the case of a hot ionized gas containing CO_2 and water-vapour (*e. g.*, Bunsen flame) the radiation may be divided up into three parts. First, the negative ions which exist at high temperatures as free corpuscles† are retarded and accelerated during collisions, and pulses will therefore be emitted along the Faraday tubes attached to them. This would give rise to a continuous spectrum in the way described when dealing with the radiation from solid bodies. This part of the radiation would obey the Stefan-Boltzmann fourth power law if the amount of ionization did not vary with the temperature. But in all probability ionization is a function of the temperature, and the radiation due to the retardation and acceleration of the negative ions would then increase at a greater rate than that given by the fourth power law.

* Very few gases seem to emit thermal radiation. The most important, from an engineering point of view, are CO_2 and water vapour. The thermal radiation from air seems to be very small.

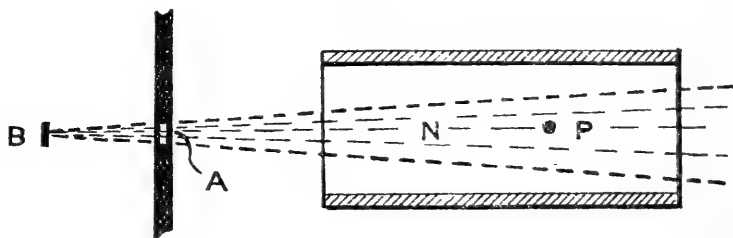
† J. J. Thomson, 'Engineering,' April 3, 1908, p. 447.

The energy in this part of the radiation is, however, generally small, for the number of negative ions is generally only a small proportion of the number of molecules in the gas*. The second part of the radiation is luminescence. It is due to the shaking up of the intra-atomic corpuscles by ionic bombardment, and also by ionization and recombination, which is continually going on as explained above. The energy in this part of the radiation is also generally small. The third part is the thermal radiation which is emitted if the molecules possess low-frequency vibrations like those of CO_2 and water-vapour. The emission of this infra-red radiation may be due to molecular collisions or ionic bombardment of the molecules. The energy in this part of the radiation may be very considerable.

Paschen's Experiments.

Paschen, as we mentioned above, heated CO_2 in a metal tube with open ends, and measured the radiation emitted by the hot gas by means of a bolometer. The arrangement of his apparatus was somewhat as shown in fig. 1, but the rock-salt prism used to disperse the radiation is not shown. The

Fig. 1.



bolometer at B does not "see" any part of the hot tube, it "sees" only a small cone N of the gas through the small aperture at A. The emission from the gas was measured at various temperatures between 150°C. and 500°C. , and after passing it through a rock-salt prism he found that the radiation of wave-length 4.4μ emitted by a thickness of 7 cm. of gas was only a little below that of a black body at the same temperature. He concluded that CO_2 has a pure temperature emission—that the intra-molecular vibrations are excited during molecular collisions. The writer doubts whether this conclusion drawn from these experiments is justifiable.

* In a metal, on the other hand, the number of free corpuscles is comparable with the number of atoms it contains.

The hot walls of the metal tube emit radiation of all wave-lengths, and some of this is absorbed by the CO_2 —viz. that of wave-length in the neighbourhood of $2.8\ \mu$, $4.4\ \mu$, and $14.1\ \mu$. This absorption by the gas goes primarily to excite the low-frequency vibrations of its molecules corresponding to radiation of these wave-lengths, and these vibrations cause radiation of the same wave-lengths to be emitted in all directions. Some of this will reach the bolometer.

To make this clear imagine a molecule of CO_2 at some point P within the cone of gas seen by the bolometer. Radiation from all parts of the interior surface of the hot metal tube passes through P, but none of this radiation can reach the bolometer at B because the aperture at A was made small enough to prevent any part of the tube surface being seen by the bolometer. The internal parts of the CO_2 molecule at P will be set in vibration owing to the absorption of $2.8\ \mu$, $4.4\ \mu$, and $14.1\ \mu$ radiation. These intra-molecular vibrations give rise to the emission of radiation in *all* directions*. Some of this obviously will reach the bolometer.

Paschen also found the emission from CO_2 just as it issued from a heated platinum tube, but in this case also the emission by the hot CO_2 may have been due to absorption of radiation from the hot solid body (the platinum tube) near it. It is not, therefore, possible to decide from these experiments whether the intra-molecular vibrations, which give rise to the emission by the hot CO_2 , are excited by molecular collisions or by absorption of radiation from the hot metal walls. Tyndall's experiments on the emission from adiabatically compressed CO_2 † give perhaps more satisfactory information on this point. The CO_2 was compressed in a glass tube with its ends closed by means of two rock-salt plates, and the emission measured by means of a thermopile. But even here it is conceivable that the emission by the gas is due to its absorbing radiation from the glass tube‡, which, being a bad conductor of heat, would have its interior surface heated up very quickly to a temperature nearly equal to that of the gas, especially as it was in turbulent motion during compression.

* Wood has detected lateral emission from sodium vapour when a beam of light from a sodium flame is sent through it. Also cf. curves in fig. 14 of paper "Radiation in Explosions of Coal-gas and Air," Phil. Trans. A. cxxi. p. 396. Lateral emission will explain why curve A lies above the curve C, and the B above the D.

† See Poynting and Thomson's 'Heat,' p. 236 (1908 edition).

‡ Glass is a good radiator in the infra-red region.

Discussion of further Work on the Emission of Infra-red Radiation from CO₂ and H₂O.

Most chemists seem to hold the view that a gas can only emit radiation (infra-red as well as luminous) when it is undergoing chemical or a quasi-chemical reaction* ; disruption of molecules or violent combination are necessary according to them to excite the intra-molecular vibrations. R. von Helmholtz held the view that the radiation from a flame came mainly from molecules which had just been formed, and which are in a state of vigorous vibration. According to this view the infra-red radiation emitted by flame, like the radiation of higher frequency which gives rise to luminosity, is due to violent chemical combination, and not to purely thermal causes. In support of his view R. von Helmholtz brings forward the experimental fact discovered by him that the radiation from a flame is diminished when the gas and air are heated before entering the burner, although the temperature of the flame must be higher. This he explains as being due to the quicker approach to the state of equilibrium owing to the more frequent collisions of the freshly-formed compound molecules with their neighbours.

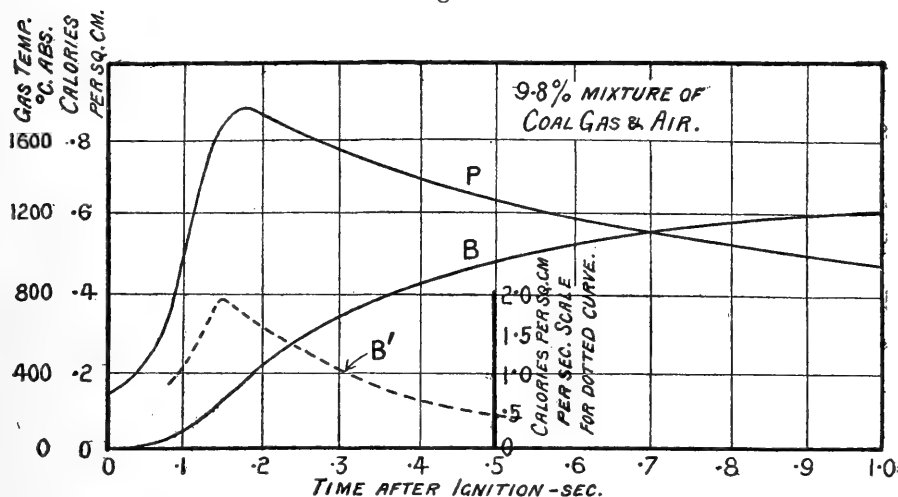
Some experiments made by Prof. Hopkinson and the writer may be mentioned here †. They measured the radiation emitted during explosion and subsequent cooling of a mixture of coal-gas and air, and found that considerable radiation was emitted as the gaseous mixture cooled. The radiation emitted by the hot gaseous mixture was measured by means of a bolometer placed behind a fluorite window let into the walls of the explosion vessel. The result of an experiment made by the writer on a 10 per cent. mixture of Cambridge coal-gas and air exploded in a cylindrical cast-iron vessel 30 cm. in length and 30 cm. in diameter is shown in fig. 2. Curve P gives the mean gas temperature deduced from the pressure record (taken on a revolving photographic film by means of a Hopkinson optical indicator) by means of the gas equation $pv = R\theta$ after making allowance for the small contraction of volume which takes place during combustion. Curve B shows the heat received by radiation by the walls of the vessel (which were painted black) per sq. cm. of wall surface ; this curve was traced by a galvanometer whose deflexions were proportional to the rise of temperature of the bolometer. Both curves are to a time base, and were simultaneously recorded on the same photographic film.

* In which case it is ionized.

† Hopkinson, Proc. Roy. Soc. A. vol. lxxxiv. p. 155 ; David, Phil. Trans. A. vol. cxxi. p. 375.

Curve B' is the differential of curve B, and shows the rate at which the gaseous mixture emits radiation at various times after ignition in calories per sq. cm. of wall surface per sec.

Fig. 2.



It will be noticed that the emission is a maximum sometime during explosion, just before the gas temperature attains its maximum value. During this time chemical combustion is rapidly proceeding, and this must be to a very large extent responsible for the intensity of the emission at this point. It cannot be due wholly to temperature, for the emission is less at the moment of maximum gas temperature than at this point, and Prof. Hopkinson has shown that every part of the gaseous mixture has a higher temperature at the moment of maximum temperature than at any other time *. It is possible that the violence of combustion causes a considerable part of the energy of combination to pass into the form of intra-molecular vibrations. Part of the energy in these vibrations is lost by radiation, but the greater part is converted into the two other kinds of molecular energy—rotational energy and translational or pressure energy.

During the cooling of the gaseous mixture the emission is still very considerable, at any rate until the gas temperature has fallen to 1000° C. abs., and it seems highly probable that the emission during this time is mainly thermal in origin (*i. e.* that the molecular vibrations are for the most part excited during molecular collisions). It is difficult to believe that this large emission is wholly due to continued combustion (or after burning). Mr. Dugald Clerk's experiments seem

* Roy. Soc. Proc. A. vol. lxxvii. p. 389.

to prove definitely that all the gas has not entered into combination at the moment at which the gaseous mixture attains its maximum pressure and temperature ; but it seems hardly possible that the combustion proceeding after this time is sufficient to account for this large emission. Neither would it seem to be due to any large extent to dissociation and recombination of the CO_2 and water-vapour, for it seems very probable that the amount of dissociation of CO_2 and steam at temperatures under 2000°C . is very small.

The increase of the specific heats of CO_2 and steam with temperature seems to give fairly reliable evidence that some of the intra-molecular vibrations of these gases are excited by molecular collisions. When a gas absorbs heat the translational, rotational, and vibrational energies of its molecules are increased. According to the Maxwell-Boltzmann law of equipartition of energy, the heat energy absorbed by a gas is equally distributed amongst the various degrees of freedom possessed by its molecules, or rather amongst those degrees of freedom which share in the heat motion of the molecules, and the specific heat of a gas is therefore proportional to the number of those degrees of freedom possessed by its molecules which share in the molecular heat motion. The number of translational and rotational degrees of freedom possessed by molecules must be independent of the temperature of the gas (unless the nature of the molecules changes with the temperature, in which case we should have a different gas or mixture of gases), but the number of the vibratory degrees of freedom of the molecules, which have energy given to them during collision, may vary with the temperature without affecting the composition of the gas. At any given temperature the molecular collisions may be too soft to excite any but the very low-frequency vibrations which the molecules may possess ; but as the temperature is raised the collisions become harder (*i. e.*, the duration of collisions becomes smaller), and consequently vibrations of higher frequency may be excited*. The specific heat of a gas would also increase with temperature, even though only one type of vibration could be excited during collisions. The

* It is not supposed here that the very high-frequency vibrations giving rise to luminous radiation (which absorption spectra show to be very numerous) are excited by molecular collisions as the gas-temperature is raised. The vibrations referred to are those only which give rise to infra-red variation. It seems probable that the vibrations of CO_2 molecules corresponding to radiation of wave-length 15μ are excited by molecular collisions at ordinary temperatures, and that as the temperature of the CO_2 is raised the vibrations corresponding to 4.4μ radiation, and later those corresponding to 2.8μ radiation, are excited during collisions.

duration of collision between pairs of molecules decreases as the velocity with which they approach one another increases, and since the velocities of the molecules of a gas at any temperature have widely different values (grouped about the mean according to the law of errors), the collisions between slowly moving pairs may be too soft to excite the vibrations within those molecules, but the collisions between the fast moving pairs may be short enough to excite their vibrations. As the temperature of the gas is raised the molecules will all move with greater velocities, with the result that the proportion of collisions soft as regards this type of vibration will be decreased, and the number of molecules which have their vibrations excited will therefore be increased. The specific heat will therefore increase, not suddenly, but gradually with the temperature, though, of course, the rate of increase will not be constant. It will be greatest at the temperature at which the mean molecular velocity is just great enough to make the duration of collisions short enough to excite the vibrations, for the proportion of molecules moving with the mean velocity is far greater than the proportion of molecules moving with other velocities.

Infra-red Spectrum of the Bunsen Flame.

Julius made a very complete analysis of the infra-red emission from various kinds of flame. He examined the spectrum of the flame by means of a rock-salt prism, and found that in all flames producing both CO_2 and water-vapour that the infra-red spectrum consisted of two emission bands whose maxima are at 2.8μ and 4.4μ *. Of these the 4.4μ band was considerably stronger than the 2.8μ band. The 4.4μ band is absent from the spectrum of a pure hydrogen flame, but it contains the 2.8μ band; while the spectrum of a pure CO flame contains both the 2.8μ and 4.4μ bands, but the 2.8μ band is very weak. Infra-red flame spectra seem to be independent of the nature of the combustible gas; they depend solely on the products of combustion.

Paschen found that the 4.4μ emission band of CO_2 has its maximum shifted towards the *long* wave-lengths with rise of temperature†, the maximum being at 4.27μ at 17°C .

* There is also a small emission band in the neighbourhood of 14μ due to CO_2 (corresponding to the absorption band of cold CO_2 in the neighbourhood of 15μ), but the energy in this band at the temperature of the Bunsen flame is small in comparison with the energy in the 2.8μ and 4.4μ bands.

† The emission band of CO_2 in the neighbourhood of 14μ shift towards the *short* wave-lengths with rise of temperature, as is usual.

(absorption), $4.3\ \mu$ at 600°C ., $4.388\ \mu$ at 1000°C ., and $4.4\ \mu$ at the temperature of the Bunsen flame. Coblenz has confirmed this, and finds that in the arc the maximum goes up to $4.55\ \mu$. This shift is most peculiar, and Coblenz commenting on it says: "Since the absorption band of CO_2 is at $4.3\ \mu$ and that of CO is at $4.6\ \mu$, if the emission band is due to a pure thermal effect, then one would expect to find that with rise of temperature and the consequent dissociation of CO_2 into CO the maximum of the emission band of CO_2 will shift towards that of CO ." It is interesting to notice in this connexion that the maxima of the emission bands of both CO and CO_2 are at the same point, viz. $4.75\ \mu$, in a vacuum-tube*. Coblenz believes that this is due to the dissociation of CO_2 . It may be mentioned that the intensity of the CO emission band from the vacuum-tube is much greater than that of CO_2 for all pressures.

R. von Helmholtz made some very interesting experiments on the radiation from hydrogen, CO , marsh-gas, ethylene, and coal-gas flames. He found that CO_2 produced in the CO flame emitted about 2.4 times as strongly as an equal volume of water-vapour produced in a hydrogen flame, and shows that this ratio is preserved in the other flames whose products of combustion consist of CO_2 and water-vapour. The flames in these experiments were just rendered non-luminous by adjusting the air supply, and the temperatures of all of them were probably pretty much the same. A rough analysis of the radiation from a mixture of coal-gas and air after explosion made by the writer supports this result. He measured the emission from identical gaseous mixtures first through a fluorite window, and secondly through a quartz window†. The fluorite transmits practically all the radiation emitted by the hot gaseous mixture, which contained about 8.5 per cent. of CO_2 and 20 per cent. of water-vapour, while the quartz cuts off practically all the radiation from CO_2 and transmits about 65 per cent. of that from water-vapour. The radiation from the gaseous mixture transmitted by the quartz window was about 50 per cent. of that transmitted by the fluorite, and the CO_2 therefore emitted about twice as strongly as an equal volume of water-vapour at the same temperature.

Theoretical.

Some experiments made by the writer show that the intrinsic radiance from thicknesses of gas containing the

* Coblenz, 'Investigations of Infra-red Spectra,' Part II. p. 313.

† Phil. Trans. A. vol. ccxi. p. 388.

same number and kind of radiating molecules does not depend upon the temperature alone, even after correcting the radiation for absorption. This implies that the vibratory energy which gives rise to the radiation is not solely dependent upon the gas temperature (which is proportional to the translational energy). It seems to depend upon the lateral dimensions and density of the gas as well*. An explanation in terms of the kinetic theory of gases which has been suggested by the writer to account for this may be briefly stated thus:—A molecule as it describes its free-path loses energy owing to the emission of radiation and gains energy owing to the absorption of radiation energy from the æther†. The rate at which it emits radiation is a function of its vibratory energy, say $\xi(V)$, and the rate at which it absorbs energy is a function of the density of radiation energy in the æther, say $\phi(E)$. During the free-path, therefore,

$$\frac{dV}{dt} = \phi(E) - \xi(V),$$

and the vibratory energy, V , will increase or decrease according as the rate of absorption of energy, $\phi(E)$, is greater or less than the rate of emission of radiation, $\xi(V)$. During collision with another molecule there will be a transference of energy between the vibratory degrees of freedom and the rotational and translational degrees of freedom, and the vibratory energy of the molecule will tend to take up during this time a value, which we will call V_0 , such that the energy in each of the vibratory degrees of freedom equals that in each of the translational and rotational degrees of freedom. During collision, therefore, the vibratory energy of the molecules will tend to take up a value which is proportional to the absolute temperature of the gas, but during the free-path there will be a considerable departure from this value if the density of radiation energy in the æther is above or below a certain value, and the time of description of free-path is not very short. If τ is the time of description of free-path the gain in the vibratory energy, V ,

* Phil. Trans. A. vol. ccxi. (1911) pp. 402 & 406.

† The molecule gains energy from the æther in two ways:—(i.) The absorption of energy by its vibratory degrees of freedom, and (ii.) a direct transfer to its translational degrees of freedom due to the pressure of radiation. Of these (ii.) is possibly small in comparison with (i.) in the case of thermal radiation from carbonic acid gas and steam, and is neglected in this discussion.

during τ is

$$\delta V = \int_0^\tau [\phi(E) - \xi(V)] dt,$$

and the average value of V over a time τ is roughly

$$\bar{V} = V_1 + \delta V/2,$$

where V_1 is the vibratory energy possessed by the molecule as it enters on its free-path, that is, immediately at the end of collision. If the transference of energy during collision is exceedingly rapid (as it probably is in the case of the low-frequency vibrations of carbonic acid gas and steam molecules*) V_1 will approach the value V_0 . But if the rate of transfer of energy is not sufficiently rapid to reduce V to V_0 at the end of a single collision, it will be obvious that the greater the departure of V from V_0 before collision the greater will be the departure of V_1 from V_0 after collision. In either case \bar{V} will be appreciably different from V_0 (which is proportional to the absolute temperature of the gas) if the gain of vibratory energy, δV , during the free-path is appreciable.

From this theory it appears that at any given gas temperature the greater the gain of vibratory energy during the free-path the greater will be the average vibratory energy of the molecules, and therefore of the radiating power of the gas; and that, *other things being the same*,

- (i.) the greater the density of radiation energy in the æther (which depends among other things upon the transparency and volume—or virtual volume—of the gas) the greater will be the radiating power of the gas;
- and (ii.) the smaller the time of description of free-path (or, in other words, the greater the density of the gas) the nearer will the average vibratory energy of the molecules approach a value which is proportional to the absolute temperature of the gas. In a very dense gas, therefore, as in the case of solids and liquids, the radiation would depend on the temperature alone.

The radiating power of a gas which emits thermal radiation thus appears to be a function of the absolute temperature of the gas, the value of the density of radiation energy in the æther, the rate at which the molecules emit radiation, the time of description of free-path (inversely as the density of the gas), and the rate of partitioning of energy during collisions.

* Phil. Trans. A. vol. cxxi. (1911), footnote p. 409.

Conclusion.

In this paper the writer has briefly reviewed and criticized the experimental work which has been done on the emission of thermal radiation from hot gases. Probable theories of the origin of radiation from gases have also been dealt with. The question as to whether a hot gas can emit radiation in virtue of its temperature alone has been rather fully discussed, and, although it is impossible to settle this question definitely until further experimental work has been done, it seems highly probable that the low-frequency vibrations of CO_2 and water-vapour giving rise to infra-red radiation are excited by molecular collisions. Paschen's experiments on the emission from hot CO_2 and water-vapour have been looked upon as affording conclusive evidence that molecular collisions excite the low-frequency intra-molecular vibrations of these gases, but the writer shows that in these experiments the absorption of radiation from the hot tube walls *might* be wholly responsible for the exciting of these vibrations. The writer believes that this question could be definitely settled by experiments such as the following:—

- (i.) By measuring the emission (if any) from a gas like CO_2 heated by adiabatic compression during compression and subsequent cooling. Many of the experiments made by the writer* on the radiation emitted in explosions of coal-gas and air might with advantage be repeated, imitating the explosion by adiabatic compression;
- (ii.) By measuring the rise of pressure (if any) or temperature of CO_2 when it is absorbing radiation at a known rate†.

Some experiments by Prof. Hopkinson and the writer are of interest in this connexion. Hopkinson finds a greater maximum pressure and a slower rate of cooling of a gaseous mixture after explosion when the walls of the explosion vessel are reflecting than when they are black‡; and the writer finds that the radiation emitted from a certain thickness of the gaseous mixture is greater when the walls of the vessel are reflecting than when they are black§. The most natural interpretation of these experiments is that the radiation

* See Phil. Trans. A. vol. ccxi. pp. 375–410.

† The air is warmed by sunlight, but air has no marked absorption bands, and in this case it is believed that the transfer of energy is direct from the æther to the translational degrees of freedom owing to the pressure of radiation. (See Jeans's 'Dynamical Theory of Gases,' p. 212.)

‡ Proc. Roy. Soc. A. vol. lxxxiv. p. 155.

§ Phil. Trans. A. vol. ccxi. p. 394.

reflected back into the gaseous mixture from the polished walls goes primarily to increase the energy in the vibratory degrees of freedom of the molecules, and that this excess is then partitioned off into the translational and rotational degrees during molecular collisions.

The writer desires to tender his thanks to Prof. Hopkinson, to whom he is greatly indebted for so much kindly advice and valuable criticism upon the main suggestions made in this paper.

XXXI. *The Disintegration of Metals at High Temperatures. Condensation Nuclei from Hot Wires.* By JOSEPH H. T. ROBERTS, M.Sc., Oliver Lodge Prizeman; late Isaac Roberts Scholar; Oliver Lodge Research Fellow in Physics in the University of Liverpool*.

[Plate II.]

Introductory.

IN a letter to 'Nature,' August 29th †, the writer gave a brief account of experiments upon the disintegration of metals, more particularly the platinum metals, and put forward the theory, with a short account of evidence to support it, that the disintegration of the platinum metals was due to direct oxidation. The following paper contains an account of the continuation of those experiments, and shows how the results provide further evidence in support of the same view. Throughout this paper the word disintegration simply means loss of weight; it is not intended to convey any theory as to the manner of the loss.

The disintegration of platinum and iridium is a phenomenon which cannot have escaped the notice of users of platinum pyrometers, and platinum and iridium furnaces. Many direct experiments have been performed by different investigators upon the loss of weight of wires of the platinum metals in different gases; as a result of these experiments, the great influence of oxygen upon the rate of disintegration has long been recognized, but in view of the very general opinion of scientists (in some cases clearly expressed ‡) that platinum does not, under any circumstances, combine directly with oxygen, there has been a diffidence in suggesting that the influence of the oxygen is other than

* Communicated by the Author.

† This letter was also reproduced and discussed by 'Engineering,' October 25, 1912, p. 577.

‡ Deville and Debray, *Comptes Rendus*, 1878, vol. lxxxvii. p. 441.

catalytic. There are in addition, moreover, certain experimental facts which at first sight appear to militate against a theory that the disintegration is due to direct oxidation:—

1. No matter how much a platinum wire is heated it remains clean and bright.
2. Under certain conditions (along the edge of the platinum strip in a resistance furnace) platinum crystals may be formed; this would seem to point to volatilization of the metal.
3. Under some circumstances the rate of disintegration is more rapid in the early heatings than in the later ones. Since the platinum metals absorb hydrogen readily, this might seem to be due entirely to the loss of weight of hydrogen; or again, since platinum in a finely divided state is black, the black deposits on the walls of a (comparatively cool) vessel containing a glowing platinum wire might be thought to be due to the spontaneous emission of minute metallic particles from the wire, or to such particles being detached by the escaping gas.
4. Since the platinum metals absorb other gases, such as oxygen, to a certain extent, hydrogen and oxygen might form explosive mixtures in minute cells near the surface of the metal, and on heating the metal the explosions might cause particles of metal to be ejected. This is the view of two French scientists*. I do not think, however, that this is likely to be the true explanation of the phenomenon.

The disintegration of the platinum metals has been investigated gravimetrically by Berliner †, Elster and Geitel ‡, Nahrwold §, Stewart ||, Holborn and Austin ¶, and Sir W. Crookes **, who have shown that:—

1. The amount of disintegration in a given time at a given temperature diminishes after prolonged heating.
2. If, however, wires of pure metals are used, there is no diminution in the rate of disintegration (Holborn and Austin, and Crookes).
3. The disintegration is practically zero in the absence of oxygen. In the case of palladium, however, the disintegration increases with diminution of pressure of surrounding gas.

* Reboul and Bollemont, *Journal de Physique*, July 1912.

† Berliner, ‡ Elster and Geitel, § Nahrwold, *Wied. Ann.* 1887, 1888.

|| Stewart, *Phil. Mag.* 1889.

¶ Holborn and Austin, *Phil. Mag.* 1904.

** Crookes, *Proc. Roy. Soc.*, May 1912.

The more rapid disintegration in the early stages is due to the small quantities of iridium which are usually present in commercial platinum. Iridium disintegrates much more rapidly than platinum.

Expansion Method of Detecting Disintegration.

The disintegrated particles serve as centres for the condensation of water vapour, as was found by Aitken*. The emission of particles is certainly complicated with the emission of positive and negative ions. That the electric charges are not carried entirely by the particles is now well known†. It has been suggested by Child‡ that so far from carrying the charges the particles load them up, and so hinder their motion. Though this effect may exist, it cannot be to any important degree, for I have found that the passing of hot-wire nuclei through a strong electric field on their way to the expansion chamber is entirely without detectable effect.

As the super-saturation of water-vapour is an extremely delicate test for the presence of particles, I have used this method to investigate the minimum temperature at which disintegration begins. As a proof of its superiority over weighing methods, it may be mentioned that Sir W. Crookes was unable to detect the slightest loss of weight in a platinum crucible kept for 20 hours at 900°C .; on repeating the experiment with a platinum wire, I was unable to detect any alteration of weight after 13 hours at 650°C . On inserting the wire in the nuclei-chamber, and heating by means of the same current for *two seconds*, a dense cloud was obtained at expansion of 1.15, showing that the wire was disintegrating. This result is confirmed by tests under various circumstances.

Condensation Nuclei from Hot Wires.

Apparatus.—The general form of the apparatus is shown in fig. 1. The experimental wire W was not placed in the expansion chamber G, but in a separate nuclei-chamber C, so that no water-drops could fall on it; experiments could be performed with the wire in different gases and in a vacuum; the wire was supported in two platinum electrodes, P P, 2 mm. diameter and 10 cm. long. The temperature of the hottest part of the wire was determined by means of a platinum-platinum-rhodium thermocouple, the wires being

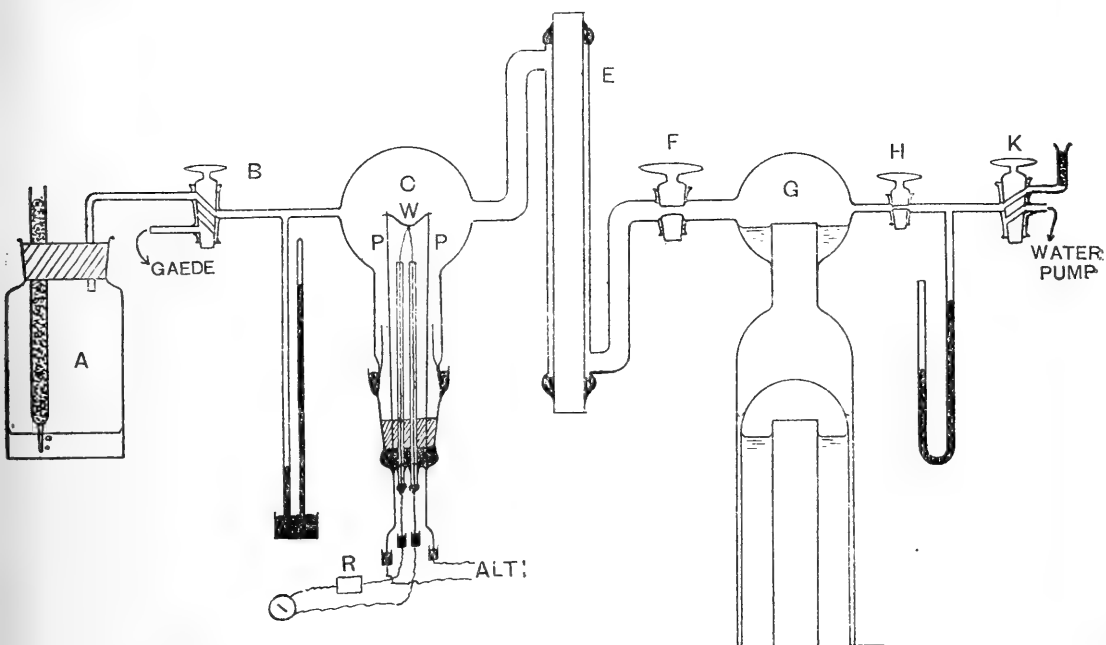
* Aitken, Trans. R. S. E. 1883.

† J. J. Thomson, 'Conduction through Gases,' 1903, p. 184.

‡ Child, Phys. Rev. 1902.

0.0013 inch diam. The two thermocouple wires do not lie across the wire W exactly at right angles to its axis, and as the drop of potential in the wire W is considerable there is an E.M.F. introduced between the thermocouple wires on this account. Consequently direct current was not used; the wire was heated by the current developed from an alternator and transformer set.

Fig. 1.



Immediately after a set of observations, an alternative thermocouple of the same wires, and on a circuit of the same total resistance, was calibrated at the temperatures of boiling water, oil at different temperatures, boiling mercury, melting Na_2SO_4 and K_2SO_4 and melting platinum. In order to prevent slight variations of the temperature of the wire W, the resistances in series with it were immersed in oil; this was found to work very satisfactorily; the temperature could be adjusted with considerable accuracy and remained constant.

On their way to the expansion chamber, the nuclei passed through the annular space, 2 mm. wide, between two brass tubes E, insulated from one another, the outer one earthed and the inner one at -230 volts. The nuclei were tested with the field on and off, and with the tubes E present and absent; it was never found, however, that the tubes required to be removed, as they offered no mechanical difficulty to the passage of the nuclei.

The expansion apparatus was of the ordinary Wilson type *. It was, however, fired by means of a trigger which was worked electromagnetically, so that all expansions could be relied upon as being of the same degree of suddenness.

The tap B enabled the apparatus to be put into communication with a Gaede rotatory mercury pump, or with a source of nuclei-free air. The simple device A is worth bringing to the notice of persons using expansion apparatus. It consists of a bottle of 2 litres capacity, very carefully sealed round the stopper, and having a tube 2 cm. diameter, fairly loosely packed with cotton-wool soaked with glycerine, passing through and dipping into glycerine at the bottom. As will be seen later, in the description of the nuclei obtained in a vacuum, it was necessary, after the nuclei-chamber C was evacuated, to have it filled instantly with nuclei-free air; this was impossible with the ordinary cotton-wool plug. After the reservoir A has been in use a few days, the air drawn from it can be subjected to an expansion of 1.20 without a single drop being seen; the writer has never found this to be possible with a cotton-wool plug, except at great waste of time.

The method of making a test of the nuclei was as follows:—The tap F being closed, the expansion chamber G was pumped down to a pressure much lower than that required for the pressure drop of the expansion; H was then closed, and the pressure in C having been adjusted, the wire was heated. When the heating current was cut off, C was put into communication with A, B was closed, and F was opened, with the result that a puff of gas went from C to G.

Experiments.—When the experiments upon the nuclei from hot wires were first begun, it was found impossible to obtain consistent results. The temperature required to give nuclei of a definite size, for example, or the minimum temperature at which the emission of nuclei could be detected, was extremely variable, and the behaviour of the wire after treatment in various gases, for various intervals of time, and at various temperatures, seemed to be entirely capricious. After a considerable amount of preliminary work, it was decided to keep the wire in air, and to try the variation of the effects with time, no variation being made in the conditions, other than that of heating up the wire to make the tests.

In the earlier stages of the work, when the conditions under which the wire was placed were varied somewhat at

* C. T. R. Wilson, *Phil. Trans. A.* 1897; *A.* 1899.

random, the temperature required to produce nuclei of a definite size, say, was found to depend very much upon the recent treatment of the wire. When the conditions were varied on more definite lines, as, for example, when the wire was kept in air with no variation other than was incidental to testing, it was found that the temperature required to produce nuclei of a definite size depended upon the length of time since the commencement of the experiments. Thus there are two well-marked conditions governing the production of nuclei :—

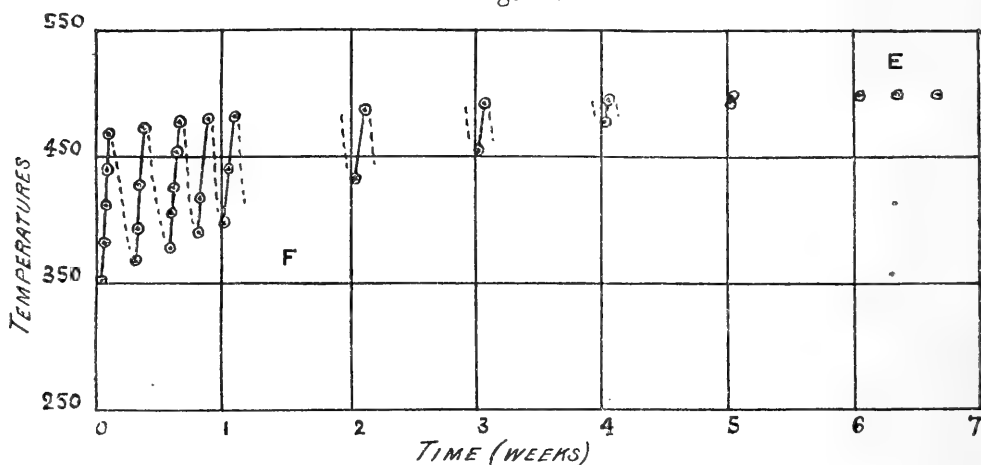
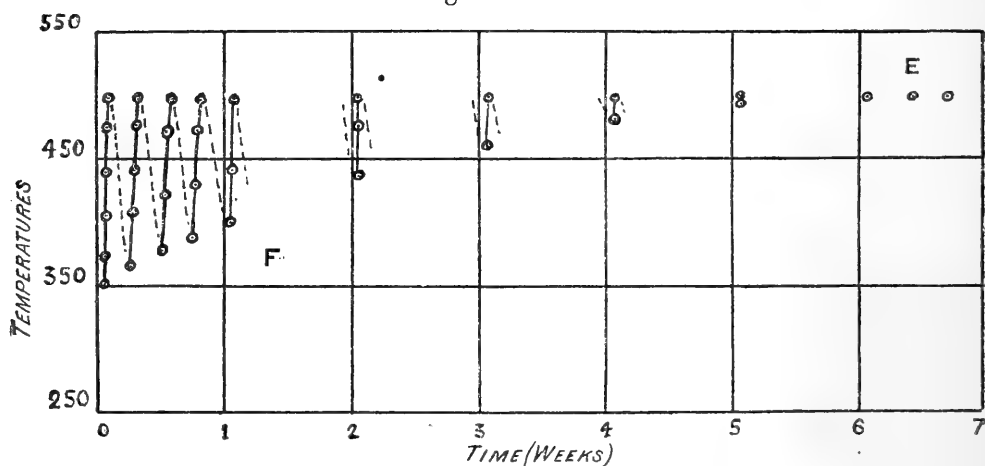
1. The recent history of the wire previous to the commencement of the experiments.
2. The length of time since the commencement of the experiments.

If the wire had been standing in air, and had not been heated for some hours or days, a comparatively low temperature was all that was required to produce nuclei of a definite size. If, however, the wire had just been heated, then a second heating to the same temperature would produce practically nothing, for this definite expansion; a little higher temperature would again produce nuclei, a second heating at this new temperature would give practically nothing, but a little higher temperature would again give nuclei, and so on. Eventually a temperature would be reached at which nuclei could be produced time after time.

For simplicity it may be stated at once that there are two sets of nuclei: the first set, which are got rid of after continuous experimenting, depend upon the presence of hydrogen and other gases in the wire; the second set depend upon the presence of oxygen round the wire: below a certain temperature the second set are never obtained; above this temperature they are always obtained in the presence, but never in the absence, of oxygen.

If the wire were left until the following day similar results were again obtained, beginning, however, at a somewhat higher temperature than the previous initial temperature, and ending at a slightly higher temperature than the previous final temperature. This effect was very marked in the earlier stages of the work, and decreased gradually until, after about six weeks' experimenting, it became inappreciable. At the same time that this variability dies away, the upper temperature, that is, the minimum temperature, for a given occasion, at which nuclei can be produced repeatedly, attains a limit from which it never afterwards departs, provided that hydrogen is carefully

excluded from the vicinity of the wire ; the same precaution prevents the recurrence of the variations described. The curves shown in fig. 2 give an idea of the nature of these variations. Fig. 2*a* is for commercial platinum ; fig. 2*b*

Fig. 2*a*.Fig. 2*b*.

for pure platinum. Various other metals were tried, including palladium, rhodium, iridium, and ruthenium. All these metals were found to give nuclei in air and oxygen, but not (eventually) in a vacuum.

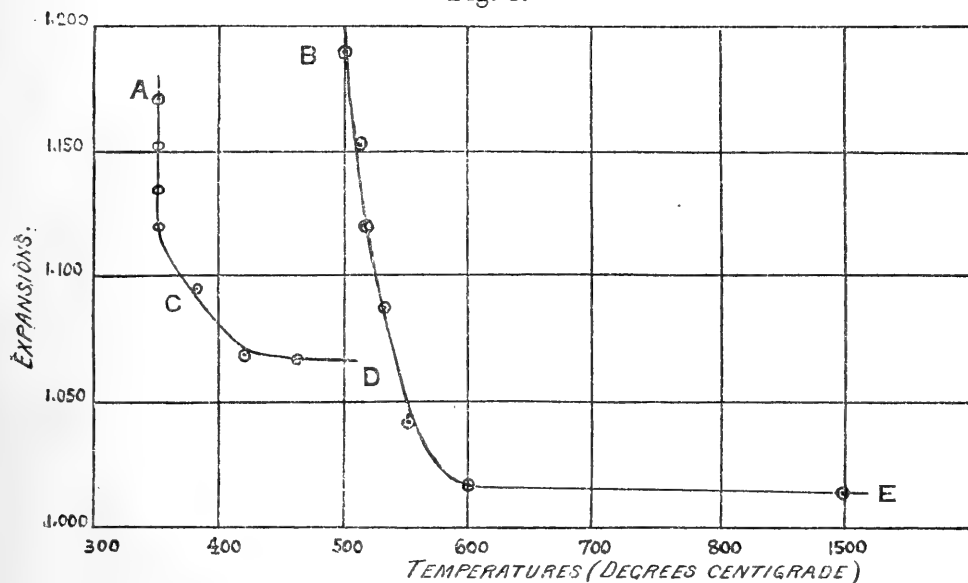
Relation between Temperature of Wire and Size of Nuclei.*

Experiments were made in order to see how the size of the nuclei given out depended upon the temperature, for a

* It has been shown by G. Owen (Phil. Mag. 1903) that nuclei are emitted from platinum wires at very low temperatures ; that the size of the nuclei increases with rise of temperature ; that nuclei are not produced in hydrogen below $1000^{\circ}\text{C}.$; and that the nuclei are uncharged.

given pressure, in air. Numerous sets of observations were taken; it is extremely difficult to get the effects definitely marked, but the curve in fig. 3 shows the chief features of the results which were always obtained. Fig. 3 represents the relation between the temperatures and the minimum expansions required to catch the nuclei given out at those temperatures, for a pure platinum wire containing hydrogen, that is, for a wire whose behaviour is represented by fig. 2 *b*.

Fig. 3.



It is noticed from the curve that :—

1. No nuclei are obtained at a temperature below 350° C. in air at atmospheric pressure.
2. The nuclei caught at this temperature are of a maximum size represented by an expansion of 1.119 and a minimum represented by an expansion of 1.152, and higher expansions beyond 1.152 do not produce any more drops.
3. As the temperature is raised, nuclei of the same size, and of larger sizes, are produced.
4. At a temperature of about 500° C., in addition to the nuclei caught with expansions between 1.02 and 1.152, other nuclei begin to be produced, which are first caught at 1.188, but when the wire has reached a temperature of about 600° C. they are caught by an expansion of 1.016.
5. No matter how hot the wire is made, no nuclei are caught by an expansion of 1.014.

After some little experience, the difference between the two kinds of nuclei is very easily observable: the nuclei produced from 350°C . onwards are very easily got rid of; they diminish in size very rapidly after their production, and will entirely disappear in less than five minutes; they can be preserved to some extent, however, by causing condensation of water-vapour to take place upon them. The nuclei which begin to be produced at about 500°C ., however, are very persistent, and they do not alter in size.

The nuclei represented by the portion ACD, fig. 3, are the ones which are got rid of after many weeks of experimenting; thus a wire whose condition was represented by the part E of curve, fig. 2, would give the curve BDE, fig. 3, the portion ACD being absent.

If a wire which has been got into the condition represented by BDE, fig. 3, and by the part E, fig. 2, is heated and cooled in hydrogen, the wire goes back to its original condition, represented by the whole of fig. 3 and by F, fig. 2, and on repeated heatings all the variations there represented are gone through as before. No treatment with any other gas, or in any other way, has the effect of bringing back the variations represented by fig. 2.

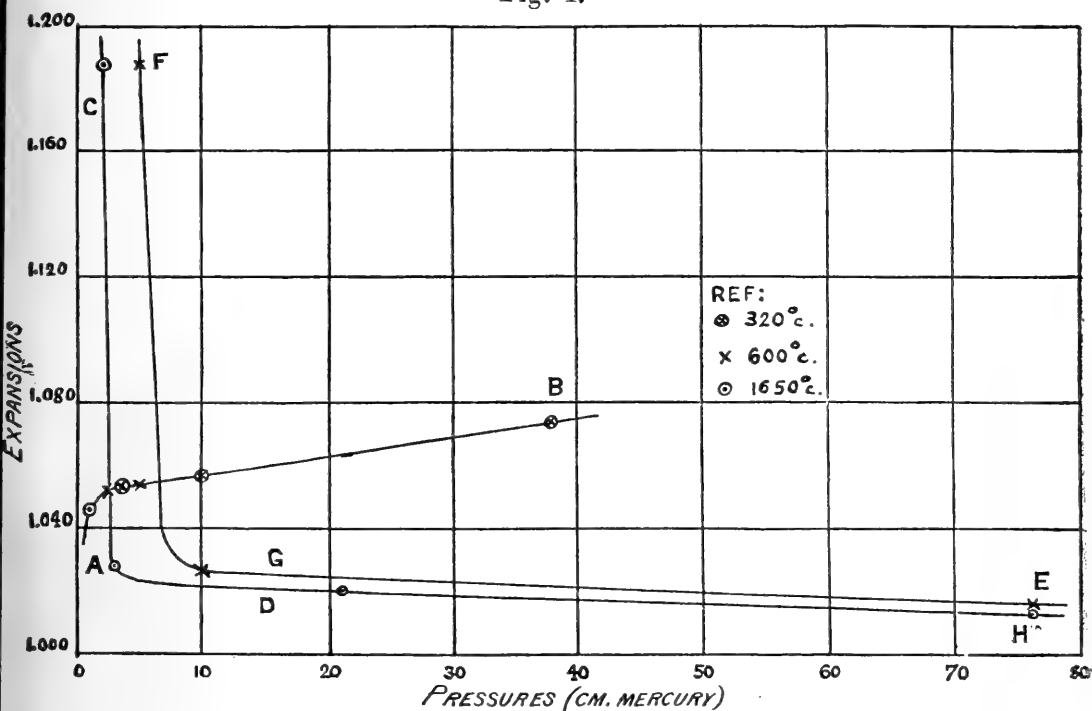
Relation between Pressure of Air and Size of Nuclei.

Fig. 4 shows the results of experiments upon the relation between the pressure of the air round the wire, and the size of the nuclei produced, for different temperatures. The curve for a temperature of 320°C . is AB, the curve for 600°C . is FGE together with two points practically on AB, while the curve for 1650°C . is CDH, together with one point on AB. By comparing fig. 4 with fig. 3 it will be seen that the first set of nuclei are obtained at 320°C . and expansion of 1.041 as against 340°C . and expansion 1.119 at atmospheric pressure, and that the expansion required increases, that is, the size of the nuclei decreases, as the pressure of the surrounding gas increases. At 600°C . none of the second set of nuclei are produced when the air is at a pressure below 5 cm.; two points corresponding to the first set of nuclei lie on AB, showing that the temperature is of less importance than the pressure in determining the size of these first nuclei. At 5 cm. pressure the second set begin at expansion 1.188 and rapidly increase in size with increase of pressure.

At 1650°C . there is one point on AB at a pressure of 1 cm.: the second set of nuclei are produced at a pressure of 1.5 cm., and require an expansion of 1.188 to catch them;

they rapidly increase in size with increase of pressure, until at 2.5 cm. pressure they are caught with expansions of 1.016.

Fig. 4.



Before discussing the nature of these nuclei, let us consider the effect of heating the wire in the highest vacuum, as it was in this way that the existence of two different sets of nuclei was first detected. We have seen that the first set of nuclei are got rid of after prolonged experimenting, while the second set are never got rid of in air. The experiments upon the heating of a wire in a vacuum were conducted as follows:—The chamber C was pumped out to a high vacuum by means of a Gaede pump; B was closed and the wire was heated. The heating current was then shut off, and the moment the wire lost its colour B was reversed, with the result that C was instantly filled with nuclei-free air at atmospheric pressure.

For simplicity we will anticipate the results by assuming that the platinum wire has been well soaked in hydrogen. On heating in a vacuum, large nuclei caught by expansions of 1.027 are produced at very low temperatures; in some cases nuclei were detected after the wire had been raised to a temperature between 150° C. and 200° C. After one or two heatings at any temperature, no more nuclei are obtained for that temperature, but nuclei will be given for a higher

temperature and so on, and eventually no more will be given, no matter how high the temperature may be raised. If the wire be now left for a few hours in the vacuum, nuclei will be again obtained on heating to a temperature very little higher than the previous initial temperature, and after successive heatings the wire will again cease to give nuclei at any temperature. In other words, the behaviour of these nuclei is exactly the same as the behaviour of what we have called the first set of nuclei obtained in air. They are ultimately got rid of entirely, the only difference being that by the use of the vacuum the emission of these nuclei can be prevented after about three days' experimenting, whereas in gases (excluding hydrogen) at atmospheric pressure it takes several weeks to attain this result.

Suppose a platinum wire has been heated repeatedly in a vacuum until the first set of nuclei have been entirely got rid of, then the wire can be left, heated or cold, in a vacuum for an indefinite period, or it can be left for an indefinite period, heated or cold, in air, nitrogen, or oxygen at any pressure, and on again testing in a vacuum no nuclei will be obtained at any temperature. Thus we see that in the production of the first set of nuclei the action of the hydrogen is *unique*.

If a wire which has ceased to give nuclei in a vacuum is now tested in air or oxygen, it is found that the first set of nuclei are entirely absent, that is, the behaviour indicated by fig. 2 is not observed; the second set of nuclei begin at the usual temperature, about 500°C. , and increase in size as the temperature is raised.

We see, then, that the wire is capable of emitting two kinds of nuclei, in addition to the positive and negative ions. One set of nuclei depends upon the presence of hydrogen in the wire, and the other upon the presence of oxygen round the wire. In working with the expansion apparatus it is quite easy to tell which nuclei are being dealt with; the first set of nuclei rapidly diminish in size, and disappear in two or three minutes after their production, but last longer if condensation of water-vapour has taken place upon them than otherwise; in general, they are not so great in number, at any rate by the time the expansion takes place, as are the oxygen nuclei; the latter nuclei are very great in number, except at the temperature at which they just begin to be produced; they are of a fairly definite maximum size for each temperature, and of smaller sizes in addition, as can be shown by following up with higher expansions; and they are extremely persistent.

Nuclei in Pure Oxygen.

Tests were made upon hydrogen-free wires, and it was found that the minimum temperature at which the second nuclei began to be produced was not altered, but that the nuclei produced at that temperature were more numerous in the oxygen than in the air.

Nuclei in Pure Electrolytic Hydrogen.

At a bright yellow heat a small shower was obtained in hydrogen, doubtless formed upon nuclei of the first set produced by the absorbed hydrogen. Before the introduction of the hydrogen, the wire had been hydrogen-free, according to the vacuum test.

Nuclei in Nitrogen.

If the nuclei depend upon hydrogen and oxygen respectively, no nuclei should be obtained when a hydrogen-free wire is heated in pure nitrogen. In view of the delicacy of the expansion method of detecting particles, it is essential that the nitrogen be absolutely free from hydrogen and oxygen. For the tests in nitrogen a special form of nuclei-chamber was employed, containing two platinum wires, which were hydrogen-free according to the vacuum test, and could be heated independently. Atmospheric air was introduced into the apparatus through KOH, P_2O_5 , and cotton-wool and glycerine tubes; by means of mercury reservoirs it was then passed to and fro through a tube of palladium asbestos, prepared according to the method of Winkler *, and the oxygen was finally combusted by bringing dry phosphorus, floating on the surface of the mercury, sufficiently near to one of the platinum wires, which was heated, to cause it to ignite. After the combustion was complete, the second wire was heated for a few minutes, and the whole apparatus was left until all nuclei must have disappeared; the second wire was then heated to a white heat, and the expansion test made, expansion 1.188; a few drops only were seen. Considering the delicacy of the expansion method, this may be regarded as a zero effect; it is probable that the wire was not absolutely hydrogen-free, and that in a vacuum the very few nuclei were produced at the beginning of the heating and were lost before the end of the heating; whereas when surrounded by a gas, as in the nitrogen tests, they would be much more likely to be caught.

* Technical Gas Analysis.

Effect of Light on Nuclei.

The nuclei obtained in a vacuum from various platinum wires containing hydrogen were allowed to remain, in air at atmospheric pressure, in the nuclei-chamber, for various intervals of time before the expansion was made. Experiments were tried alternately with the chamber strongly illuminated by means of a Nernst lamp and other sources of light, and with the chamber in darkness. It was found that there was no difference in the behaviour of these nuclei in the dark and in the light.

Effect of Electric Field on Nuclei.

The nuclei obtained under various conditions were tested for electrification by means of the tubes E, fig. 1. No difference was ever detected between the behaviour with the field on and that with the field off. The nuclei, however (particularly the second set, that is, the oxygen nuclei), are usually so numerous that if only a few of them were removed there would not be any appreciable alteration in the nature of the cloud formed upon the remainder. Thus, if any nuclei are attached to ions, the number of such nuclei must be a very small percentage of the total number of nuclei.

The behaviour of iridium, rhodium, and ruthenium was in general similar to that of platinum—that is, nuclei were produced in air or oxygen, but not in a vacuum, after all the hydrogen had been got rid of. There is one important point of difference: platinum gives no nuclei in a vacuum after being heated in oxygen; iridium and ruthenium, however, will give nuclei in a vacuum after being heated in oxygen, these nuclei being due to the removal of the oxide, which, in the case of iridium, forms a film upon the cooler ends of the wire. After a few heatings, with the Gaede pump working, these nuclei cease to be emitted.

Nature of the Nuclei.

1. We see that the properties of the first set of nuclei are as follows:—

- (a) They are emitted by the wire at comparatively low temperatures.
- (b) The minimum temperature required to produce them is lower the less the pressure of the surrounding gas.
- (c) They alter in size and disappear very soon after their liberation, but last longer if water-vapour has been caused to condense upon them.

- (d) The ability of the wire to emit them is temporarily lost after an emission, but is slowly regained after the lapse of time.
- (e) The wire immediately regains the ability to produce them on hydrogen being brought into contact with it; air, oxygen, and nitrogen do not produce this effect.
- (f) If the wire has been kept at a white heat in a vacuum for a very long time, the admission and withdrawal of pure hydrogen does not revive the power to emit nuclei in a vacuum.

These nuclei are obviously not of the nature of solid particles ; they are particles which are able to evaporate or break up. They may be :

- (a) Minute water-drops.
- (b) Traces of compound gases produced by the combination with hydrogen of other occluded gases *.

These nuclei are not necessarily produced by heat ; they may be produced by the catalytic action of the metal, which is well known, and may be merely liberated by the heat. It is easy to see why they should last longer if condensation of water-vapour takes place upon them, as extremely small drops evaporate rapidly and the condensation, by increasing the size of the drops, would diminish their rate of evaporation.

Recent investigations have shown that the occluded gases in a metal wire are partly absorbed in the metal, and partly adsorbed, that is, condensed or entangled upon the surface ; and I have to thank Prof. Donnan for the following suggestion in explanation of the curves in fig. 2 :—On first heating the wire to a fairly low temperature, some of the adsorbed gas quickly goes off, but on again heating immediately afterwards to the same temperature, practically no more is liberated ; on heating to a higher temperature more adsorbed gas goes off, but not again on a second heating at that temperature, and so on. The amount of the adsorbed gas which can be got rid of by this process has now been removed. Now leave the wire for a day, and some of the absorbed gas slowly diffuses out and becomes adsorbed, and on a second set of heatings, results of the same nature as before are obtained ; eventually the quantity of gas remaining in the wire is too small to give nuclei. Thus it is the adsorbed gas which goes off, and the absorbed gas slowly diffuses out in the longer intervals of rest. On this view it

* See 'Electrical Properties of Flames,' H. A. Wilson, p. 26.

seems likely that in a vacuum the process of diffusion will be hastened, and that the minimum temperature for nuclei will be lower than in gas at atmospheric pressure ; and these, as we have seen, are among the observed experimental facts.

There is still one point which requires explanation. Why is it that when a wire has ceased to give nuclei in a vacuum, the single process of admitting and removing hydrogen, provided the wire has not been heated in the vacuum too long, at once revives the power of the wire to emit nuclei, while the admission and removal of oxygen, air, or nitrogen does not have this effect ? We may imagine the mechanism of occlusion and liberation to be pretty much the same in the cases of the other occluded gases as in that of hydrogen, except that in the case of hydrogen the processes, both of occlusion and liberation, are more rapid. Thus it is probable that when the hydrogen has been almost entirely removed, and consequently traces of compounds with hydrogen cease to be formed, there are nevertheless, remaining in the metal, quantities of other occluded gases liberated with more difficulty. On bringing hydrogen into contact with the wire, the ability to form hydrogen compounds (possibly H_2O) would be at once restored *.

This explains why the action of pure hydrogen fails if the wire has been kept white hot in a vacuum for a long time, as the other occluded gases would then be removed. The effect of hydrogen in reviving the nucleating power in air is easily understood, as, in the experiments in air, the wire, on account of the frequent heatings, would have every opportunity of absorbing oxygen, &c. It has been mentioned that the nuclei may be *produced* by the action of the metal and merely *liberated* by the heat.

If a wire has been heated in a vacuum so long that the admission of hydrogen fails to revive the power of emitting the first set of nuclei, the subsequent admission of *air* will restore the power.

2. The second set of nuclei are in all probability particles of an unstable oxide of the metal. The formation of this oxide will be considered later. The formation of an oxide agrees with the facts that :—

- (a) The second set of nuclei are not formed in nitrogen, hydrogen, or a vacuum, but only in the presence of oxygen.
- (b) The rate of loss of weight of the metal is zero in nitrogen, hydrogen, or a vacuum. For platinum

* H. A. Wilson, *loc. cit.*

and rhodium the rate of disintegration at a given temperature is roughly proportional to the oxygen pressure ; for iridium, which is very oxidizable, the rate of disintegration increases much more rapidly with the oxygen pressure. The disintegration of palladium is of a different nature and will be considered later.

- (c) At low pressures of oxygen the nuclei are very small.
- (d) The nuclei begin to be formed (that is, the disintegration begins) at a fairly definite temperature.
- (e) The nuclei are very persistent and do not alter in size ; they are unaffected by light or by an electric field.

Disintegration of Metals.

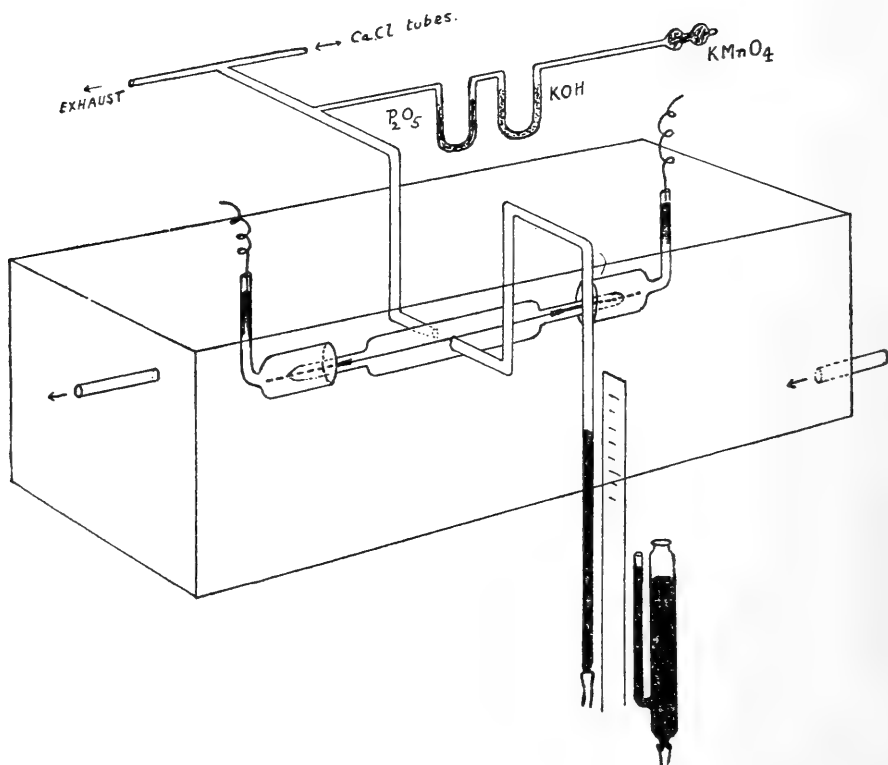
If the hot platinum combined with the oxygen, it would be expected that there would be, after some hours, a detectable diminution in the pressure of the enclosed oxygen in a constant volume gas-chamber, containing a platinum wire maintained at a bright heat ; and that some atomic relation would exist between the loss of weight of the platinum wire and the loss of weight of the oxygen in the apparatus. It will be as well to mention at once, however, that the oxide is unstable at temperatures lower than that at which it is formed *, dissociation will be taking place, and some of the oxygen will be set free. The oxygen which enters into combination, and is then liberated by the dissociation, acts merely as the temporary carrier of the metal. If the volatile oxide could be instantly drawn away and cooled very rapidly ("frozen"), practically no dissociation would take place, and an atomic relation would be obtained. The further the actual conditions of cooling fall short of the ideal conditions of cooling, however, the further the weight of oxygen lost will fall short of that required for an atomic relation: until, in the limiting case, when the temperature gradient is very small, all the oxide will be dissociated ; in this case we may consider that the oxygen has a purely catalytic effect upon the volatilization of the metal. The latter conditions are approximated to in the case of the platinum strip in a resistance furnace, where the temperature gradient in the gas round the strip is very small. In this case, as is well known, crystals of the metal are deposited in the immediate vicinity of the strip, and this fact has caused

* As the oxide is only obtained at high temperatures, it seems probable that its formation is accompanied by an absorption of heat: a slight lowering of temperature would therefore shift the equilibrium in the direction, oxide \longrightarrow metal + oxygen.

the phenomenon of the disintegration of the platinum strip to be mistaken for one of simple volatilization *.

The constant-volume gas-chamber used for the following experiments is shown in fig. 5. It consists simply of the

Fig. 5.



cylindrical glass bulb containing the glowing wire, with connecting tubes for the withdrawal and admission of gas, the shape of the tubes being such that the bulb can be immersed in running water in a trough. The pressure at constant volume is read in the usual way by means of the sliding mercury reservoir.

The behaviour which would be expected from the above considerations as to the nature of the oxide was exactly what was observed. Before the water-cooling arrangement was employed, the small glass vessel used to get exceedingly hot and the weight of oxygen lost was always too small for a simple atomic relation. Many precautions were taken to try to improve the relation between the weights of oxygen and platinum, but it will be interesting to mention the precautions which most readily suggest themselves, as the most important precaution (that of water-cooling the small glass vessel) was stumbled upon in endeavouring to eliminate an error which seemed negligible. Conditions (other than

* Crookes, *loc. cit.*

dissociation) which would prevent a correct result from being obtained are :—

1. Change of barometer and temperature.
2. Presence of unsaturated water-vapour in the apparatus, pressure unknown.
3. Absorption or evolution of gas by the wire.
4. Oxidation of parts of the leads not made of platinum.
5. Large volume of apparatus rendering diminution of pressure inappreciable.
6. Evolution or absorption of gas by the glass.
7. Absorption and adsorption of gas by deposit, whether deposit be oxide, metal, or mixture*.

(1) was corrected with great care, (2) overcome by drying, (3) by heating the wire for 30 to 40 hours in the same gas before the initial weighing, (4) by making the leads entirely of thick platinum rods, and (5) by using an apparatus of small volume. Still the amount of oxygen taken up was always too small even for the formation of the oxide Pt_2O , (6) seemed negligible, but it was decided to overcome it by having the vessel water-cooled as shown in fig. 5; on this being done the weight of oxygen lost was increased. With air in the apparatus, the weight of oxygen lost sometimes approximated very closely to that required for Pt_2O : it was never equal to it, and it never exceeded it. The following figures give the results of two very careful experiments made in air on platinum :—

	Beginning of Expt.	End of Expt. (42 hrs.).
Barometer	754.4 mm.	754.8 mm.
Temperature	18°·2 C.	18°·2 C.
Position of mercury in apparatus ...	900.0 mm.	900.0 mm.
Position of mercury in reservoir ...	640.0 mm.	588.0 mm.
Weight of wire	175.80 mgms.	164.9 mgms.
Volume of apparatus	20.40 cc.
Loss of weight of oxygen	0.3884 mgm.
Weight of platinum corresponding to Pt_2O	9.477 mgms.
Actual loss of weight of platinum ...	10.90 mgms.
	Beginning of Expt.	End of Expt.
Barometer	764.7 mm.	764.3 mm.
Temperature	17°·1 C.	17°·8 C.
Position of mercury in apparatus ...	855.0 mm.	855.0 mm.
Position of mercury in reservoir ...	639.2 mm.	621.6 mm.
Weight of wire	158.60 mgms.	151.20 mgms.
Volume of apparatus	36.53 cc.
Loss of weight of oxygen	0.261 mgm.
Weight of Pt corresponding to Pt_2O .	6.638 mgms.
Actual loss of weight of platinum ...	7.40 mgms.

* The conditions are further complicated by the formation of solid solutions of the gas in the oxides, and of the oxides in one another. See Wohler, *Zeit. für Elektrochemie*, 1909.

Platinum in Pure Oxygen.

	Beginning of Expt.	End of Expt.
Barometer	754.7 mm.	761.5 mm.
Temperature	14° 8 C.	15° 1 cc.
Position of mercury in apparatus ...	740.0 mm.	740.0 mm.
Position of mercury in reservoir.....	572.0 mm.	537.3 mm.
Weight of wire	209.1 mgms.	199.1 mgms.
Volume of apparatus	27.41 cc.
Loss of weight of oxygen	1.39 mgms.
Weight of Pt corresponding to PtO ₂ ..	8.478 mgms.
Actual loss of weight of platinum ...	10.00 mgms.

It is impossible, after the most careful experiments, to obtain an exact simple atomic relation with platinum: the results obtained in air, and the fact that the weight of oxygen taken up frequently approximated to, but never exceeded, that required for the lower oxide Pt₂O, might seem to indicate the formation of this oxide in air and its partial dissociation. Since in an atmosphere of oxygen the ratio of platinum to oxygen approximates to that required for PtO₂, it is possible that the oxide formed is in all cases PtO₂, and that in air so much dissociation takes place that the ratio approximates to that required for Pt₂O. Since in air the partial pressure of the oxygen is less, we should expect a greater amount of decomposition of the oxide, as is easily seen by applying the law of mass action to the equation



whence we obtain

$$P_{\text{PtO}_2} = K(P_{\text{Pt}} \times P_{\text{O}_2}).$$

The dissociation will be compensated for to an unknown, but probably small, extent by the adsorption of oxygen by the dissociated platinum particles*. As mentioned above, this platinum will be the result of the dissociation of the oxide.

Iridium in Pure Oxygen.

The effect with iridium is very striking; the deposit upon the glass is perceptible after two or three minutes. The following experiment took about 30 minutes:—

	Beginning of Expt.	End of Expt.
Barometer	761.2 mm.	762.0 mm.
Temperature	13° 5 C.	13° 3 C.
Position of mercury in apparatus ...	740.0 mm.	740.0 mm.
Position of mercury in reservoir.....	549.9 mm.	454.5 mm.
Weight of wire	431.00 mgms.	402.15 mgms.
Volume of apparatus	28.99 cc.
Loss of weight of oxygen	4.89 mgms.
Weight of iridium corresponding to IrO ₂	29.51 mgms.
Actual loss of weight of iridium.....	28.85 mgms.

* It is worth noticing that if the deposit formed on the walls of the vessel consisted of platinum particles, the absorption of the oxygen corresponding to PtO₂ would represent the enormous absorption by the platinum of 2470 volumes.

Thus it seems as though too little iridium has been lost ; this is due to the deposition of a slight film of oxide on the cool ends of the wire, which diminishes the observed loss of weight.

*Black Deposit upon the Walls of Vessel containing
Glowing Wire.*

The oxide formed deposits itself upon the walls of the glass vessel as a soft black or greyish-black powder. The manner in which the deposit is disposed about the vessel gives every indication that it is the result of the condensation of a vapour ; it gives no support to the view that particles are ejected from the wire. For the deposit is not distributed equally round the vessel nor is it mostly upon the bottom or top. It is frequently found that the vapour has to be cooled considerably before it deposits. Thus although the thin water-cooled glass must be at practically the same temperature at all parts, the vapour rising upward with the convection currents is not sufficiently cooled to deposit on first striking the upper surface, but on flowing over the surface for a short distance it begins to form the deposit at a sharply defined line ; this shows that it has to be cooled to a definite temperature before condensation takes place ; the greatest amount of deposition is usually found to take place where the cooling vapour is on its downward journey over the *sides* of the vessel*.

** Description of Plate II.*

The plate shows photographs of the small glass vessels containing the glowing wires after the deposits had been formed. Nos. 1 to 5 show the deposits due to an iridium wire, Nos. 1 and 2 being after five minutes heating of the wire, Nos. 3, 4, and 5 after half an hour. As the iridium wire remained straight when heated, and coincident with the axis of the tube, the convection currents in the heated gas would be symmetrical with respect to the cylindrical vessel. As the vessels were 1 cm. in radius and were water-cooled, the convection circulation was probably very vigorous. No. 1 shows the view from above, and it is seen that the black deposit begins at a fairly sharply defined line on the upper surface ; as the cooling vapour circulates round the tube the two streams meet together and the deposit at the bottom of the vessel shows a sharp line of demarcation vertically below the wire : this is well shown in Nos. 1, 2, and 4, which are all views from above, the deposit showing this line of demarcation being on the surface of the vessel furthest away from the reader. In Nos. 1 and 2, which are photographs of the same vessel, it is seen that the side tubes have interfered with the symmetry of flow. Nos. 3, 4, and 5 are different views of the same vessel, and it is seen that the deposit is greatest near the centre of the wire, which was the hottest part. The most important point in all the figures, however, is that the deposit is not formed on the upper surface of the vessel, with which the ascending vapour first comes into contact, but the deposit

After different experiments the apparatus was broken up and the deposit examined in the microscope. A high-power immersion microscope revealed a vast number of particles of various sizes, individually black, and looking exactly like particles of soot. By means of a scale in the eyepiece of the microscope, the particles were seen to range in size from 10μ down to about $\frac{1}{50}\mu$. There was no evidence of crystallization.

In order to remove the black deposit from a piece of glass, the glass was boiled in aqua regia, but this did not remove the black powder by any means completely. Another piece of glass from the same apparatus was heated in the Bunsen flame, when the black deposit quickly assumed the form of a metallic film. On treating this with aqua regia, the film was almost immediately dissolved. Another metallic film, obtained by heating the black powder in the same way, was examined in the microscope, and found to consist of a more or less continuous film, which, however, had drawn up here and there, leaving a large number of roughly circular holes; the film had, in fact, behaved as if it had possessed surface tension; light was able to pass through the film*.

These black deposits are also obtained, whenever oxygen is present, by heating iridium, rhodium, and palladium. The effect with iridium is very striking; an iridium wire 430 mgms. in weight lost 30 mgms. in 30 minutes. The deposit upon the glass began to be perceptible two or three minutes after putting on the heating current, and at the end of 30 minutes was thick and almost opaque; the same result

begins to be formed as the vapour is cooled on its downward journey along the sides of the vessel. This disproves at once any theory of the emission of solid particles from the hot wire, as, if this were the case, there would be a deposit on the upper surface of the glass. Nos. 6 and 7 show the deposits from a platinum wire in the form of a spiral; as the wire bent on heating it was nearer to one side of the vessel than to the other, and consequently the convection currents went up one side of the vessel and down the other; hence the vapour was cooled on its *upward* journey and deposits were in this case obtained on the top surface. In other experiments with the spiral wire, when the spiral has remained along the axis of the tube, deposits of the same pattern have been obtained, but in these cases, as in Nos. 1 to 5, the deposits were not produced upon the upper surface.

* In this connexion see the interesting papers by Stone (Phys. Rev., July 1905), and by Turner (Proc. Roy. Soc. 1908), where it is shown that thin films of other metals, such as silver and gold, on being heated to very moderate temperatures, below 500°C ., also draw up, leaving holes; the metallic parts are still opaque, but the light is transmitted through the holes. The reflecting power of the film is diminished and the electrical resistivity is greatly increased.

with platinum and rhodium takes many hours. No deposits are obtained from platinum, rhodium, and iridium if these are heated in a vacuum.

The behaviour of palladium at low pressures is different from that of the other three metals named. It has been found by Stewart * and by Holborn and Austin * that :—

1. The rate of loss of weight of platinum, rhodium, and iridium is practically zero when oxygen is absent, and when oxygen is present the rate of loss of weight diminishes with diminution of pressure of the oxygen.
2. The rate of loss of weight of palladium increases with diminution of pressure, and is practically independent of the nature, of the surrounding gas.
3. With palladium the deposit is always black when oxygen is present, but is bright and metallic in hydrogen at a pressure of 1.25 mm.

It is evident that the mechanism of the disintegration in the case of palladium is different from that in the cases of the other metals. Several explanations of this phenomenon in the case of palladium suggest themselves :—

1. Since palladium absorbs gases to a greater degree than the other platinum metals, the greater rate of loss of weight at low pressures might be due to the greater rate of escape of these gases, the loss of weight being equal to the weight of escaped gas.
2. The evolution of the gas might cause particles of the metal to be loosened and detached.
3. The bright deposits mentioned by Holborn and Austin in hydrogen at 1.25 mm. might be due to the reduction of an oxide.
4. The effects might be due to simple volatilization of the metal.

In order to decide between these possible explanations, I have repeated Holborn and Austin's experiment and found that 1 and 3 are disposed of by the fact that the greater rate of loss of weight at low pressures continues indefinitely, and the bright deposits are obtained in a maintained vacuum, where they cannot be due to the reducing action of hydrogen. 2 and 3 are disproved by the fact that no nuclei whatever are detected from palladium in a vacuum. I think that 4 is the true explanation. Incidentally it may be noticed that volatilizing palladium does not give nuclei. This agrees with Aitken's observations on camphor, and suggests that a pure solid substance does not give nuclei when

* *Loc. cit.*

volatilizing, contrary to Owen and Hughes' result with solid CO_2 *.

If the palladium volatilizes rapidly in a vacuum, it might be expected that the bright metallic deposit would prove to be crystalline. Examined under the microscope, however, it was found to be perfectly uniform; there were no holes, and yet the film was semi-transparent. A careful microscopic examination of the glowing wire, in this and in other cases, did not reveal any of the glowing particles mentioned by Reboul and Bollemont. In order to see if crystalline structure in the film was to be expected as a necessary result of sublimation, I made a test in which the deposit was known to be the result of sublimation. I fused a palladium wire in a vacuum, and the surface of the glass was instantly covered with a perfect bright palladium mirror, which under the microscope showed no signs whatever of crystallization; the microscope used in all these experiments was a high power Zeiss with vertical illuminator. Examination of the fused wire at the point of fusion showed that the metal was covered with small mounds as though it had boiled; there was no evidence of crystallization here. Probably the reason that these deposits are not crystalline is that the vapour has been in too rapid motion, and has been cooled too quickly. In platinum resistance furnaces the vapour produced by the dissociation of the volatile oxide of the platinum is entirely confined, and almost stationary; it therefore slowly condenses upon the hot clay cylinder of the furnace in the form of crystals.

On dipping pieces of the broken glass, having these deposits, into nitric acid, the palladium films were instantly dissolved, and produced the usual bronze coloration of the acid. Three samples of the palladium films were heated (1) moderately with a bunsen, (2) strongly with bunsen, (3) strongly in blow-flame. On examining these in the microscope 1 and 2 showed no special features, but 3 had a fern-like pattern depending upon crystallic action, though no individual crystals were seen †.

* Phil. Mag. 1908.

† It is impossible to exaggerate the beauty of these films as seen in the microscope. The patterns are similar to those produced by frost upon glass, and interference colours are seen by transmitted light. If the film is gently breathed upon, the patterns go through most beautiful transformations, both as to colour and arrangement, these effects being due to the thickening and distortion of the film with the heat of the breath.

Discussion of Results.

By the delicate test of the expansion apparatus it is found that platinum begins to disintegrate at so low a temperature as 500°C . (just below the dull red heat), but in such infinitesimal quantities that no loss of weight would be detected even after days of heating. The disintegration does not begin to come within range of the balance until 1900°C . or 1100°C . The fact that the second set of nuclei, even in the region of 500°C ., are so persistent, and that they do not change in size or character, together with the fact that they are produced in pure oxygen, no matter how long the heating has been continued, and are not produced in the absence of oxygen, either in nitrogen, hydrogen, or in a vacuum, shows that they are not likely to be either particles of the metal brought off by the escaping gas or traces of compounds of different gases.

The fact that the rate of loss of weight of the platinum wire is roughly proportional to the oxygen pressure points to the formation of an endothermic oxide. The experiments in the constant-volume gas-chamber in which the ratio of the loss of platinum to the loss of oxygen was determined, gave results which approximated in the case of air to $2\text{Pt}:\text{O}$ and in the case of oxygen to $\text{Pt}:2\text{O}$. It does not seem probable that this large amount of oxygen is simply adsorbed; it must be combined chemically, at any rate for the most part. During the cooling of the oxide after its formation at the hot wire, some decomposition takes place, and the amount of this decomposition will be greater the lower the oxygen pressure. If we assume that the quantity of oxygen adsorbed by the deposit is small, the composition of the oxide in the experiments in oxygen must be either PtO_2 or some higher oxide. If this oxide is also present in the deposit obtained in air, there must be a considerable amount of platinum mixed with it, this platinum being the result of dissociation of the oxide during cooling.

According to the observations of Nahrwold, Stewart, and Holborn and Austin, the rate of disintegration of the platinum metals (excluding palladium) diminishes with the pressure of the surrounding oxygen; this is in accordance with the oxidation theory. Palladium, however, as has been shown in the course of this paper, volatilizes; it oxidizes if there be any oxygen present: this agrees with the observations of Stewart, and Holborn and Austin, that the rate of disintegration of palladium is practically independent of the nature, but increases with diminution of the pressure, of surrounding gas.

If oxidation be the mechanism of the disintegration of the platinum metals, the rate of disintegration should not alter with time; that this is so with pure metals is confirmed by Sir W. Crookes' curves* and by the observations of Holborn and Austin on pure metals, and on alloys containing small percentages of iridium; the more rapid rate of disintegration, in some cases observed in the early heatings, is due to the presence of traces of more easily oxidisable impurities.

Sir W. Crookes, in his paper on "The Volatility of Metals of the Platinum Group" (*loc. cit.*), discusses the possibility of the formation of an oxide in the case of platinum, but discards the view on account of his theory that an oxide formed at a high temperature would only dissociate at a still higher temperature, not at a slightly lower temperature. Speaking of the crystals which occur in a platinum resistance furnace in the vicinity of the platinum strip, that is, upon the porcelain tube, which is at a slightly lower temperature than the strip itself, Sir W. Crookes says: "the mode of occurrence of the beautiful crystals of platinum is against the supposition that they are a product of the decomposition of an oxide, for the crystals deposit upon a part of the apparatus that is at a slightly lower temperature than the bulk of the metal, and it is inconceivable that platinum should combine with oxygen to form a volatile oxide at one definite temperature, and part with this oxygen, and come down in metallic crystals, at a little lower temperature." Later on Sir W. Crookes says: "I must therefore come to the conclusion that platinum is absolutely non-volatile at 900° C., a temperature easily obtainable in an analytical laboratory, and that the formation of crystals of the metal in the electric furnace is a true case of sublimation."

It must be pointed out, however, that if the disintegration of platinum were a simple case of volatility, it would not become zero in a vacuum; and that there are many examples recognized in physical chemistry and in accordance with the laws of thermodynamics, of the formation of compounds at high temperatures, and their dissociation at lower temperatures provided the cooling is slow. In a platinum resistance furnace, since the hot air round the strip is confined, we have exactly the right conditions for the dissociation of the oxide and the formation of crystals; the oxygen being used over and over again and acting merely as the temporary carrier of the metal. *In this sense,*

* Proc. Roy. Soc. 1912.

and under these circumstances, truly, the influence of the oxygen is catalytic.

We see that this theory of the formation of an endothermic, volatile, and dissociable oxide explains all the observed facts in a perfectly simple manner and without any other assumptions.

The formation of an oxide of platinum would also explain certain facts in the discharge of negative and positive electricity from hot platinum wires at low pressures. It is well known that a metal plate placed in the neighbourhood of a hot platinum wire acquires an electrical charge. "If the wire be not too hot, then at high pressures the plate will be charged positively; on exhausting the vessel, a point will be reached where the positive charge begins to decrease, then vanishes, and finally is replaced by a negative charge. This change in the sign of the charge on the plate occurs at much higher pressures in hydrogen and nitrogen than in oxygen, where this reversal is difficult to obtain unless the wire be very hot. When the reversal of sign has been obtained in hydrogen or nitrogen, the addition of a surprisingly small quantity of oxygen is sufficient to make the charge on the plate positive again. It is possible that part of the diminution in the positive leak may be due to the burning up of the oxygen. The increase in the positive electrification produced by oxygen is easily explained if there is any oxidation of the metal at a red heat; for in the oxide thus formed, the oxygen carries the negative, the metal the positive charge: thus if the oxygen in the neighbourhood of the platinum wire got ionized by the heat, the platinum, by combining with the negative but not with the positive oxygen ions, would leave an excess of positive ions in the neighbourhood"*.

There are many other observations in the discharge of electricity from hot metal wires which would receive their most satisfactory explanation on the theory of the formation of an unstable oxide†.

The results of these experiments have obvious bearings upon the means to be adopted for the preservation of the various metallic heating strips used in resistance furnaces.

I desire to offer my very best thanks to Prof. Donnan, F.R.S., and to Mr. R. E. Slade, M.Sc., for their kind

* J. J. Thomson, 'Conduction of Electricity through Gases,' 1903, p. 181.

† See various parts of Ch. 2-5 of 'Electrical Properties of Flames and Incandescent Solids,' by H. A. Wilson. University of London Press, 1912.

criticism of many chemical points; to my colleague Dr. G. Owen for much practical assistance; and, as usual, to Prof. Wilberforce for valuable advice and facilities always so readily placed at my disposal.

Messrs. Johnson, Matthey & Co. went to great trouble to prepare for me specimens of the pure platinum metals in suitable form; in the cases of iridium and ruthenium the specimens were difficult to produce.

George Holt Physics Laboratory,
University of Liverpool.

XXXII. *The Photographic Effect of X-rays and X-ray Spectra.* By C. G. BARKLA, M.A., D.Sc., F.R.S., and G. H. MARTYN, B.Sc.*

AS the fundamental phenomena accompanying the transmission of Röntgen radiation through matter,—those of absorption, secondary radiation, and ionization,—are all intimately connected with the X-ray spectrum characteristic of the particular matter traversed, it is to be expected that chemical actions should exhibit similar dependence on the characteristic radiations.

In general a very penetrating radiation during transmission through a photographic plate produces little photographic effect, while an easily absorbed radiation of the same intensity produces considerable photographic action, increased absorption of energy being accompanied by increased photographic action. Selective effects are, however, not readily observed when heterogeneous beams are used. By the use of homogeneous Röntgen radiations,—the characteristic radiations (series K) for various elements,—the connexion between the photographic action and the absorbability (or wave-length) may be easily studied.

Primary radiation from an X-ray tube was allowed to fall on a plate of substance the fluorescent radiation of which was to be used.

A portion of this fluorescent radiation, after passing through a rectangular aperture with aluminium edges (5 cm. \times 5 cm.) in a lead screen, was allowed to fall on a rapid photographic plate† enclosed in an envelope of black paper.

Another pencil of the fluorescent X-radiation passed through a small square aperture of about .5 cm. edge in a lead screen on to the thin paper face of an electroscope

* Communicated by the Authors.

† "Griffin's Professional."

which it traversed. The angles which the axes of these two pencils of radiation—one producing photographic action, the other ionization—made with the normal to the plate were approximately equal.

The photographic action and the ionization were produced simultaneously until the electroscope deflexion reached a suitable definite value obtained by preliminary experiments. The radiating plate was replaced by another, the photographic plate was moved over its aperture so that a fresh portion was exposed to the fluorescent radiation, and the electroscope was re-charged. Again, the exposure lasted until the same deflexion was produced in the electroscope by the fluorescent X-radiation from the second substance. In this way the photographic plate was exposed to various homogeneous radiations for periods sufficient for these to give identical ionizations in the air contained in the electroscope. After development of the plate it was seen that the various radiations had not produced equal photographic effects. In order to get a standard for comparison of these photographic effects, a photographic wedge was made with a similar plate exposed to a uniform light for periods proportional to the distance from one end of the wedge. By comparing the various exposed portions of the plate affected by X-rays with this wedge, the relative exposures required to produce the effects observed for the various homogeneous X-radiations were obtained. The results given in Table I., column 3, are the mean values obtained from a number of experiments, the number varying from three to eight for different radiations.

TABLE I.

X-radiation producing photographic action.	Absorbability of radiation in Al $\left(\frac{\lambda}{\rho}\right)$.	Relative Intensity of Photographic Effect (measured as indicated) for equal ionizations in air (8 cm. thickness).
Mn X-rays (series K)	1.77
Cu " " " "	47.7	1.73
Zn " " " "	39.4	1.67
Br " " " "	16.4	1.75
Mo " " " "	5.3	2.25
Ag " " " "	2.5	2.25
Sn " " " "	1.57	2.75
Sb " " " "	1.21	4.22
I " " " "	.92	4.62
Ce " " " "	.6	4.67

If we attempt to plot the absorbability of the homogeneous
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radiations as abscissæ and the photographic effect (measured as indicated) as ordinates, the features of the curve become crowded at one end of the figure. But though no direct determinations of the wave-lengths of the fluorescent X-radiations have hitherto been possible, if we extend the conclusions arrived at with regard to ultra-violet light to these Röntgen radiations we may arrive at the wave-lengths indirectly. As to the essential identity of ultra-violet light and X-rays there can be no doubt, and there is no reason to even suspect that the law connecting frequency of light and the velocity of emission of electrons by substances exposed to that light is not applicable also to X-rays. There is much evidence of the applicability, and, as far as we are aware, none against. We shall, at any rate, accept it provisionally.

The work of Whiddington has shown that the maximum velocity of the electrons set free from a plate by a fluorescent radiation (series K) from an element of atomic weight w is about $w \times 10^8$ cm. per sec.* But if this is the whole energy of a quantum on Planck's theory

$$\frac{1}{2}mv^2 = hn,$$

where m and v are the mass and velocity of the electron, h is Planck's unit 6.55×10^{-27} , and n is the frequency of light. We can thus calculate the frequency and hence the wave-length.

The wave-length λ is found to be $\frac{43.7 \times 10^{10}}{v^2}$.

$$\text{But } v = w \times 10^8.$$

Hence, assuming the whole energy of a quantum goes into an electron,

$$\lambda = \text{about } \frac{.437 \times 10^{-4}}{w^2} \text{ centimetre.}$$

If, however, we accept the experimental results of A. L. Hughes, $\frac{1}{2}mv^2 = h'n$ †, where h' is about $\frac{6}{7}$ of Planck's constant, we get a value for λ of about $\frac{.38 \times 10^{-4}}{w^2}$ cm.

Accepting this experimental value,—Hughes suggests that

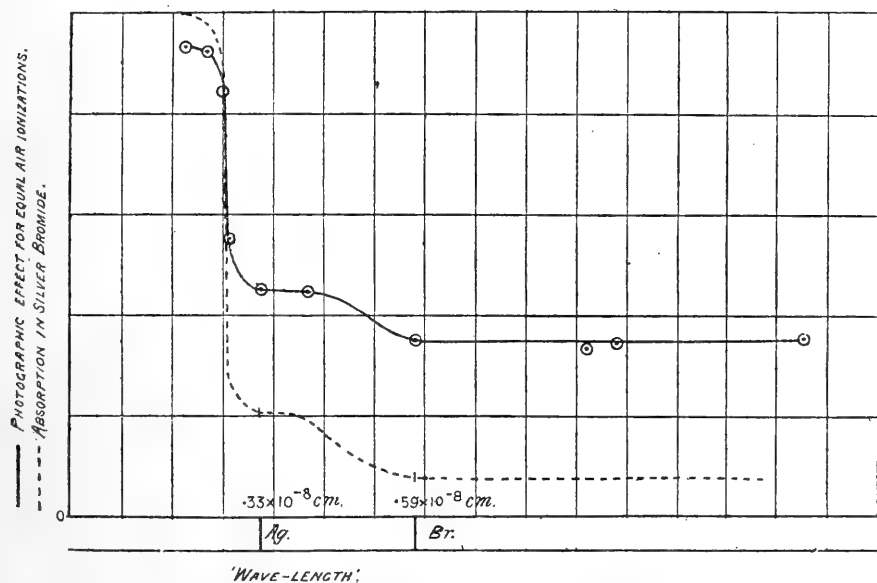
* This is probably the velocity of *all* electrons when *just* freed from the atom.

† The relation found by Hughes is written $\frac{1}{2}mv^2 = h'n - E_0$, but E_0 is negligible in this case. The value of h' was found to vary slightly with the substance emitting the electrons. The average of these values is taken above.

the difference may be due to absorption of energy by the parent molecule,—we get for the wave-length of bromine X-radiation (series K) the value $\frac{.38 \times 10^{-4}}{(79.9)^2}$ cm., that is $.59 \times 10^{-8}$ centimetre about; and of silver X-radiation (series K) $.33 \times 10^{-8}$ centimetre.

If now we plot “wave-length” so obtained and photographic effect for beams producing equal ionizations in an air-electroscope 8 cm. in length, we get a curve as shown in fig. 1.

Fig. 1.



Showing relative photographic effects for X-radiations of various “wave-lengths” producing equal ionizations in air (8 cm. thickness). Discontinuous curve shows relative absorptions of these radiations in silver bromide.

Lower portion of figure shows spectral lines (series K) of Br and Ag.

It is seen that, commencing with long waves (absorbable radiations), the photographic effect for equal ionizations is practically a constant until the radiation becomes of shorter wave-length (more penetrating) than bromine X-radiation, when the intensity rises. Again, it approaches a constant but higher value until, when the radiation becomes of shorter wave-length (more penetrating) than the radiation characteristic of silver, a second increase of photographic effect occurs. The first increase occurs when there is additional absorption of the primary radiation and re-emission of secondary radiations from the *bromine* of silver bromide, the second when the absorption in *silver* increases and the energy re-emitted in the form of secondary rays from silver increases

also. The connexion with the spectral lines (series K) of Br and Ag is shown in the lower portion of the figure.

As might be expected, the photographic effect is not proportional to the absorption of Röntgen rays, in silver, bromine, or silver bromide. For silver bromide is surrounded by gelatine consisting of light elements. On the one hand, a portion of the photographic effect is undoubtedly due to the secondary rays from this ; and, on the other hand, a portion of the energy originally absorbed in silver bromide is re-emitted and ultimately absorbed by the gelatine. It is significant that when the absorption in silver bromide relative to that in air increases either through the bromine or through the silver, the *increase* in photographic effect is approximately proportional to the *increase* in absorption.

The curve is thus of the same general shape as an absorption curve for silver bromide. This is shown by a broken line in fig. 1. It is probable that there would be a much closer similarity between the photographic curve and an absorption curve for the whole emulsion of silver bromide and gelatine.

As the values given in column 3, Table I., and plotted in fig. 1, give the photographic effect for equal ionizations produced by the beams in a few centimetres thickness of air, they give us little idea of the relative photographic effects produced in equal times by beams of equal intensity ; for, of course, the more absorbable radiations produce much larger ionizations in an electroscope which absorbs only a small fraction of the radiation passing through it than do the more penetrating radiations of equal intensity. If we assume that the total energy of a beam is proportional to the total number of ions it produces in a given gas when completely absorbed—an assumption which is probably not far from the truth for the radiations considered,—the relative photographic effects of beams of equal intensity are given by the product of the numbers in columns 2 and 3 of Table I.

The penetrating radiations of course produce small photographic effects owing to the small amount of energy absorbed.

The effect of the secondary radiations from other elements in the emulsion will probably be shown by adding salts containing heavy elements. We intend to make a more complete investigation of the subject.

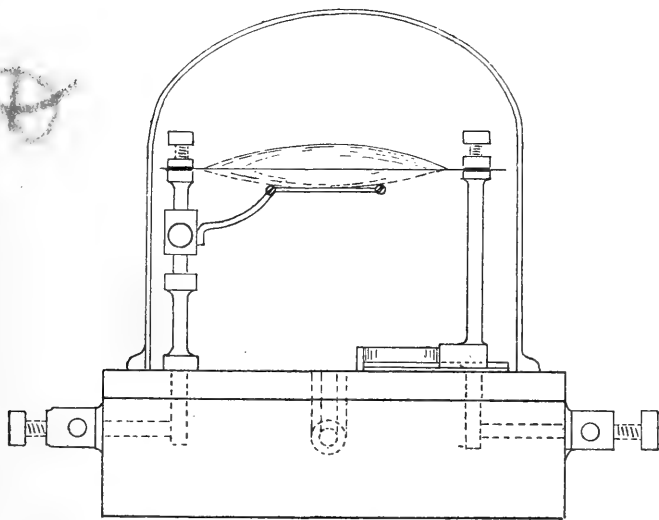
King's College, London.

Note.—I wish to express my thanks to the Solvay International Physical Institute for a grant in aid of these researches.—C. G. B.

XXXIII. *The Apophorometer* *. By J. JOLY, F.R.S.†

WHEN recently looking over some of my records of experimental work dating back to 1885–86, I came across a suggestion of an apparatus which, as I now believe, deserves to be disinterred and suitably named. The name at the head of this paper means a measurer of sublimates. The instrument is, in fact, one for enabling sublimates obtained from substances at high temperatures to be collected in their entirety and weighed on the chemical balance for purposes of chemical analysis, identification, or research.

The apophorometer is a very simple instrument. A ribbon of thin platinum, about 6 cm. in length and 4 or 5 mm. in width, is stretched between two forceps which are provided with binding-screws so that a current can be sent through the ribbon, raising its temperature to any desired degree up to the melting-point of platinum. One of the forceps is



movable parallel to itself, and is so acted on by a light spring that the ribbon is kept stretched. The substance to be volatilized is placed in the form of powder upon the ribbon or hob. Beneath the ribbon a watch-glass is held in position by a support which can be raised or lowered or rotated to one side. When this watch-glass is in contact with the ribbon a second watch-glass is placed on the lower one. The ribbon is, thus, enclosed between the glasses for nearly its entire length. Over all a receiver fits enabling an

* 'αποφορά (ἀποφέρω): a sublimate. I owe the suggestion of this name to Professor Henry H. Dixon, F.R.S.

† Communicated by the Author.

indifferent gas to be introduced around the heated substance or a vacuum to be established.

The procedure is as follows :—The lower watch-glass is raised till it is in contact with the ribbon. From 5 to 30 milligrams of the substance are distributed over the ribbon so as to extend nearly over its entire length. The upper glass is then laid on. All is now ready for the experiment. In some cases it is desirable to weigh the platinum ribbon before placing it in position. And, again, in some cases it is advisable to make a preliminary experiment on a portion (not weighed) of the powder in order to observe the behaviour of the substance.

A current is now passed through the ribbon and gradually increased. It may be that more than one sublimate is obtainable from the substance by careful regulation of the temperature ; or it may be that only the one is to be expected, and the residue being non-volatile very great care in raising the temperature is unnecessary. When the sublimate is coming off freely the high temperature is maintained unaltered for from 10 to 15 minutes or until the sublimation is seen to be completed. The current is then cut off and the glasses let cool ; but while still considerably above air-temperature the upper glass is lifted off, the lower one let down and removed, and both glasses are clipped together for weighing. This is important, as some sublimates are hygroscopic. It is well to use watch-glasses which are ground to meet accurately.

I have assumed that the presence of oxygen is not injurious. In many cases it is not. If it is, the receiver must be taken into use and the air excluded.

If there is any uncertainty as to the completion of the process, a second pair of watch-glasses should be placed around the ribbon and the current again turned on. We can thus make sure that the volatile constituent has been completely removed.

The whole process is one of ease and simplicity. In most cases the nature of the sublimate is anticipated, and in others its character enables it to be determined ; and, of course, chemical tests may be applied to it after its weight has been ascertained. Knowing the nature of the sublimate, the combined oxygen may be calculated out.

The weight of residue left upon the ribbon is in some instances of importance. But it is necessary to bear in mind that the residual element may be oxidized in those cases where access of oxygen has been permitted. It will sometimes be found that from this cause the residue

may actually weigh more than the original sample of the substance.

Certain substances may alloy with the platinum and, owing to the extreme thinness of these wide ribbons, cause it to fuse. These may be dealt with either on heavier platinum ribbon or on carbon. Moulded strips of carbon would, doubtless, be obtainable. In point of temperature-range carbon has also advantages, but this is of minor importance, for there are few sublimates not obtainable by the use of platinum. It should be remembered that ordinary carbon may contain volatile impurities. If we desire to deal with very high temperatures, the watch-glasses should be of transparent vitreous silica.

I will now quote a few recent results as illustrating the uses of the apophorometer.

Clausthalite. PbSe . Pb 72.4; Se 27.6. Weight taken 21.5 mgrms.

(1) The substance fused at a very low red heat, and a brick-red sublimate collected (Se). Weight of sublimate 6.2 mgrms.

(2) The residue on the ribbon presented the appearance of litharge. A reheating at former temperature gave no further sublimate. But when the temperature was brought to a full red a copious white sublimate was formed. Weight 12.4 mgrms.

Some litharge still adhering to the ribbon, this was weighed and found to weigh 6.6 mgrms.

Taking the sublimate as PbO and the residue as approximating to the same composition, we have $\text{Pb}=17.6$ and $\text{Se}=6.2$. On the formula the weights should be $\text{Pb}=15.6$; $\text{Se}=5.9$. This was the first gravimetric experiment on sublimates which I made.

Proustite. Ag_3AsS_3 . Ag 65.4; As 15.2; S 19.4. Weight taken 11.3 mgrms.

(1) At a temperature below visible red a rapidly formed white sublimate collected (As_4O_6). Weight 2.1 mgrms.

(2) No further sublimate was obtained at temperature of (1). The residue was a blackish slag suggesting Ag_2S . Raised to a dull red the residue slowly whitened and took on a metallic lustre (Ag). A very small trace of whitish sublimate also appeared. On weighing the ribbon the silver was found to amount to 8.3 mgrms.

Taking the white sublimate as As_4O_6 we have $\text{As}=1.5$. Also $\text{Ag}=8.3$. By difference 1.5 mgrms. of S have passed

off as SO_2 . On the formula the weights should be $\text{Ag}=7.4$; $\text{As}=1.7$; $\text{S}=2.2$. In Nature considerable departures from the theoretic proportions occur in substances such as the above.

Niccolite. NiAs . $\text{Ni } 43.9$; $\text{As } 56.1$. Weight taken 26.5 mgrms.

At a sub-red heat a white sublimate of As_4O_6 was formed. Weight 16.7 mgrms. This contains 12.7 mgrms. of As , and, by difference, $\text{Ni}=13.8$. On the formula $\text{As}=14.8$ and $\text{Ni}=11.7$.

In this experiment the precaution of reheating was not at first carried out. The result shows a deficiency of As , and it was afterwards found that more sublimate was obtainable from the residue. A fresh experiment was made:—

Niccolite, as above: weight taken 30 mgrms.

(1) Raised to dull red; weight of sublimate obtained 22.1 mgrms. (2) No further sublimate formed.

From this $\text{As}=16.7$ mgrms., and, by difference, $\text{Ni}=13.3$ mgrms. From the formula the quantities should be $\text{As}=16.8$; $\text{Ni}=13.2$.

Sylvanite. $(\text{Au}, \text{Ag}) \text{Te}_2$. $\text{Ag } 13.4$; $\text{Au } 24.5$; $\text{Te } 62.1$. Weight taken 9.2 mgrms.

(1) At a sub-red heat a grey-black sublimate formed: weight 1.4 mgrms. The temperature was now raised to full red, when a copious sublimate of a white colour came off. Weight 4.9 mgrms. No further sublimate was obtainable up to an orange-yellow heat.

There can be little doubt that the iron-black sublimate is the monoxide TeO , and that the white sublimate is the dioxide TeO_2 . On this view 5.3 mgrms. of Te have been obtained. By difference $(\text{Au}, \text{Ag})=3.9$ mgrms. The formula affords $\text{Te}=5.6$; $(\text{Au}, \text{Ag})=3.6$ when $\text{Au} : \text{Ag}=1 : 1$.

This experiment suggests that a part of the Te is more loosely combined than the rest, and hence passes into that oxide which is formed at the low temperature. It may be that this part is associated with one of the two metallic elements present. The proportions in which Ag and Au occur in sylvanite vary considerably; the gold being, however, always predominant in weight. This would imply that a selenide of silver represented the more unstable body. Some confirmation of this is found in the fact that at the conclusion of the first heating the appearance of the residue suggested the complete separation of the metallic silver; there was less evidence for the separation of gold. At the conclusion of

the experiment the latter element is abundantly present. The silver appears as a brilliant frosting, the gold in fibres and, perhaps, crystals.

Bornite. Cu_3FeS_3 (variable). Weight 25.6 mgrms.

At lowest red heat SO_2 emitted; recognized by the odour. Oily drops were formed on the glasses. [This liquid was found to be a strong acid and is doubtless H_2SO_4 , the water being obtained mainly from the atmosphere.] The residue fuses and gives off no further sublimate up to a bright yellow heat. Loss of weight found to be only 2 mgrms.

Bornite (as above).—The last result suggested a gain in weight by the oxidation of the residue. To test this another quantity (18.5 mgrms.) was roasted on a weighed ribbon in free air. The result was an increase of weight by a fraction of a milligram. This substance should be dealt with in the absence of oxygen.

Realgar. As_2S_2 .—Although heated at a very carefully graduated temperature, the substance did not appear to decompose generally into S and As. There was some liberation of S, however, the characteristic odour of SO_2 being detectable. As the heating continued the remarkable effect was observed of a deposit of what was evidently orpiment on the upper glass and of realgar on the lower. Examination with the microscope showed that the minute globules composing the realgar were in general considerably larger than those composing the orpiment. There were also beads of a black vitreous substance on the ribbon: probably As. There has, therefore, been a loss of S and some separation of As and a redistribution of the S so that the trisulphide As_2S_3 (orpiment) is formed along with the realgar. The gravitational separation of the two sulphides is remarkable.

Embolite. Ag (Cl, Br).—This melted to an oily brown liquid which appeared to sublime bodily. The whole of the sublimate was easily soluble in strong ammonia. The platinum was left clean.

Tetradymite. $\text{Bi}_2(\text{Te}, \text{S})_3$. Bi 51.9; Te 48.1; S small in amount or absent. Weight taken 27.1 mgrms.

(1) Black-grey sublimate formed at a sub-luminous temperature. It was allowed to collect for 10 minutes. Weight 2.3 mgrms.

(2) No further black sublimate could be obtained at the former temperature. Raised to a full red, a white sublimate collected. The sublimate after 20 minutes' heating was removed and weighed : weight 6.4 mgrms.

If the black sublimate be TeO and the white be TeO_2 , the weight of Te is 7.3 mgrms.

The residue on the ribbon was of a yellow colour and was fluid at the final temperature. The weight of it was found to be 24.7 mgrms. Assuming that it is Bi_2O_3 the weight of Bi is 22.2 mgrms. The added weights are about 8 per cent. too great. As for the proportions, the mineral is variable in composition, and species exist closely resembling it in appearance which are also bismuth telurides but with largely preponderating amounts of bismuth, *e. g.* jösöite and wehrlite.

Smaltite. CoAs_2 . Co 28.2; As 71.8. Weight taken 15.2 mgrms.

A white sublimate at very low red heat. The lower glass broke before the experiment was quite completed. Weight of sublimate 9.8 mgrms. This is As_4O_6 and contains 7.3 mgrms. of As , or 49 per cent. This being too little according to the formula, a second experiment was made on the same specimen :

Smaltite, as above ; weight taken 25 mgrms. Care was taken to complete the sublimation. Result 54.4 per cent. of As .

Hence the first experiment is sustained. A borax bead made with the residue on the platinum gave a muddy brown colour. The substance, although labelled smaltite and greatly resembling that ore, cannot be the cobalt arsenide. This specimen was from the collection in Trinity College. It was resolved to try one from another source.

Smaltite, specimen recently purchased from an American dealer and labelled with the formula $(\text{Co}, \text{Ni}) \text{As}_2$ which should give the same proportion of As as before.

Weight taken 22.1 mgrms. Total weight of sublimate obtained after raising to a yellow heat, 15.6 mgrms. or 11.8 mgrms. of As . This is 54 per cent. The weight of the residue was found to be 12.4 mgrms. This, which is black in colour, is doubtless Co_3O_4 and contains 9.3 mgrms. of the metal. The added weights come to 21.1 mgrms. It is noteworthy that this corresponds very nearly to the formula $(\text{Co}, \text{Ni}) \text{As}$. It seemed possible that these smaltites correspond to the highly nickeliferous varieties having the formula $\text{RAs} + \text{RAs}_2$ which have been recorded with as little as 58 per cent. of As . As it was desirable to deal with

a more normal specimen, one was chosen which gave the characteristic cobalt bead with borax.

Smaltite highly cobaltiferous. Weight taken 14.7 mgrms. As in the case of the other smaltites there was some deflagration at very low red heat and a copious sublimate collected. This white sublimate weighed 13.2 mgrms. and contained 10.1 mgrms. of As. The weight of the residue, which was a very dark ash-red colour, was 7.2 mgrms. If this is Co_3O_4 it contains 5.4 mgrms. of Co. The added weights amount to 15.4 mgrms. and the As found was just 70 per cent. of the weight dealt with, and therefore agrees with the formula.

Molybdenite. MoS_2 . S 40; Mo 60. Weight taken 20.8 mgrms.

Having found by trial that only SO_2 was evolved at a low red heat, the substance was roasted with the upper glass removed. A crystalline residue of MoS_3 remained on the ribbon. This was swept off and weighed: = 19.1 mgrms. Hence Mo = 12.7 and S = 8.1 by difference. The formula gives Mo 12.5; S 8.3.

Argentite. Ag_2S . Ag 87.1; S 12.9. Weight taken 14.1 mgrms.

At a cherry-red heat SO_2 escaped and Ag was left. This was swept into the lower glass and any still adhering silver sublimed off the ribbon. Weight of Ag = 12.4 and, by difference, S = 1.7. On the formula Ag = 12.3; S = 1.8.

These few initial results will be sufficient to illustrate the applications and uses of the apophorometer. I do not think there is any doubt that for rapid determination of mineral species it will be found of use. Percentage estimates as cited above would take many hours to obtain by the ordinary processes of chemical analysis. A good result can easily be obtained in an hour by the apophorometer and on a very few milligrams of material. A very large number of mineral species may be partially analysed by its means and, by weighing and qualitatively testing the residue, complete analyses can, in many cases, be obtained, to a degree of accuracy sufficient for determining the species or investigating new ones.

But it will, I think, be found that something more than the discrimination of substances, mineral or other, may be accomplished with it. We can by its means determine the relative stabilities of the constituents of many volatile compounds at high temperatures. It is not improbable that light will in this way be thrown on the internal constitution

of the substance. An instance in point seems to be forthcoming in the case of the telurides dealt with above.

With further experience there will be more to be said about the uses of this instrument. I hope to deal with its applications in a more systematic way in another paper. The temperature at which the sublimates are given off should be determined. In my earlier work, before I used the expansion of platinum (as in the meldometer) and employed carbon or platinum for the hob, I determined temperature by optical pyrometry or by electrical resistance. The first method has the fatal objection, as regards the apophorometer, that some of the most useful temperatures are sub-luminous. The second is very troublesome. In the case of the apophorometer I find the readings of the amperemeter afford the temperature to a sufficient degree of accuracy. It is only requisite to use in every case platinum or carbon of the same length and cross-section. In the case of platinum this, I find, presents no difficulties. By observation of the melting of a few substances of known melting-point, placed on the hob under exactly the same conditions as obtain when an ordinary experiment is being made, and simultaneous observations of the current, a graph is readily constructed which gives the approximate temperature corresponding to any strength of current.

The uses of the apophorometer are not by any means restricted to gravimetric measurements. All that class of work which I formerly assigned to the meldometer and which does not call for microscopic observation and accurate temperature readings, can be effected by its means. The brief summary of this work, which appears in a former paper *, may be reprinted here; for although other work on the meldometer has been since carried out in my laboratory and elsewhere, this subsequent work has, so far as I know, been largely restricted to the revision of melting-points. The earlier summary of qualitative work is, I think, still fairly comprehensive. In what follows we may read at pleasure "apophorometer" for "meldometer."

"SUBLIMATION.

"This apparatus affords a means of obtaining sublimates much transcending the blowpipe (used either with carbon or aluminium) in delicacy, range, and purity. Sublimates

* Joly, "The Uses of the Meldometer," *Proc. Royal Irish Academy*, 3rd ser. vol. xi. No. 1, May 1891, p. 44 *et seq.*

may, in fact, easily be obtained from substances which treated in the blowpipe would appear to afford none, as will appear. The mode of procedure is as follows:—A circular cover-glass—not too thin—grasped in a forceps, is held horizontally above the platinum ribbon, as the temperature is being raised. If the sublimate is one which oxidizes, we obtain the oxidized sublimate alone; or the unoxidized sublimate bordered by the oxide, according as we hold the glass further from or nearer to the ribbon.

“The more volatile elements often afford as sublimates both the element and an oxide of it. The elemental sublimate may often be obtained nearly pure by suitably regulating the temperature. Thus, at low temperatures *arsenic* sublimates as a rich grey-black sublimate, showing the mirror when viewed through the glass. At a higher temperature, especially if the glass is held at a distance of three or four centimetres above the ribbon, the white oxide—the trioxide—only is obtained. Sometimes both element and oxide are together on the one glass, affording an ‘eye,’ the pupil of which is the element. This results from the screening action of the outer parts of the ascending column of vapour, the central parts being, in fact, sublimed in the absence of oxygen, which is all absorbed in the outer layers of the vapour. *Magnesium* affords similar eyes surrounded by the white oxide, or in many cases veiled over by it, so that the dark metal is only seen through the glass. The great avidity of this element for oxygen is shown in this fact. *Tin* also affords ‘eyes.’ *Thallium* throws a rich black velvety sublimate, fringed with deep ash-red (the oxide?). This is a very beautiful sublimate, but very fleeting, the black soon fading into a pale greyish-brown colour. If immediately enclosed from the air it retains its original tints a longer time. *Cadmium* may also be sublimed as the metal and its oxide. *Indium* affords a white sublimate, dashed with pink and yellow.

“While the metal is thus sometimes obtained with the oxide it more generally affords the oxide only. This is the case, so far as I have observed, with *vanadium*, *lead*, *wolfram*, *bismuth*, *tellurium*, *zinc*, and *antimony*. But, again, sometimes the element appears to sublime without oxidizing. Thus *silver* affords a grey-black veil of the metal, iridescent where thinly deposited. *Gold* is also sublimed. *Sulphur* is another case, the oxide being a gas at atmospheric temperatures. *Mercury* gives a sublimate of a grey colour, consisting of globules of the element.

“As regards compounds, the command we have over the temperature in the meldometer enables many very distinct separations to be effected. Thus, dealing with *realgar*, at low temperatures, the substance is sublimed in a rich yellow sublimate. Somewhat higher a decomposition is effected, the free arsenic showing as a white sublimate of the oxide round an eye of sublimed *realgar*. As the temperature rises the effect is more and more that proper to arsenic only, the liberated sulphur not appearing; but the eyes remain most generally distinctly touched with *realgar*. *Orpiment* behaves in a similar manner. *Pyrargyrite*, a compound of silver and antimony sulphides, throws off the antimony first in a rich white sublimate of the oxide, touched more or less with a pale pink cloud, probably the unaltered compound. A bead of silver is left upon the ribbon, which ultimately volatilizes to the grey-black sublimate of silver. *Clausthalite*, the selenide of lead, affords first a sublimate of selenium, a fine ash-red; this then becomes veiled over and intermixed with the rich yellow and whites of the lead oxides, so that a very beautiful marbling is produced, which shows stronger tints of red seen from the back of the glass than from the front.

“Many such effects are seen in a similar order with the blowpipe, but are not produced with the ease, certainty, and cleanliness obtaining with the meldometer. Tests may very conveniently be applied to these sublimate as they repose upon the glass, in the knowledge that the only addition to the original substance can be oxygen. Sublimates also may be obtained from very minute quantities of the substance. This is an advantage in more ways than one. . . .

“But the meldometer is capable of affording sublimate which the blowpipe very certainly will not reveal. Thus, for example, *tourmaline* affords a pale whitish-yellow sublimate, the nature of which I have not determined; and *enstatite* volatilizes at the highest temperatures obtainable, very nearly, giving a pale brown sublimate. An addition may be made to this form of the meldometer, which will permit of sublimate being obtained in the absence of free oxygen.”

[Here follows the description of a closed sublimation vessel with tubulures by which an indifferent gas may be admitted and which has glasses supported both above and below the ribbon for catching the sublimate.] “In this manner sublimate of *realgar* and arsenic may be made to afford the unoxidized substances.”

“PYRO-CHEMISTRY.

“Before passing from the subject of the secondary uses to which this form of the meldometer may be put, it remains to add that much of the pyro-chemical work done with the blowpipe may with greater ease and delicacy be effected upon the meldometer. Thus, glasses with microcosmic salt or with borax may be made readily upon the ribbon, the colours produced being well seen, and that, too, however deep in tint, where they thin out at the ends along the bright platinum strip.

“Again, abandoning the use of the ribbon, we may substitute a platinum wire carrying a loop at its centre, and clamping it in the forceps, form beads of great beauty of the usual form from the action of the hot wire. These may be observed, under the microscope, while hot. Changes of colour, often so characteristic, are very distinctly observed through the microscope [or lens] directed upon the platinum ribbon. For example, the changes of tint of a glass formed of copper oxide (CuO) with borax, coating the ribbon, as the temperature is *slowly* raised, is from a fine blue through every gradation of tint to a greenish yellow. The command we possess over the temperature enables these successive changes to be very readily observed. Similarly, the oxidizing effects of the blowpipe may be obtained by addition of oxidizing substances, such as potassium nitrate. Thus, as with the blowpipe, a glass formed of the sesquioxide of cerium and microcosmic salt which is a pale yellow when hot, passing to colourless when cold, may by the addition of KNO_3 be intensified to a vivid yellow when hot, to colourless when cold. By the use of reducing agents deoxidation may, of course, be effected. In this way a mixture of cupric oxide with carbonate of soda and cyanide of potassium yields, first the lower cuprous oxide as a transparent red crystalline body, and finally the metal which alloys with the platinum. The most minute quantities may be used.”

Iveagh Geological Laboratory,
Jan. 17, 1913.

XXXIV. *Heating Effect of Radium and its Emanation.* By Prof. E. RUTHERFORD, F.R.S., and H. ROBINSON, M.Sc., Demonstrator and Assistant Lecturer in the University of Manchester*.

SINCE the initial discovery of the rapid and continuous emission of heat from radium by P. Curie and Laborde in 1903, a number of investigations have been made by various methods to determine with accuracy the rate of emission of heat. Among the more important of these may be mentioned the determination of Curie and Dewar† by means of a liquid air and liquid hydrogen calorimeter; of Angström‡; and of Schweidler and Hess§ by balancing the heating effect of radium against that due to an electric current; and of Callendar|| by a special balance method. It is difficult to compare the actual values found on account of the uncertainty as to the relative purity of the radium preparations employed by the different experimenters. The most definite value is that recently obtained by Meyer and Hess¶ using part of the material purified by Hönigschmid in his determination of the atomic weight of radium. As a result of a series of measurements, they found that 1 gram of radium in equilibrium with its short-lived products produces heat at the rate of 132.3 gram calories per hour.

Rutherford and Barnes** in 1904 made an analysis of the distribution of the heat emission between radium and its products. They showed that less than one quarter of the heat emission of radium in radioactive equilibrium was due to radium itself. The emanation and its products, radium A, B, and C, supplied more than three quarters of the total. The heating effect of the emanation was shown to decay exponentially with the same period as its activity, while the heating effect of the active deposit after removal of the emanation was found to decrease very approximately at the same rate as its activity measured by the α rays. The results showed clearly that the heat emission of radium was a

* Communicated by the Authors. This paper was read before the KK. Akad. d. Wissenschaft. in Wien, July 4, 1912; and published in the *Wien. Ber.* October 1912.

† Curie and Dewar, *Mme. Curie, Recherches sur les substances radio-actives*, p. 100, 2^{me} Edition, Paris, 1904.

‡ Angström, *Ark. f. Mat. Astr. och Fysik*, i. p. 532 (1904); ii. No. 12 (1905); *Phys. Zeit.* vi. p. 685 (1905).

§ Schweidler and Hess, *Wiener Berichte*, 117, p. 879 (1908).

|| Callendar, *Phys. Soc. Proc.* xxiii. p. 1 (1910).

¶ Meyer and Hess, *Wiener Berichte*, 121, p. 603, March 1912.

** Rutherford and Barnes, *Phil. Mag.* vii. p. 202 (1904).

necessary consequence of the emission of α rays, and was approximately a measure of the kinetic energy of the expelled α particles. If this were the case, all radioactive substances should emit heat in amount proportional to the energy of their own radiations absorbed by the active matter or the envelope surrounding them. This general conclusion has been indirectly confirmed by measurements of the heating effect of a number of radioactive substances. Duane* showed that the heating effect of a preparation of polonium was of about the value to be expected from the energy of the α particles emitted, while the experiments of Pegram and Webb† on thorium and of Poole‡ on pitchblende showed that the heat emission in these cases was of about the magnitude to be expected theoretically from their activity.

It is of great interest to settle definitely whether the heat of radium and other radioactive substances is a direct measure of the energy of the absorbed radiations. Since the emission of the radiations accompanies the transformation of the atoms, it is not *a priori* impossible that, quite apart from the energy emitted in the form of α , β , or γ rays, heat may be emitted or absorbed in consequence of the rearrangements of the constituents to form new atoms.

The recent proof by Geiger and Nuttall§ that there appears to be a definite relation between the period of transformation of a substance and the velocity of expulsion of its α particles, suggests the possibility that the heating effect of any α -ray product might not after all be a measure of the energy of the expelled α particles. For example, it might be supposed that the slower velocity of expulsion of the α particle from a long-period product might be due to a slow and long-continued loss of energy by radiation from the α particle before it escaped from the atom. If this were the case, it might be expected that the total heating effect of an α -ray product might prove considerably greater than the energy of the expelled α particles.

In order to throw light on these points, experiments have been made to determine as accurately as possible:—

- (1) The distribution of the heating effect amongst its three quick-period products, radium A, radium B, and radium C
- (2) The heating effect of the radium emanation.

* Duane, *Comptes Rendus*, cxlviii. p. 1665 (1909).

† Pegram and Webb, *Phys. Rev.* xxvii. p. 18 (1908).

‡ Poole, *Phil. Mag.* xix. p. 314 (1910).

§ Geiger and Nuttall, *Phil. Mag.* xxii. p. 613 (1911); xxiii. p. 439 (1912); xxiv. p. 647 (1912).

(3) The agreement between the observed heat emission of the emanation and its products and the value calculated on the assumption that the heat emission is a measure of the absorbed radiations.

(4) The heating effect due to the β and γ rays.

It was also of interest to test whether the product radium B, which emits no α rays but only β and γ rays, contributed a detectable amount to the heat emission of the active deposit.

Method of Experiment.

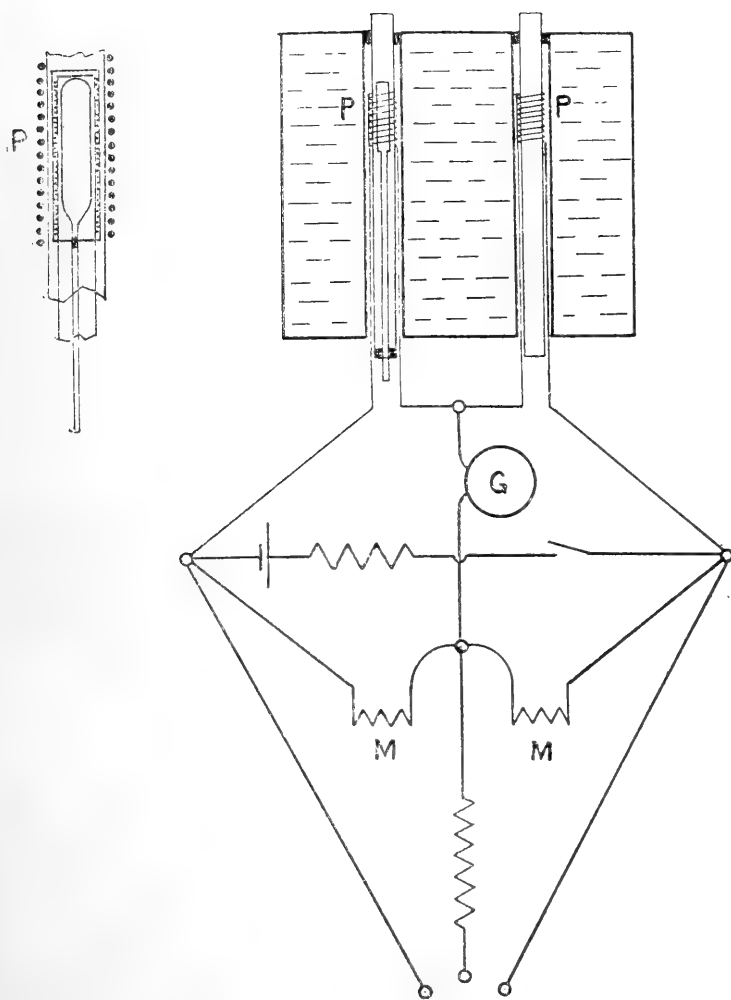
In order to test these points, it was essential to employ a method whereby rapidly changing heating effects could be followed with ease and accuracy. A sufficient quantity of radium emanation was available to produce comparatively large heating effects. It was consequently not necessary to employ one of the more sensitive methods for measuring small heating effects, such as have been devised by Callendar and Duane.

The general arrangement was similar to that employed in 1904 by Rutherford and Barnes for a like purpose. Two equal coils, P, P, fig. 1, about 2.5 cm. long, were made of covered platinum wire of diameter .004 cm. and length 100–300 cm., and wound on thin glass tubes of 5.5 mm. diameter. These platinum coils of nearly equal resistance formed two arms of a Wheatstone bridge, while the ratio arms consisted of two equal coils, M, M, of manganin wire, each of about the same resistance as the platinum coils, and wound together on the same spool and immersed in oil. The platinum coils had a resistance varying between 15 and 45 ohms in the various experiments. The glass tubes on which the platinum coils were wound were placed in brass tubes passing through a water-bath. When a specially steady balance was required, the water-bath was completely enclosed in a box and surrounded with lagging to reduce the changes of temperature to a minimum. In most of the experiments the correction for change of balance during the time of a complete experiment was small and easily allowed for. By means of an adjustable resistance in parallel with one of the coils, a nearly exact balance was readily obtained. A Siemens and Halske moving-coil galvanometer was employed of resistance 100 ohms. This had the sensibility required, and was found to be very steady and proved in every way suitable.

The current through the platinum coils never exceeded $1/100$ ampere, and was generally about $1/200$ ampere.

A calibration of the scale of the galvanometer was made by placing a heating-coil of small dimensions of covered manganin wire within one of the platinum coils, and noting the steady deflexion when known currents were sent through it.

Fig. 1.



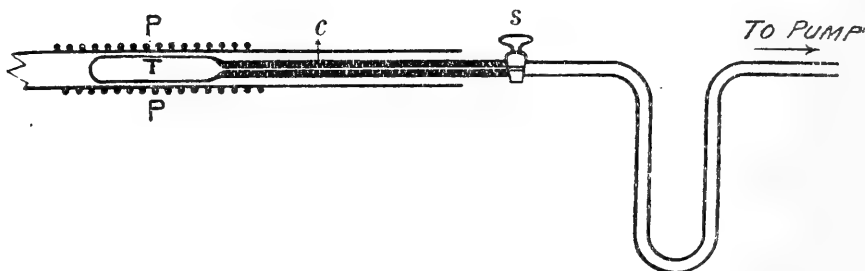
It was found that the deflexion of the galvanometer from the balance zero was very nearly proportional to the heating effect of the manganin coil, for the range of deflexion employed, viz. 400 scale-divisions. The deflexion thus served as a direct measure of the heating effect.

§ 1.

Distribution of the Heat Emission between the Emanation and its Products.

A quantity of emanation of about 50 millicuries was introduced into a thin-walled glass tube T (fig. 2) connected by a capillary tube C to a small stopcock S. The tube was attached to a mercury-pump by the aid of which the emanation could be purified and compressed into the emanation-tube. The position of the latter was adjusted to lie in the centre of one of the platinum coils.

Fig. 2.



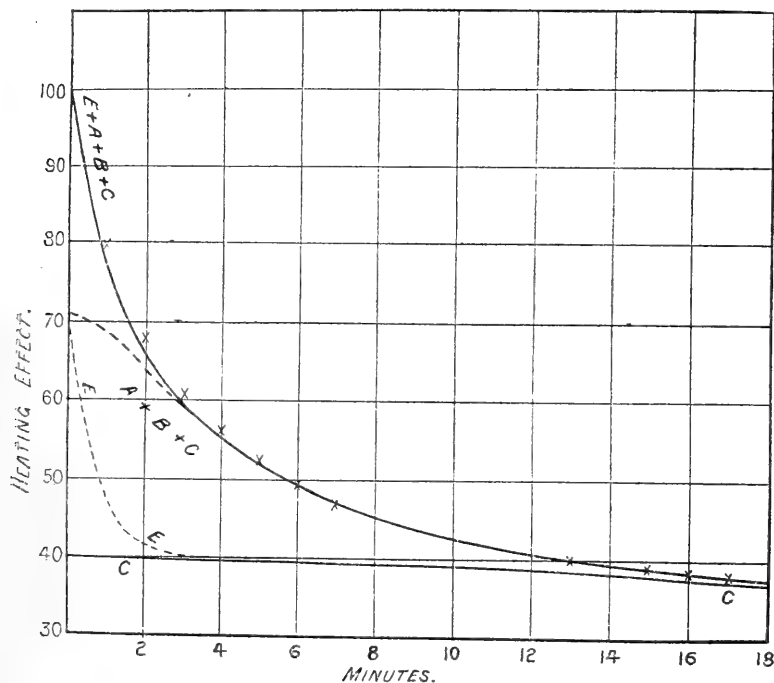
As it was necessary to leave the emanation for about 5 hours in the tube for equilibrium to be reached with its successive products, it was desirable to arrange that the emanation-tube could be removed outside the water-bath at intervals to test for any change in the balance. The emanation-tube was kept fixed to the pump, but the water-bath was moved backwards along the direction of the axis of the emanation-tube. For this purpose, the water-bath was mounted on metal guides, and was moved backwards or forwards by means of a screw.

The general procedure of an experiment was as follows. The balance was adjusted as nearly as possible and the tube, which had been filled with emanation for more than five hours, was introduced within the platinum coil. In about ten minutes a steady deflexion of the galvanometer was obtained, proportional to the heating effect of the emanation. The emanation was then suddenly expanded into the exhausted pump by opening the stopcock S, and condensed in a U-tube by liquid air. The removal of the emanation caused a rapid decrease of the deflexion, followed by a slower decrease due to the decay of activity of the deposit. Observations of the deflexion were continued in some experiments for over two hours. In this time the heating effect had decayed to about 6 per cent. of the initial value. At the conclusion of the experiment, the emanation-tube was removed and the balance point

again obtained. Special experiments showed that any change of balance was very slow and regular, so that a correction of the readings for the small change of balance during the observations could be made with accuracy. The readings of the galvanometer were remarkably steady, and observations of the deflexion could be made to about $\frac{1}{5}$ of a scale-division.

A typical example showing the variation of the deflexion with time for the first 18 minutes after removal of the emanation is shown in fig. 3, curve E + A + B + C.

Fig. 3.



On account of the lag of the apparatus, the deflexion of the galvanometer at any moment is always greater than corresponds to the heat emission of the emanation-tube. A number of experiments were made to determine the amount of this lag. For this purpose a manganin coil was wound on a glass tube of the same size and thickness as the emanation-tube T and introduced into the platinum coil. A current from an accumulator was sent through this coil so as to give an effect of about the same magnitude as that of the emanation used in the experiments. The circuit was then broken and the decrease of deflexion with time was noted. For this coil the deflexion fell to half value in about 45 seconds, and after that decreased approximately according to an exponential law with a half-value period of about 30 seconds. The lag of the manganin coil was found by experiment to be

slightly greater than the lag of the bare emanation-tube. It was found that for a slow decrease of heating effect the deflexion lagged about one minute behind the actual heat emission.

Analysis of the Curve.

The curve given in fig. 3 is typical of a number of curves obtained which agreed closely with one another. The relative heating effects of the emanation and its products can be deduced from the observed curve by comparison with the theoretical curve of decay of the components of the active deposit.

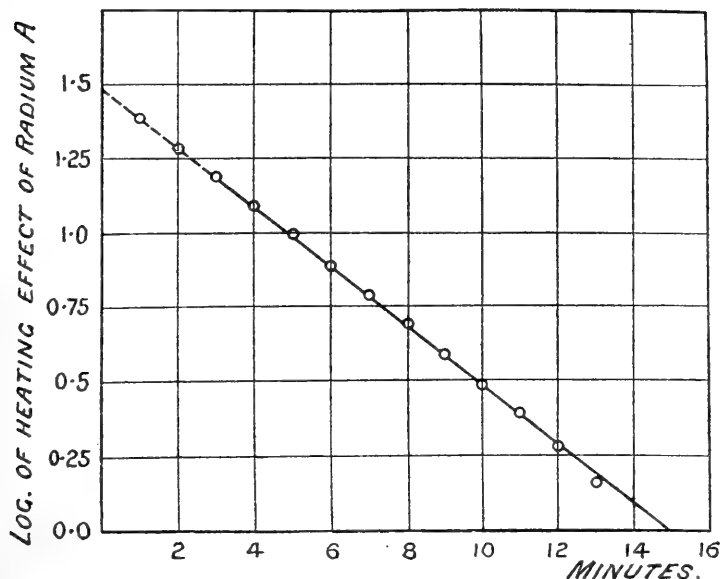
The heating effect of the emanation itself has practically disappeared three minutes after its removal. The variation of the heating effect of the tube C resulting from the removal of the emanation alone is shown in the dotted side curve EE, where the maximum heating effect is taken as 29 per cent. of the total. This curve was deduced from a knowledge of the cooling curve of the tube under the experimental conditions when heated above its surroundings.

After subtracting the heating effect due to the emanation alone, the resulting curve A + B + C gives the heating effect due to radium A + B + C. After about 20 minutes the heating effect due to radium A has practically vanished, and the effect observed is then due to radium B + C. It was found that the curve after 20 minutes followed closely the theoretical curve to be expected if the heating effect was provided mainly by radium C. Assuming this to be the case, the heating effect due to radium C alone is shown by the curve CC, which cuts the axis of ordinates at 40. A lag of 1 minute is assumed between the observed and true heating effects after 20 minutes. The difference of the ordinates of the curves A + B + C, and CC, must be due to the heating effect supplied by radium A. After an initial lag, the heating effect of radium A should ultimately decay exponentially with its known period of transformation, viz. 3 minutes. This is shown clearly in the curve of fig. 4. The difference-curve is plotted, allowing an initial interval of 3 minutes for the emanation effect to decay. Plotting the logarithms of the deflexions as ordinates and the time as abscissæ, the curve is a straight line, showing that the heating effect due to radium A decays exponentially with a half-value period of 3 minutes. The maximum heating effect of radium A was deduced to be 31 per cent. of the total.

The variation of heating effect of the emanation-tube with time brings out clearly that about 29 per cent. of the initial

heating effect of the tube is due to the emanation alone, 31 per cent. to radium A, and 40 per cent. to radium B + C together. It should be mentioned that it is difficult to deduce

Fig. 4.



with certainty the exact ratio of the heating effects due to the emanation and radium A on account of small errors in the determination of the lag. It is clear, however, from the experiments that the heating effects are nearly equal.

These deductions were verified by another method which avoided the necessity of any correction for lag or for galvanometer or scale errors. The emanation-tube was replaced by a glass tube of the same dimensions, over which was wound a layer of fine insulated manganin wire whose resistance was determined. The variation of the heating effect of the emanation-tube after removal of the emanation was then calculated from the known periods of transformation of radium A, B, and C, assuming that the emanation provided 29 per cent. of the total, radium A, 31 per cent., radium C, 40 per cent. The current through the resistance-coil to give a corresponding heating effect was then calculated, and the external resistance to be added in the battery-circuit at any moment deduced. The initial amount through the coil was adjusted to give nearly the same deflexion of the galvanometer as that due to the emanation. By means of a dial resistance-box, the resistance could be rapidly varied to give at any moment the required heating effect. For example, to imitate the removal of the emanation the resistance was

suddenly increased so that the heating effect of the current changed to 71 per cent. of the initial amount.

In this way the variation of the deflexion of the galvanometer to be expected for the assumed distribution of the heating effect was directly determined. The values obtained are marked by crosses in the main curve fig. 3. It is seen that the observations lie close to the curve throughout the whole range. The lag of the resistance-coil was slightly greater than that due to the emanation-tube, and in consequence the initial points lie slightly above the curve. The agreement between the two curves shows clearly that the assumed distribution of heating effect between the emanation and its products is in close accord with direct experiment.

It is seen from the curve fig. 3 that the heating effects due to the emanation and radium A have practically vanished after 20 minutes, and the remaining heating effect is due to radium B and radium C together.

A number of experiments were made to test whether radium B provided an appreciable part of the heating effect observed. For this purpose the decay of the heating effect was carefully followed for about three hours after removal of the emanation and the results compared with those to be expected theoretically for any assumed distribution between the heating effects of radium B and radium C. The decay curve observed was found to agree closely with that to be expected if all the heating effect arose from radium C alone. The experiments were rendered difficult by the fact that a small fraction of the emanation adhered to the walls of the emanation-tube, and was gradually released during the time of the experiment. The effect of this became appreciable after two hours, when the heating effect due to radium C had decayed to about 14 per cent. of its initial value.

In addition, the method is not very sensitive, for the decay curve over the region examined is not much affected even if radium B provides 5 per cent. of the heating effect of radium C. It was concluded from the observations that radium B could not provide *more* than 5 per cent. of the heating effect due to radium C; but for the reasons mentioned the actual percentage could not be deduced with any confidence.

Agreement of Experiment with Calculation.

The relative heating effects of the emanation, radium A and radium C in equilibrium can be readily calculated if it be assumed that the heating effect is a measure of the kinetic energy of the expelled α particles. Since the expulsion of

an α particle causes a recoil of the residual atom, the kinetic energy of the latter should be included in the calculation. If m , M be the masses of the α particle and recoil atom respectively, and u , U the corresponding velocities, $mu = MU$, and the kinetic energy of the α particle and recoil atom is given by $\frac{1}{2}mu^2\left(1 + \frac{m}{M}\right)$. The ratio m/M is slightly less than $\cdot 02$, so that the heating effect due to recoil is about 2 per cent. of that due to the α particle itself.

When the emanation is in transient equilibrium with its products, it has been shown* that radium C is in excess of the true equilibrium amount by 0.89 per cent., so that a slight correction is necessary for this factor. The velocity u of the α particle is deduced from the relation found by Geiger, $u^3 = KR$, where R is the range in air. Taking the ranges of the α particles from the emanation and its products given by Bragg and correcting for the factors mentioned above, it can be simply shown that the heating effect of the emanation in transient equilibrium with its products is distributed as follows:—

Emanation ...	28.8 per cent.
Radium A ...	30.9 ,,
Radium C ...	40.3 ,,

The experimental values observed are 29, 31, and 40 per cent. respectively, and thus appear in good accord with theory.

In this comparison no account is taken of the heating effect contributed by the β rays from radium B and radium C. From experiments described later, it appears probable that the β rays from these two products contributed under the experimental conditions about 4 per cent. of the total heating effect. It follows that the percentage of the heating effect included under radium C should be 42.6 per cent. instead of 40.3.

As the result of a number of observations, the heating effect due to radium B + C was found to be certainly not greater than 40.5 per cent. and probably nearer 40.0 per cent. It thus appears that radium C provides slightly less heating effect than that to be expected theoretically. While the difference between observation and calculation is not large, it may prove to be significant; for in making the calculations no account is taken of the heating effect of the β rays or of a possible small heating effect due to radium B.

* Rutherford and Chadwick, Proc. Phys. Soc. xxiv. p. 141 (1912).

If the heating effect of radium B were 5 per cent. of that contributed by C, the discrepancy between theory and experiment would be quite marked, and would indicate that the heating effect of a product was not entirely a measure of the energy of the expelled α particles and the recoil atoms.

In order to settle this point with certainty, it would be necessary to isolate radium C from radium B, and to measure accurately its heating effect. It is hoped to continue experiments in this direction, for the question to be settled is of great importance in connexion with the general theory.

§ 2. *Heating Effect of the Radium Emanation.*

A series of experiments were made to determine accurately the heating effect of the radium emanation in absolute measure in order to test how far the calculated heating effect is in agreement with experiment. The general method employed was similar to that described in the earlier part of the paper. A quantity of emanation of 100 to 150 millicuries was concentrated in a small glass tube about 2.2 cm. long, 2 mm. bore, and of thickness 0.2 mm. This was attached to a long thin glass cylinder of small diameter for convenience of handling. In order to calibrate the heating effect observed, a coil of silk-covered manganin wire about 127 cm. long and 41.45 ohms resistance was wound uniformly for a length of 2.2 cm. on a long thin glass tube of 2.5 mm. bore. The heating-coil was of exactly the same length as the emanation-tube, but in order to make sure that the heat distribution was the same for the emanation-tube and for the heating-coil, a copper cylinder 2.7 cm. long and 0.2 mm. thick was placed over the heating-coil. The whole arrangement was placed symmetrically in the glass tube of 5 mm. bore, over which was wound one of the platinum balance coils P (fig. 1).

The procedure of an experiment was as follows. The balance of the platinum coils was accurately adjusted and the current through the coils kept constant. The emanation tube in equilibrium with the active deposit was introduced in the platinum coil in a definite position, and the maximum deflexion of the galvanometer observed. A steady deflexion was reached in less than ten minutes. The emanation-tube was then withdrawn by the glass handle, and a known constant current from a storage-cell passed through the manganin coil to give nearly the same maximum deflexion as that due to the emanation. The current was then cut off and the emanation-tube again introduced. Alternate measurements

of the heating effect of the emanation and of the current were made for a period of two hours. The emanation-tube was then removed and the change of the balance in the interval determined. The change of balance due to slight alterations of the temperature of the room was usually found to be quite regular and small, and could be easily corrected for if necessary.

In order to determine the heating effect, it was necessary to measure accurately the amount of emanation at any moment in the tube and the current through the heating-coil. The γ -ray effect of the emanation-tube at a definite time was compared in terms of the Rutherford-Boltwood standard by the electroscopic method, and also by the balance method developed by Rutherford and Chadwick. The authors are indebted to Mr. Chadwick for his kind assistance in these measurements. The results obtained by the two methods were in good agreement. A correction of 0.3 per cent. was made for the absorption of the γ rays in the walls of the emanation-tube. The heating effect of the emanation was assumed to decrease exponentially with a half-value period of 3.85 days. This period of decay was verified on several occasions by direct measurement of the heating effect. The current through the heating-coil was determined by measurement of the E.M.F. of the accumulator by a carefully standardized voltmeter, and the total resistance of the circuit.

The measurements of the heating effect made with different quantities of emanation were in close accord, and the mean of each series of measurements agreed within 1 part in 500. In this way it was found that the heating effect of a quantity of emanation which gave the same γ -ray effect as one gram of radium (Rutherford-Boltwood standard) was 95.95 ± 0.05 gram calories per hour under the experimental conditions.

It is necessary, however, to correct this value to obtain the heating effect of one curie of emanation, *i. e.* of the quantity of emanation in radioactive equilibrium with one gram of radium. The amount of the products radium A, B, and C in transient equilibrium with the emanation are somewhat greater than the amounts in equilibrium with the same quantity of emanation which is maintained constant. This point has been discussed by Moseley and Makower*, and by Rutherford and Chadwick†. The amount of radium B is 0.54 per cent. and of radium C 0.89 per cent. in excess of the true equilibrium amount. Moseley and Makower showed

* Moseley and Makower, *Phil. Mag.* xxiii. p. 302 (1912).

† *Loc. cit*

that under ordinary experimental conditions, radium B provides about 11 per cent. of the γ -ray effect due to the emanation, and radium C 89 per cent. We have seen earlier that radium C contributes about 40 per cent. of the heating effect of the emanation. Taking these factors into account, it can be deduced that the heating effect of the emanation which gives a γ -ray effect equal to that of one gram of radium is about 0.54 per cent. less than corresponds to one curie of emanation in equilibrium with radium.

The heat emission of one curie of emanation thus reduces to 98.5 gram calories per hour in terms of the laboratory standard. By the kindness of Professor Stefan Meyer of Vienna, the laboratory standard has been compared in terms of the pure radium salt prepared by Hönigschmid. Expressed in terms of the Vienna standard, the heat emission of one curie of emanation is equal to 103.5 gram calories per hour. In the experimental arrangement the β rays traversed a thickness of glass, copper, &c., equivalent to a weight of .354 gram per square cm. More than 90 per cent. of the energy of the β rays was absorbed and added its heating effect to that of the α rays.

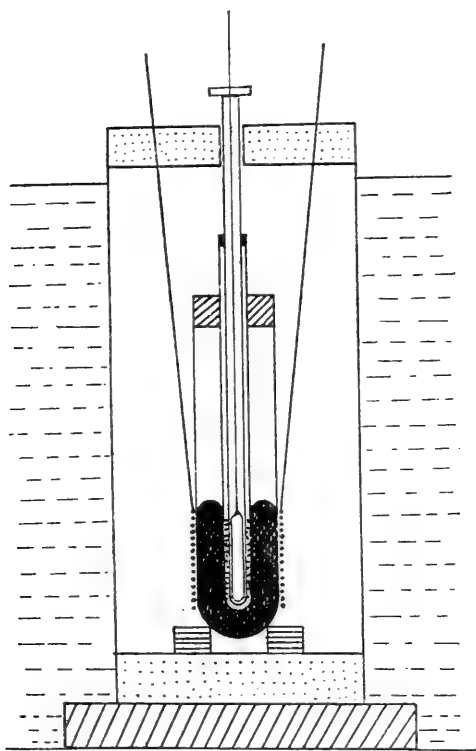
Heating Effect of the β and γ Rays.

Before comparing the observed heating effect with the calculated value, it is necessary to determine how much of the heating effect observed is to be ascribed to β and γ rays. A number of experiments were made to form an estimate of the magnitude of these effects. In the experimental arrangement described the greater part of the β rays was absorbed in the glass tubes, heating-coil, and copper tube surrounding it. The heating effect under these conditions will be taken as 1. Experiments were first made to determine the alteration of the heating effect when a lead cylinder 1.2 mm. thick, which completely absorbed the β rays and some of the soft γ rays, was substituted for the copper cylinder. As a result of a series of measurements, the heating effect was found to be 1.02.

A series of measurements were then made to determine the heating effect of the γ rays. For this purpose about 4 metres of platinum wire were wound on the outside of two similar thin-walled test-tubes of 1.5 cm. diameter. Each of these was inside a metal cylinder of 6.5 cm. diameter, closed at one end and immersed in a water-bath (fig. 5). Each of the test-tubes was filled with mercury so that the mercury extended about 5 mm. above and below the platinum coil. After the balance had been obtained the emanation-tube, surrounded by its heating-coil, as in previous experiments, was fixed in

the centre of one of the mercury columns and the steady deflexion of the galvanometer determined. The thickness of mercury traversed by the rays was 4.4 millimetres. On account of the large quantity of mercury and the distance between the platinum coils and the outside cylinder, there was a marked lag between the deflexion and the heating effect. For example, the deflexion reached half its maximum value in ten minutes.

Fig. 5.



It is difficult to determine the heating effect with the same accuracy as for smaller coils ; but a number of fairly concordant experiments gave a heating effect of 1.034. Similar experiments were made with a thickness of mercury of 1.46 cm. The deflexion in this case reached half its maximum value in 23 minutes. On account of the large lag, the small variations in the balance point during the time of observation became more important. Suitable corrections were made for the lag of the apparatus, and also for the effect of the decay of the emanation. As a mean of several observations the heating effect was found to be about 1.05. It is, however, difficult to fix the value of the heating effect in this case closer than half of one per cent.

The heating effect due to the γ rays from radium could be determined with greater accuracy with a preparation of radium in equilibrium, for under such conditions there is no

necessity, as in the case of the emanation, to take into account the decrease of the heat emission of the source.

It is now necessary to consider what fraction of the energy of the β rays was absorbed in the arrangement of the heating apparatus shown in fig. 1, by which the heating effect of the emanation was accurately determined.

Eve* has made an estimate of the relative energy emitted by the α , β , and γ rays from one gram of radium on the assumption that the energy of the radiation emitted is proportional to the total ionization produced. By this method he deduced that the β rays from radium contributed about 2 per cent., and the γ rays about 4.5 per cent. of the total heat emission. In his arrangement, however, the radium was enclosed in a glass tube which must have absorbed a considerable fraction of the soft β rays, and the correction for the ionization of these soft rays was uncertain. It was thought desirable to repeat the experiments made by Eve, using the radium emanation in place of radium, and compressing the former in a very thin glass tube, which allowed the α rays to escape freely. The stopping power of the glass tube corresponded to only 2 cm. of air. Mr. Moseley kindly assisted in these experiments, a more detailed account of which will be published later by Mr. Moseley and Mr. Robinson.

The method originally used by Eve is very suitable for the purpose for which it was designed, and was employed in these experiments. The ionization produced by the β and γ rays from the emanation-tube in a thin-walled ionization-chamber supported in the middle of a room was measured for different distances of the tube extending up to 12 metres. The ionization current in the chamber was directly measured by an electrometer using a balance method. Taking the ionization in air due to the α rays from radium in equilibrium as 100, the total ionization in air due to complete absorption of the β rays was about 3.8, and for the γ rays about 5.2. The ionization due to the γ rays is somewhat greater than that found by Eve, but the ionization due to the β rays is nearly twice as large. In Eve's experiment a large part of the soft β rays was absorbed in the radium tube. By placing over the emanation-tube the copper and glass tubes &c. used in measuring the heating effect of the emanation, it was found that about 85 per cent. of the total ionization due to the β rays was cut out. This was an unexpectedly large fraction, but was confirmed in several experiments.

Remembering that the α rays from the emanation and its products provide about 80 per cent. of the heating effect due

* Eve, Phil. Mag. xxii. p. 851 (1911).

to the α rays from radium in equilibrium, it follows that the heating effect of the β and γ rays absorbed in the experimental arrangement described in § 2 was 4.2 per cent. of that due to the α rays. This is, of course, based on the assumption that the total ionization produced by the α and β rays is a measure of their relative energy.

From the ionization measurements, it follows that the total heating effect of the γ rays from the emanation should be 6.5 per cent. of that due to the α rays. It is difficult to estimate with certainty the fraction of the γ rays absorbed by the thickness of mercury of 1.46 cm., but it was probably about 70 per cent. The heating effect of the γ rays should thus be about 4.6 per cent. of that of the emanation. This is in fair accord with the observed increase of heating effect of 5 per cent., of which probably about .5 per cent. was due to β rays.

It should be pointed out that the increase of the heating effect of 2 per cent. observed when the copper cylinder was replaced by a lead cylinder 1.2 mm. thick, is greater than would be expected from the ionization results. The value was undoubtedly nearly correct, for it was verified in a number of experiments. It is well known that lead shows an abnormal absorption for soft γ rays, and the heating effect observed is no doubt due partly to the absorption of the more penetrating β rays and partly to the soft γ rays. The heating effect observed for γ rays is in reasonable accord with the value calculated from the ionization, and indicates that the underlying assumption is not much in error. Since the ionization observed for γ rays is mainly, if not entirely, due to the liberation of β rays from the matter which the γ rays traverse, it seems probable that the ionization method can be used with confidence to estimate also the energy of the β rays.

In 1910 Pettersson* made a number of careful observations by balance methods of the heating effect of β and γ rays from a radium preparation. The heating effect of the radium preparation was 116.4 when the rays were absorbed in 4 mm. of lead, and 114.5 when the lead was replaced by aluminium 2 mm. thick. The rays in both cases passed through absorbing material equivalent to 4 mm. of aluminium before entering the lead or aluminium cylinder. From the measurement of ionization, it is clear that the difference is due not to the heating effect of the β rays as assumed by Pettersson, but mainly to the absorption of the γ rays by the lead. It seems certain that nearly all the energy of the β rays is absorbed in traversing aluminium 4 mm. thick.

* Pettersson, *Ark. f. Mat. Astr. och Fysik*, vi. p. 26, July 1910.

The results obtained for the heating effect of one curie of emanation under various conditions are tabulated below.

Screen.	Heat emission of one curie of emanation in gram calories per hour.			
	α rays.	β rays.	γ rays.	Total.
Equivalent to 1.3 mm. of aluminium	99.2	4.2	0.1	103.5
0.7 mm. Al + 1.2 mm. of lead.....	99.2	4.8	1.5	105.5
„ + 4.4 mm. of mercury ...	99.2	4.8	3.0	107.0
„ + 14.6 mm. of mercury ..	99.2	4.8	4.7	108.7

These results are expressed in terms of the Vienna Radium Standard.

§ 3. Calculation of Heating Effect of Radium and its Emanation.

The energy of the α particles and recoil atoms liberated from one gram of radium or of any of its products in equilibrium with it can readily be calculated. This energy is equal to

$$\frac{1}{2}mnu^2\left(1 + \frac{m}{M}\right) = \frac{1}{2} \frac{mu^2}{e} \cdot ne \cdot \left(1 + \frac{m}{M}\right)$$

for each of the α -ray products concerned. The value $\frac{mu^2}{2e}$ was directly determined by Rutherford for the α particle from radium C by measurement of the electrostatic deflexion of the rays, and found to be 4.21×10^{14} . Taking the velocity of an α particle to be proportional to the cube root of its range, the corresponding values of $\frac{mu^2}{2e}$ for radium, emanation, and radium A, are $2.56, 2.95, 3.13 \times 10^{14}$ respectively. The masses of the recoil atoms from radium, emanation, radium A, and radium C, are 222, 218, 214, and 210 respectively. The value of $1 + \frac{m}{M}$ is consequently slightly less than 1.02 for each product.

The value of ne , the total charge carried by the α particles from one gram of radium itself, has been found by Rutherford and Geiger to be 1.054×10^{-9} e.m. unit. Substituting these values, the emission of energy is for one gram of radium in equilibrium 1.38×10^6 ergs per second, and for the emanation in equilibrium with it 1.19×10^6 ergs.

The corresponding heating effect of one gram of radium

for complete absorption of α particles is 118 gram calories per hour, and for the emanation 94.5 gram calories per hour.

These results are expressed in terms of the Rutherford standard, for the value ne depends on this standard. Correcting in terms of the Vienna standard, the corresponding heating effects are 124 and 100 gram calories per hour.

We have seen (§ 2) that the heating effect of one curie of emanation on the Vienna standard is 103.5 gram calories per hour. Since under the experimental conditions probably 5 per cent. of this is due to the β rays, it is seen that the calculated and measured values for one curie of emanation are in good agreement.

St. Meyer and Hess found that the heating effect of one gram of radium in terms of the Vienna standard was 132.3 gram calories per hour. This includes the heating effect of the β rays and 15 per cent. of the γ rays. This is in excellent accord with the value deduced from the observed heating effect of the emanation. The heating effect of one curie of emanation surrounded by 1.2 mm. of lead was 105.5 gram calories per hour. The heating effect due to α particles and recoil atoms is probably about 98.5 gram calories. The theoretical rates of the heating effects for radium in equilibrium compared with its emanation is 1.255. The heating effect of one gram of radium surrounded by 1.2 mm. of lead thus comes out to be $123.6 + 7 = 130.6$ gram calories per hour. Allowing a small correction for the extra absorption of γ rays in the Vienna experiments, this value is in close accord with that found by Meyer and Hess.

Too much stress should not be laid on the agreement of the calculated value of the heating effect of radium with that deduced experimentally, for the data used in the calculations are not fixed with the accuracy required. For example, the calculation depends on the accuracy of the values $\frac{mu^2}{e}$ and $n.e.$

The former was determined by measuring the electrostatic deflexion of the α rays. A combination of the value so found with the value $\frac{mu}{e}$ found by deflexion of the same rays in a magnetic field gave a value $e/m = 5.07 \times 10^3$. There is now no doubt that the α particle is a helium atom carrying two charges, and the value of e/m should be 4.84×10^3 .

Taking the value $\frac{mu}{e} = 4.06 \times 10^5$ found by Rutherford for the α particle from radium C as correct, and assuming $e/m = 4.84 \times 10^3$, the value $\frac{mu^2}{2e} = 3.99 \times 10^{14}$ instead of the value 4.21×10^{14} used in the calculation. Taking the new

value, the calculated heating effect is reduced 5 per cent., and the agreement between calculation and experiment is not so good. In order to settle this point, experiments are now in progress to redetermine the values of u and e/m of the α particle from radium C.

From the data already given, the distribution of the heating effect between radium and its products and radiations is given below.

	Heating effect in gram calories per hour corresponding to one gram of radium.			
	α rays.	β rays.	γ rays.	Total.
Radium*	25.1	25.1
Emanation	28.6	28.6
Radium A	30.5	30.5
Radium B }	39.4	4.7	6.4	50.5
Radium C }				
Totals	123.6	4.7	6.4	134.7

It follows that the total heating effect of one gram of radium for complete absorption of the α , β , and γ rays should be about 135 gram calories per hour per gram on the Vienna standard.

University of Manchester, 1912.

XXXV. *Solubility of the Active Deposit of Thorium in Various Solvents.* By C. F. HOGLEY, B.Sc., A.R.C.S.†

IN this paper is described an attempt to classify the transformation products of thorium in the periodic system by means of their solubilities in various solvents.

Some thorium hydroxide was placed in a metal dish over which was suspended a small piece of platinum foil which could be easily detached. The active deposit from the thorium was collected in the usual way by connecting the platinum plate to the negative pole of a battery. After two or three days' exposure the plate was removed and its activity

* During the publication of this paper, V. F. Hess (*Wien. Ber.* cxxi. p. 1, 1912) has published the results of a direct determination of the heating effect of radium freed from all its products. The value obtained, 25.2 calories per hour per gram, is in excellent accord with the value calculated from the measurements on the emanation given above.

† Communicated by the Hon. R. J. Strutt, F.R.S.

measured by observing the rate of leak of an electroscope. It was at once placed in the solvent for an observed time, carefully dried by placing between filter-paper, and its activity again measured. It was now set aside for a few hours to enable the transformation products to get into equilibrium, after which the activity was again measured. From this third reading could be calculated the equilibrium activity of the plate at the instant it was taken out of the solvent. This was necessary in order to ascertain which of the substances had been dissolved in the greater quantity. Thus if thorium B had been dissolved more than thorium C*, the quantities of each remaining would not be in equilibrium, and the activity of the plate would be greater than that calculated from the third reading when the two substances had adjusted themselves. If the reverse of this occurred it would indicate that the thorium C had dissolved more than the thorium B. (This of course is due to the fact that the activity of the plate arises from the thorium C only.) Thus when thorium B is dissolved from the plate, the loss does not immediately affect the activity of the plate, and can only be detected by calculating backward from some value of the activity when the two have reached equilibrium. The loss of thorium C is noticed directly from the reading immediately after treatment with the solvent.

It was found that water, solutions of salts, hydroxides, and acids dissolved both products, but thorium B was always dissolved in a relatively larger amount than thorium C. This was most noticeable in the case of short treatments, as would be expected from the rates of decay of the products. The results show that the solubility in water (boiling) is small, about 35 per cent. being dissolved in 15 minutes' treatment. With an hour's treatment about 70 per cent. had dissolved; but after about $1\frac{1}{2}$ hours the rate of solution was very little greater than the rate of decay of thorium B. A solution of potassium iodide (boiling) was found to dissolve the active deposit at more than twice the rate of the water. Dilute acids (HCl, HNO₃) had a much more rapid rate of solution even at ordinary temperatures. In the case of organic solvents the rate of solution was found to be about the same as in the case of water, but the thorium C dissolved more easily than thorium B. In fact, thorium B was absolutely insoluble in carbon bisulphide and methylene iodide, whilst thorium C was soluble to the extent of 20 per cent. in

* In these experiments I had no means of differentiating between thorium C₁, C₂, and D; hence I have used the term thorium C in the paper to represent all the products after the B. The nomenclature is the amended one of Rutherford and Geiger, *Phil. Mag.* xxii. p. 621 (1911).

10 minutes. Other liquids (bromoform, benzene, &c.) had a similar effect, but in these cases thorium B was dissolved to a slight extent.

I wish to record my thanks to Prof. Strutt, who suggested the above research and to whom I am indebted for his valuable assistance.

XXXVI. *On the Photo-Electric Effect in some Compounds.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the *Philosophical Magazine* for December 1912, Dr. R. S. Willows calls attention to a possible explanation of an experiment which I made during an investigation of the photo-electric effect in compounds (*Phil. Mag.* September, 1912). The experiment referred to is one in which it is shown that moist zinc chloride has a well-marked photo-electric effect, while dry zinc chloride is quite insensitive. Dr. Willows suggests that the emission of negative electricity by the moist zinc chloride may be identical with the effect observed by Mr. A. E. Garrett some years ago, and quite independent of illumination by ultra-violet light. The procedure in my experiments, however, was to insulate the electroscope (connected with the zinc chloride plate), and then to remove a shield which was interposed between the mercury lamp and the apparatus. The leaf of the electroscope only moved when the zinc chloride plate was illuminated. Hence the effect is a direct result of illumination by ultra-violet light. I have recently confirmed this observation with a simpler and less sensitive apparatus. As before, there was a well-marked effect when the moist salt was illuminated, but there was no measurable effect in the dark—this may be due to lack of sensitiveness.

I did not look for any emission of positive electricity from the illuminated substance. Had it been at all large, it would probably have been noticed. With the type of apparatus used in these experiments, it is always possible to explain an apparent emission of positive electricity from the plate as an emission of electrons to the plate from the surrounding electrode, which is unavoidably illuminated by reflected light, Special precautions would be necessary to avoid such spurious effects.

Yours truly,

A. L. L. HUGHES.

Cavendish Laboratory,
Cambridge.
January 11th, 1913.

FIG. 1.



FIG. 2.

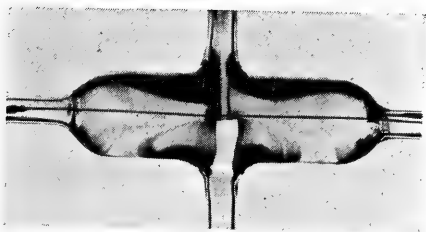


FIG. 3.

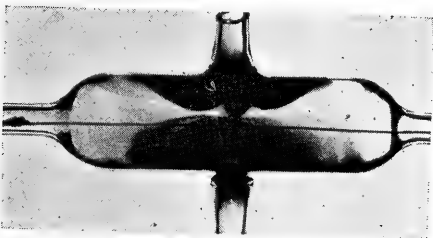


FIG. 4.



FIG. 5.



FIG. 6.



FIG. 7.



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XXXVII. *The Chemical Properties and Relative Activities of the Radio-Products of Thorium.* By HERBERT N. MCCOY, Ph.D., Professor of Chemistry, and CHARLES H. VIOL, Ph.D., Assistant in Chemistry, University of Chicago *.

I. *The Chemical Properties of the Radio-Products of Thorium.*

FROM the earliest history of radioactivity it has been recognized that the various active products of uranium, radium, and thorium have more or less definite, characteristic chemical properties. An accurate knowledge of such properties is of much importance in the study of these substances, since it forms the basis for their chemical separation from one another and from inert matter; at the same time it may throw some light on the problem of the transformation of matter. In attempting to determine the relative activities of the various radio-products of thorium, we found it necessary to study their chemical properties in some detail in order to be able to prepare them in (radioactively) pure form. A great many reactions are recorded in the literature, but, owing to the intricate and novel nature of the problem, some errors have doubtless been made; so that it becomes important that supposed facts be corroborated by independent observers.

During the writing of this paper, Soddy's monograph,

* Communicated by the Authors. Presented, in abstract, at the Eighth International Congress of Applied Chemistry.

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'The Chemistry of the Radio-Elements,' appeared *. This is a comprehensive review of published knowledge of this subject, but does not contain new material. In view of this *résumé*, we shall not dwell upon the historical aspects of the subject; we shall, however, include our results and conclusions which have previously been reported by others. In most cases our statements here are put in generalized form rather than as records of specific experiments. This is done on account of the very numerous separate experiments made during a period of three years.

The members of the thorium series with the symbols (or abbreviations) here used are as follows:—Thorium; mesothorium-one (Ms_1); mesothorium-two (Ms_2); radiothorium (Rt); thorium X (ThX); emanation (Em); thorium A (A) of period 0.145 sec.; thorium B (B) of period 10.6 hours; thorium C (C) of period 60.8 minutes; thorium D (D) of period 3.1 minutes †. The product C is doubtless complex ‡, the components being C_1 and C_2 .

Mesothorium-one.—Mesothorium-one is easily separated from thorium. So far as is now known, all reactions which separate ThX from Th also separate Ms_1 ; for it seems that the latter and ThX have essentially identical chemical properties. We have studied the following methods of separation of Ms_1 from Th:—

(1) When a dilute solution of thorium nitrate is precipitated by ammonia either in large or small excess, the greater part of the Ms_1 , 80 or 90 per cent., remains in the filtrate. This is a well-known reaction §, which we have regularly used in practice.

(2) Thorium nitrate is precipitated by a solution of sodium carbonate, but redissolves in an excess, the solubility being greater in the presence of some bicarbonate. For example, 5 g. of thorium nitrate redissolve completely in a solution of 5 g. of anhydrous sodium carbonate and 2 g. of sodium bicarbonate in 50 c.c. of water. If 2 or 3 mg. of ferric chloride in dilute solution be added, it will be precipitated as basic carbonate if the solution be warmed to 70° or 80°, and carry down all of the Ms_1 and all ThX present as well. In a similar manner, any barium present in the thorium solution

* Longmans, Green & Co., London and New York, 1912.

† Hahn & Meitner, *Verh. d. Phys. Ges.* xi. p. 55 (1909). On account of the recent changes of nomenclature, which we follow, we wish to avoid all uncertainty by mention of the periods.

‡ Hahn, *Phys. Zeit.* vii. pp. 412, 456 (1906). Barratt & Marsden, *Proc. Phys. Soc. Lond.* xxiv. p. 50 (1911). Geiger & Nuttall, *Phil. Mag.* [6] xxii. p. 613 (1911).

§ Boltwood, *Am. Jour. Sci.* [4] xxv. p. 93 (1907).

will also be left as insoluble carbonate containing, in the absence of iron, all of the Ms_1 and ThX.

(3) The precipitation of barium as sulphate in a thorium nitrate solution is not complete; but when the concentrations of barium salt and sulphuric acid are sufficient to form a precipitate, the latter carries down Ms_1 more or less completely. For example, 0.1 g. of barium sulphate removed all of the Ms_1 from 5 g. of thorium nitrate in 100 c.c. of water.

(4) The precipitation of thorium by oxalic acid does not give a definite separation of Ms_1 from thorium. In strongly acid solutions much of the Ms_1 is left in the filtrate; in a neutral solution, if the precipitate is allowed to settle out for one or two days, most of the Ms_1 is found in the precipitate.

A solution of Ms_1 which has been separated from thorium nitrate by ammonia shows the following chemical behaviour:—

(1) By the addition of a small amount of ferric chloride (5 mg. for 100 c.c.), and then an excess of sodium carbonate, the whole of the Ms_1 is thrown down with the precipitate formed when the solution is boiled.

(2) If the iron, as in (1), is precipitated by ammonia, the Ms_1 is only partially precipitated, the fraction increasing with the amount of iron and presence of carbonate.

(3) Calcium carbonate, formed by the use of ammonium carbonate, carries down Ms_1 completely.

(4) Mesothorium-one and barium are inseparable by any known chemical reactions; if barium be separated from any mixture it will be found to contain all of the Ms_1^* . According to Soddy † fractional crystallization of barium chloride leads to an enrichment in Ms_1 , just as in the case of radium.

(5) Ms_1 is not appreciably carried down with aluminium hydroxide when the latter is precipitated by pure NH_3 , free from carbonate. We use the gas obtained by warming concentrated ammonia to which barium chloride has been added.

(6) Ms_1 is not carried down with lead sulphide precipitated by hydrogen sulphide (in acid solution), and very probably also with no other sulphide under like conditions.

The Ms_1 used in our earlier experiments was obtained from thorium nitrate by precipitation of the thorium by ammonia. The filtrate always contained both ThX and Ms_1 , as the two are identical in chemical behaviour ‡. Since Ms_1 is itself inactive, its presence in such a case is established after the decay of ThX by means of the activity of the Rt, &c., which

* Soddy, *Trans. Chem. Soc. Lond.* xcix. p. 72 (1911).

† *Ibid.* See also Marckwald, *Ber. d. Chem. Ges.* xliii. p. 3420 (1910).

‡ Marckwald, *loc. cit.* Soddy, *loc. cit.*

it produces. The amount of Ms_1 obtainable from amounts of thorium nitrate at our command (2 to 3 kilos) was small ; we have obtained a large quantity of Ms_1 from another source. Through the courtesy of Mr. George P. Gilman, of the Lindsay Light Co., Chicago, to whom we wish here to express our sincere thanks, we obtained about 5 kilos of residues left from the refining of several thousand kilos of thorium. After the separation of the thorium salts from cerium &c. by the well-known carbonate process, and the ignition of the residue to remove organic dirt, there remained about 300 g. of material, of which the principal constituents were oxides of the rare earths, silicates, and about 10 per cent. of barium sulphate. The barium was separated completely by the following process. The powder was mixed with five parts by weight of an equimolecular mixture of dry sodium and potassium carbonates, and fused in portions at a red heat in iron crucibles. The melt was ground up, treated with hot water, and washed free from sulphate. The residue was dissolved in pure hydrochloric acid and the barium in the filtrate precipitated by sulphuric acid. The barium sulphate yielded 35 g. of nearly chemically pure barium chloride which contained all of the Ms_1 of the original material. After a few days the gamma-ray activity of this barium chloride was equal to that of 1.5 mg. of pure radium chloride. The Ms_1 preparation then contained the equilibrium amount of Ms_2 , and also Rt and its products in continually increasing amounts. The activity of the Rt formed per day was about ten times the uranium standard*.

Mesothorium-two.—We separated Ms_2 and Rt from the Ms_1 solution by adding 2 c.c. of a 5 per cent. aluminium chloride solution and passing in pure ammonia gas. The small precipitate of aluminium hydroxide carried down all of the Ms_2 , Rt, B, and C, together with a small amount of barium carbonate, owing to exposure to the air in filtering. The barium, of course, contained some Ms_1 and ThX. Radioactively pure Ms_2 was prepared by dissolving the alumina in acid, making the solution nearly neutral and removing Rt by means of thorium, precipitated by means of hydrogen peroxide, the Ms_2 being left in the filtrate. The alumina was then precipitated with ammonia two or three times to free it from barium, ThX, and Ms_1 ; finally, B and C were removed by means of mercuric sulphide. The details of these processes will be found under the reactions of the respective radio-products. The emanation, A, and D, which

* About 38 sq. cm. of a thick film of U_3O_8 . See McCoy & Ashman, *Le Radium*, v. p. 362 (1908); Amer. Jour. Sci. xxvi. p. 521 (1908).

are also present, cannot interfere ; even the latter will have practically all disappeared in the half hour usually occupied by the separations.

(1) Hahn* found that Ms_2 is carried down when zirconium hydroxide is precipitated by ammonia.

(2) Marckwald† found a similar behaviour with ferric iron and ammonia.

(3) We have regularly used aluminium hydroxide in the same way as a means of separating Ms_2 from solution. The Ms_2 seems to be carried down quantitatively with the aluminium. This reaction allows an easy and complete separation of Ms_2 from barium, Ms_1 , and ThX .

(4) Mesothorium-two is not carried down with the mercuric sulphide when hydrogen sulphide is passed into a slightly acid solution to which a little mercuric chloride has been added. This procedure will remove B and C completely if repeated two or three times.

(5) Mesothorium-two and Rt are closely alike in chemical properties, but not identical. The former is not carried down when a little added thorium nitrate is precipitated from a neutral solution by means of hydrogen peroxide at 60° or 70°. All the Rt is removed by the thorium. If the thorium used has been precipitated by hydrogen peroxide and changed back to nitrate before being used, it does not introduce any active impurity into the Ms_2 . This is the best method of separating Rt and Ms_2 .

(6) Barium sulphate precipitated in slightly acid Ms_2 solutions carries the latter down readily. Material for the films used in activity measurements was prepared in this way.

Radiothorium.—Since Rt cannot be separated from thorium by any known method‡, its only practical source is a preparation of Ms_1 in barium chloride, from which it can be completely separated by means of alumina, precipitated by pure ammonia. To obtain radioactively pure Rt from this precipitate it is not necessary to separate Ms_2 chemically, as the latter will decay in the course of a few days. ThX , B, and C are then easily removed, the former by precipitations of the alumina by means of ammonia, the latter two by means of mercuric sulphide. Three or four alternate precipitations of the alumina and of mercuric sulphide in the aluminium chloride solution readily give pure Rt. In addition to those reactions of Rt in which it is associated with thorium§, the

* *Phys. Zeit.* ix. p. 246 (1908). † *Ber.* xliii. p. 3420 (1910).

‡ McCoy & Ross, *Jour. Am. Chem. Soc.* xxix. p. 1709 (1907).

§ McCoy & Ross, *loc. cit.*

following, in absence of the latter element, have been studied:—

(1) Rt is completely precipitated with aluminium hydroxide by ammonia.

(2) Rt is completely precipitated with ferric hydroxide by ammonia and with basic ferric carbonate by excess of sodium carbonate.

(3) Rt is partly precipitated with barium sulphate in acid solution; under favourable conditions 50 per cent. of the Rt may be carried down.

(4) Rt is to a slight extent (about 5 per cent.) precipitated with mercuric sulphide or lead sulphide.

Thorium X.—On account of the seeming chemical identity of ThX and Ms_1 every preparation of ThX from thorium must contain more or less Ms_1 . However, the proportion of the latter will be quite small if thorium is used which has been freed from this pair of products a few days previously. A better plan is to use Rt as the source of the ThX. A single precipitation of an aluminium chloride solution of Rt by pure ammonia carries down all the Rt, and leaves nearly all of the ThX in the solution. From such a solution B and C may be removed completely by three or four precipitations in it of mercuric sulphide.

Thorium X is separated from thorium by the following reactions:—

(1) When thorium is precipitated from a nitrate solution by ammonia, pyridine, sodium thiosulphate, potassium chromate, metanitrobenzoic acid, or hydrogen peroxide, nearly all of the ThX is left in the filtrate.

(2) Precipitation of thorium by means of oxalic acid gives a partial but not complete separation. In one experiment with 25 g. of thorium nitrate about half of the ThX was left in the filtrate.

(3) Barium sulphate formed in a thorium solution carries down practically all of the ThX.

(4) Ferric iron removes all of the ThX from a solution of thorium in an excess of the carbonates of sodium under the conditions given for the separation of Ms_1 .

A solution of ThX free from Th shows the following behaviour:—

(5) ThX is carried down completely by (a) barium sulphate, from barium chloride and sulphuric acid; (b) ferric carbonate, from ferric chloride and excess of sodium carbonate; (c) calcium carbonate, from calcium chloride and ammonium carbonate; (d) ferric phosphate, from ferric chloride and secondary sodium phosphate.

(6) ThX is partially carried down with ferric hydroxide, from ferric chloride and pure carbon-dioxide-free ammonia, the fraction carried down varying with the amount of iron. If ordinary ammonia, containing carbonate, is used, all the ThX is found in the precipitate.

(7) ThX is not carried down to an appreciable extent when the following are precipitated by pure ammonia :—Aluminium, zirconium, cerium, lanthanum, yttrium, and didymium hydroxides.

(8) ThX is not carried down when the following are precipitated by hydrogen sulphide :—Lead, mercury, tin, zinc, and iron.

Thorium B and C.—(1) B and C are not separated from thorium when the latter is precipitated by most reagents ; but precipitation by pyridine* or by metanitrobenzoic acid † leaves B in the filtrate.

(2) B and C are removed very completely from a thorium solution when mercury, lead, or zinc are precipitated in it as sulphides by means of hydrogen sulphide.

As is well known, B and C are most easily obtained in free form by exposure of a negatively charged plate to the emanation. We have used very active Rt, contained in a few milligrams of ferric carbonate, as a very satisfactory source of the emanation. We found that a small amount of ThX, thrown out by recoil ‡, also accompanies the B and C in the active deposit. To exclude the ThX, the Rt was covered with a piece of tissue paper, which did not prevent the diffusion of most of the emanation. The deposit obtained in the course of a day or two was very active. It was dissolved from the platinum plate by hot dilute hydrochloric or nitric acid, and used in studying the reactions of B and C. Since B is inactive, with a period of 10·6 hours, and C gives alpha rays, with a period of 60·8 minutes, it is very easy to recognize the presence of either or both by observations of the change of activity with time. B and C behave similarly in the following reactions carried out with solutions of the active deposit :—

(3) B and C are carried down with aluminium or cerium when these are precipitated by ammonia.

(4) They are also carried down with lead, mercury, or zinc, when these elements are precipitated as sulphides by hydrogen sulphide in slightly acid solutions.

* Moore & Schlundt, *Trans. Am. Electrochem. Soc.* viii. p. 269 (1905).

† Ashman, *Amer. Jour. Sci.* [4] xxvii. p. 65 (1909).

‡ Hahn & Meitner, *Verh. d. Phys. Ges.* xi. p. 55 (1909).

(5) They are also carried down from slightly acid solutions by lead iodide or lead chromate.

(6) They are carried down when added ferric iron is precipitated by an excess of sodium carbonate or by ammonium acetate as basic acetate.

(7) They are carried down by bismuth oxychloride formed when bismuth chloride is added and the solution diluted.

(8) B and C are not carried down by mercuric iodide or silver chloride.

We can confirm the statements of Moore and Schlundt* that B and C are separated by the following reactions :

(9) Barium or lead sulphate precipitated in a solution of B and C carries down B completely and C only partially.

(10) Ferric iron precipitated by pyridine carries down C but not B.

(11) Ferric iron precipitated by fumaric acid from a boiling nearly neutral solution of B and C carries down all of the C and only a small part of the B. By three or four repetitions of the precipitation we have obtained C in which we could not detect any B after the complete decay of the former. The method seems to leave nothing to be desired as a means of preparing pure C. It is, of course, understood that the product so obtained contains the two components C_1 and C_2 , and, in addition, the beta-ray product D, which has a period of 3.1 minutes, and which will therefore accumulate rapidly in C even if it were removed by the treatment described.

In carrying out the reactions here recorded, in solutions of thorium free radio-products, the amount of precipitate was, as a rule, 10 to 50 mg. for 100 c.c. of the solution. In some cases, especially those in which the active substance is divided between precipitate and filtrate, the proportion of active substance carried down depends on the amount of the precipitate. The identity of each radio-product studied was fully established by means of the nature of its rays and its rate of decay.

II. *The Ratio of the Activity of Thorium B + C + D to that of Thorium X + Emanation + A.*

A knowledge of the relative activities of the equilibrium proportions of the active products in a given series is of importance for investigations in radioactivity. The problem has been pretty completely solved for the uranium-radium

* Trans. Am. Electrochem. Soc. viii. p. 269 (1905).

series*. The results in the thorium series are much less complete. Rutherford and Soddy were led to conclude that thorium, ThX, Em, and the excited activity contributed about equal shares of the observed activity of thorium. Since this early work was done, our knowledge of the series has been greatly extended. The complete series as we now know it is as follows:—

Thorium	Ms ₁	Ms ₂	Rt	ThX	Em	A	B	C	D
<i>a</i>	...	β, γ	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	β	<i>a</i>	β, γ

The product C is complex, the components being known as C₁ and C₂. The activity ascribed by Rutherford and Soddy to thorium alone is due to thorium plus an uncertain fraction of the equilibrium amount of Rt; while that of the excited activity is due essentially to C. Rutherford and Soddy † found that the activity of the products now known as B, C, and D was about 44 per cent. of that due to ThX and Em and (the then unknown) A (of period 0.145 sec.). Ashman ‡, working in this laboratory, found the following results:—Thorium free from Rt contributes 11 per cent. of the activity of thorium in equilibrium with its products; Rt, 20 per cent.; ThX and its products, 69 per cent. More recently Miss Leslie § has given the following figures as the relative activities of the various products:—Thorium, 5.5; Rt, 9.4; ThX, 12.2; Em, 48.6; C₁, 12.2; C₂, 12.2. She found the ratio of the activity of B, C, and D to that of ThX, Em, and A to be between 0.33 and 0.42.

In addition to the ratios determined by Rutherford and Soddy and by Ashman, it is possible to find by experiment the relative activity of Rt as compared with the subsequent products. We have made what we think to be quite accurate determinations of two of these ratios—that of B, C, and D to ThX, Em, and A, which ratio we will call *x*; and that of the activity of the radio-products of Rt to the activity of Rt alone, which we will call *y*. The principle of the determination of the ratio *x* is the same as in Rutherford and Soddy's experiment, although the details necessary to secure accuracy are different. ThX is prepared in radioactively pure form, and its activity is measured at known intervals from the time (time zero) at which the accumulation of the subsequent products begins. It is of fundamental importance that the

* McCoy & Ross, J. Am. Chem. Soc. xxi. p. 1705 (1907). Boltwood, Am. J. Sci. [4] xxi. p. 409 (1906).

† Rutherford, 'Radioactivity,' 2nd ed., p. 360.

‡ Am. J. Sci. [4] xxvii. p. 65 (1909).

§ *Le Radium*, viii. p. 356 (1911).

ThX should be entirely free, initially, from all the other radio-bodies. It is also necessary that the preparation should not lose appreciable proportions of the emanation. We used barium sulphate preparations of ThX and found them much less emanating than highly-heated oxides, such as ferric oxide. Our preparations were so active that exceedingly thin films were used, containing a milligram or less of barium sulphate. Thus, appreciable absorption of the alpha rays in the film itself was avoided.

The mathematical treatment of the problem has been given by Rutherford*. If R is the number of atoms of C formed in t seconds from n atoms of ThX originally present, then

$$R = n(ae^{-\lambda_1 t} + be^{-\lambda_2 t} + ce^{-\lambda_3 t}), \quad (1)$$

where

$$a = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)} = 1.336 \times 10^{-2},$$

$$b = -\frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)} = -1.460 \times 10^{-2},$$

$$c = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} = 1.242 \times 10^{-3}.$$

We have taken the decay constants in reciprocal seconds, as follows:—

$$\text{ThX}, \lambda_1 = 2.204 \times 10^{-6}; \quad \text{B}, \lambda_2 = 1.816 \times 10^{-5},$$

and

$$\text{C}, \lambda_3 = 1.899 \times 10^{-4},$$

the periods corresponding being 3.64 days, 10.60 hours, and 60.8 minutes. The details of our measurements to confirm these constants are given in Section IV. of this paper.

Then

$$R = n \times 10^{-2}(1.336 e^{-\lambda_1 t} - 1.460 e^{-\lambda_2 t} + 0.1242 e^{-\lambda_3 t}), \quad (2)$$

or

$$R = n \times 10^{-2} f(e),$$

where $f(e)$ is the expression in parenthesis. If n' represents the equilibrium number of atoms of C corresponding to n atoms of ThX, then

$$\lambda_1 n = \lambda_3 n'$$

if F_1 represents the fraction of the original number of atoms of ThX left after an interval t , then,

$$F_1 = e^{-\lambda_1 t}. \quad (3)$$

* 'Radioactivity,' 2nd ed., p. 360. We may neglect ThEm and A in the equation, since after ten minutes the equilibrium proportions of these products will be present with the ThX.

If F_2 represents, at the end of the same interval, the fraction which the number of atoms of C then present forms of the equilibrium number n' based on the original number n of the ThX atoms,

$$F_2 = \frac{R}{n'} = 10^{-2} \frac{\lambda_3}{\lambda_1} f(e) = 0.8620 f(e) \quad . \quad . \quad . \quad (4)$$

Let the alpha-ray activity of equilibrium amount of C be x times the activity of ThX plus Em and A. If a_0 is the initial activity of the film, and a is the activity after the interval t , then

$$\frac{a}{a_0} = F_1 + F_2 x, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$x = \frac{\left(\frac{a}{a_0} - F_1\right)}{F_2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

When the interval t is ten hours, $e^{-\lambda_3 t}$ becomes so small that its omission would cause an error in R of only 0.02 per cent., so for longer intervals this term may be neglected. Similarly, after two hundred hours the term containing $e^{-\lambda_2 t}$ becomes entirely negligible, and then,

$$F_2 = 0.8620 \times 1.336 e^{-\lambda_1 t} = 1.152 F_1. \quad . \quad . \quad (7)$$

This shows that, even after a long time, the relative amount of C present is not that which we call the equilibrium amount, which is the relative amount that would be present in an old thorium preparation, but a quantity 1.152 times as great.

In the preparation of radioactively pure ThX for these measurements, the ThX was separated from the pure Rt, which had produced it, by precipitating the Rt with aluminium hydroxide by means of pure ammonia. The filtrate contained the ThX. In order to remove any trace of Rt that might remain in this ThX solution, we acidified it with hydrochloric acid and added a few milligrams of thorium chloride which had just been reprecipitated three times by ammonia. The added thorium was then separated, thus insuring the absolutely complete removal of Rt. The ThX solution was concentrated to 20 c.c. and faintly acidified, a few drops of mercuric chloride solution were added and the mercury precipitated in the cold solution by means of

hydrogen sulphide. After boiling out the excess of hydrogen sulphide from the filtrate so obtained, this process was again carried out, being repeated in all five or six times to free the ThX from B, C, and D, all of which are precipitated with the mercuric sulphide. After the last precipitation of mercuric sulphide a few milligrams of barium chloride were added to the solution and barium sulphate precipitated in the boiling solution by means of sulphuric acid. The precipitate settled in a few minutes, and was washed several times by decantation and finally with alcohol. A very small amount, depending on the activity of the preparation but usually about 0.1 mg., was then made into a thin film on a flat metal plate. The time of the last precipitation of H_2S was taken as time zero, that is, the time when only ThX was present. Barium sulphate carried down B and a part of the C, the total amount of which formed during the time between the precipitation of the last mercuric sulphide and the barium sulphate was very small.

In order to determine what amount of B and C remained with the ThX after a series of precipitations of mercuric sulphide, a "blank" experiment was made as follows. The excited activity collected on a platinum dish was dissolved in a few c.c. of hydrochloric acid, and this solution was neutralized with pure ammonia, then made faintly acid; the volume being about 20 c.c. In this six precipitations of mercuric chloride were made, and then in the final filtrate a little ferric chloride was precipitated as basic carbonate by boiling the solution with an excess of sodium carbonate. Basic iron carbonate carries down completely ThX as well as B and C. The relative activities of the first four mercuric sulphide precipitates were 1.00; 0.026; 0.006; 0.002, the first being about twenty times as active as the uranium standard. The activity of the iron precipitate was 0.004, and this was found, from its rate of decay, to be due essentially to ThX, which must have been carried to the platinum dish by recoil. We therefore conclude that mercuric sulphide carries down B and C practically completely.

A knowledge of the activity at time zero is also required; but this cannot be found directly, as about thirty minutes elapse between the last precipitation of mercuric sulphide and the first activity measurement. By means of the now known value of the constant α , it is found by equation (5) that at $t=30$ minutes, the initial activity should have dropped to 0.998. Calculation also shows that at $t=1.15$ hours the activity should exactly equal that at time zero. We have therefore taken the observed activity at this interval after

the last HgS precipitation as equal to the true activity, a_0 , at time zero.

The activity measurements were made with the gold-leaf electroscope used by McCoy and Ashman*. The gold-leaf system was charged initially to 500 volts, and the potential fell about 100 volts during the observed discharge. The standard of activity was a thick film of U_3O_8 , as described in the same article by McCoy and Ashman. By using barium sulphate, a loss of any considerable amount of the emanation and thus of C was avoided. This error is compensatory†; since the emanation escaping in the electroscope with the A which it produces makes the observed activity greater than it would be if the emanation did not escape. But, owing to a loss of emanation, the activity of C is too small, and a calculation shows that the observed activity is approximately the true activity which would be observed if the emanation were not escaping and thereby reducing the quantity of C in the film. In our barium sulphate film not over 0.5 per cent. of the total emanation escaped.

In Table I. are given the results obtained with one of the ThX-BaSO₄ films. The first column gives the time (in hours) elapsed since time zero, the time of the last HgS precipitation. The second column gives the observed activities

TABLE I.

Interval, Hours.	Observed Activity.	Calculated Activity on basis of $x=0.427$.	Value of x calcu- lated from observed Activity.
0.000	1.000	1.000
13.65	1.121	1.120	0.430
15.70	1.130	1.124	0.437
17.52	1.127	1.127	0.428
18.15	1.124	1.127	0.422
19.82	1.127	1.127	0.427
29.08	1.102	1.104	0.424
42.22	1.034	1.033	0.429
70.62	0.8483	0.8466	0.430
87.52	0.7473	0.7430	0.434
113.68	0.6057	0.6049	0.429
165.25	0.4035	0.4017	0.433
220.93	0.2613	0.2585	0.440
286.0	0.1547	0.1542	0.431
332.9	0.1061	0.1063	0.424
381.4	0.0723	0.07240	0.426
			Mean... 0.429

* *Le Radium*, v. p. 362 (1908); Amer. Jour. Sci. xxvi. p. 521 (1908).

† McCoy & Ross, Amer. Jour. Sci. [4] xxi. p. 433 (1906).

at the various times, in terms of the activity, calculated for time zero, as unity. The third column gives the calculated values of the activity when the mean value found for x is used. The last column gives the values of x calculated from the observed activities of this film.

The average of fifteen values of x calculated from data on one film was 0.429; from seventeen values on another, 0.424; from eighteen values on another, 0.423; and from six values on a fourth, 0.431. The mean of these four is 0.427.

As will be seen from the table, the maximum activity, which is reached in about 18 hours, is 12.7 per cent. greater than the initial. In our preliminary experiments maximum activities between 9 per cent. and 19 per cent. above the initial were occasionally found. This variation was due to several causes: (1) our first films, in which ferric oxide was used, were several times as emanating as those made of barium sulphate; (2) ThX prepared directly from thorium salts always contains some Ms_1 ; (3) precipitation of thorium by ammonia does not completely separate B and C from ThX. Two possibilities then arise: if some B is left in the ThX film the initial activity is not affected, but the maximum will be too great; while if C is originally present in the film the initial activity will be too great, and in consequence the maximum apparently too small. Rutherford and Soddy* observed a maximum activity 17 per cent. above the initial, while the whole experiment led them to a value of 0.44 for x , which does not differ greatly from our value of 0.427. However, they took as periods of ThX and B 4 days and 11 hours respectively, instead of 3.64 days and 10.6 hours. Of course, any uncertainty regarding the periods of ThX, B, and C affects the value of x . The most probable values of these decay constants are considered in Section IV. of this paper. The values we have used in the calculation of x are those which seemed the most accurate.

III. *The Ratio of the Activity of the Products of Radiothorium to that of Radiothorium Alone.*

Radiothorium free from active impurities was prepared from a barium chloride mesothorium-one preparation in the following manner. After sufficient radiothorium had been produced in the solution, the aluminium from 2 c.c. of a five per cent. solution of aluminium chloride was precipitated in the Ms_1 , $BaCl_2$ solution by means of pure ammonia.

* Phil. Mag. [6] iv. p. 370 (1902).

The precipitate contained the Ms_2 , Rt, B, and C, together with traces of barium carbonate (due to the carbon dioxide of the air) and Ms_1 associated with the barium salt. This precipitate was dissolved in dilute hydrochloric acid, and the aluminium reprecipitated by means of ammonia. Several repetitions of this treatment removed all the barium and mesothorium-one. After three days, practically all the Ms_2 had decayed, and then the ThX which had formed, and the B and C which were present, were removed from the aluminium by a series of precipitations of the aluminium by ammonia, and by precipitating mercuric chloride with hydrogen sulphide in the faintly acid solution of aluminium chloride. Six to eight repetitions of each of these treatments were found to remove more than 99.5 per cent. of the ThX, B, and C which were present. After the last precipitation of the aluminium hydroxide which corresponds to time zero, the precipitate was dissolved in dilute hydrochloric acid, a few milligrams of barium chloride added, and barium sulphate precipitated in the boiling solution by the addition of sulphuric acid. After being washed by decantation several times, finally with alcohol, a few milligrams of the barium sulphate was painted on a flat metal disk so as to give a fairly uniform thin film. The activity of this film was measured at intervals in the electroscope, and was found to vary linearly during the first four hours, so that by extrapolation to time zero the initial activity could be calculated. Calling the initial activity of radiothorium free from its products a_0 , and the observed activity after an interval of t days, a : then

$$\frac{a}{a_0} = f_1 + f_2 y, \dots \dots \dots (8)$$

where f_1 is the fraction of the original number of radiothorium atoms left after the interval t days, f_2 the fraction at the time t_1 which the number of atoms of thorium X then present forms of the equilibrium number corresponding to the original number of Rt atoms, and y the activity of equilibrium amounts of the active products of Rt (including ThX, Em, A, B, C, and D) based on the activity of Rt as unity. If we take for Rt the period 737 days, and for ThX plus its products the period 3.64 days, then λ for Rt is 9.405×10^{-4} and λ_1 for ThX is 1.904×10^{-1} (day⁻¹):

$$f_1 = e^{-\lambda t}, \dots \dots \dots (9)$$

$$f_2 = \frac{\lambda_1}{\lambda_1 - \lambda} (e^{-\lambda t} + e^{-\lambda_1 t}). \dots \dots \dots (10)$$

For the values taken, $\frac{\lambda_1}{\lambda_1 - \lambda} = 1.005$.

If the interval is forty days,

$$e^{-\lambda t} = 0.9632 \quad \text{and} \quad e^{-\lambda_1 t} = 0.00057.$$

We may therefore neglect the term $e^{-\lambda_1 t}$ for intervals greater than forty days ; so that

$$f_2 = 1.005 e^{-\lambda t} = 1.005 f_1. \quad . \quad . \quad . \quad (11)$$

Equations (8) and (11) give

$$y = \frac{\left(\frac{a}{a_0 f_1} - 1 \right)}{1.005} = \frac{\left(\frac{a}{a_0 e^{-\lambda t}} - 1 \right)}{1.005}. \quad . \quad . \quad . \quad (12)$$

The significance of the last equation is interesting ; it shows that at any moment after about forty days, the amount of ThX present in the Rt originally free from the former product is 0.5 per cent. greater than the equilibrium quantity corresponding to the amount of Rt present at that moment.

Throughout the above argument there exists the tacit assumption that the products of ThX will all be present in equilibrium amounts, the amount of ThX present being the basis of reference. This will be so nearly true after forty days that the error introduced by this assumption is entirely negligible. In Table II. are given the data obtained from a

TABLE II.

Interval, Days.	Observed Activity.	Calculated Activity <i>y</i> 5.23.	Calculated values of <i>y</i> , from the observed Activity.
0.00	(1.000)	1.000
42.68	6.012	6.010	5.229
45.73	5.971	5.993	5.209
54.99	5.939	5.940	5.229
104.86	5.700	5.669	5.264

barium sulphate film of Rt. Column one gives the intervals in days, column two the corresponding activities, and column three the activities calculated by using the mean value of *y* as determined from five such films, viz. 5.23. The last column gives the values for *y* calculated from the observed

activities. The mean values obtained for y from observations on five films are as follows :—5·21, 5·19, 5·29, 5·31, 5·23; the average of these values being 5·23.

Owing to the fact that Rt is in part carried down with the mercuric sulphide precipitate, when freeing the Rt from B and C by this method it was thought desirable to try a frequent reprecipitation of the Rt-aluminium by ammonia, through a period of about a hundred and ten hours. By continually removing the ThX as fast as it formed, the B and C originally present would have practically all decayed after an interval equal to ten times the period of B. This was done, the precipitations of the aluminium hydroxide being made every six hours during the first day and a half; every four hours for the next day; every three hours for the next day; and finally every hour for a period of twenty hours. In this solution, after the final precipitation, barium sulphate was precipitated and the Rt-barium sulphate made into two films. These are the two giving average values of $y = 5·19$ and 5·21. These values for y are thought to be more nearly correct as far as the accuracy of our experimental data is concerned, because there was less uncertainty in this case as to what was time zero. Owing to the fact that about 0·5 per cent. of ThX, B, and C remain in the Rt when this is purified by the method first described, and that unless conditions are carefully controlled the quantity may even be greater, the extrapolation for the initial activity at the time of the last precipitation of the aluminium by ammonia (time zero) may lead to too high a value for a_0 . This leads to low values for y . However, C is not precipitated with barium sulphate to the extent that B is, and B has little activity as compared with the C, which it produces much more rapidly than Rt produces ThX. This causes the observed activity during the first few hours when the activity changes as a linear function of the time, to increase too rapidly. Extrapolation under these circumstances tends to give too low a value for a_0 , and this leads to high values for y . Both these effects were evident in some preliminary experiments. Any error in the decay constants of Rt will have an effect on the value of y . As our observations have not as yet been carried on over a sufficient length of time to enable us to calculate with great accuracy the period of Rt, we make use of the value found by Blanc*. It seems probable, from the description he gives of the preparation of his Rt, that his material was pure, but it is possible that it may have contained some Ms_1 , and so have given too great a

* *Phys. Zeitschr.* viii. p. 321 (1907).

value for the period. Our preliminary results show that Blanc's figure is of the right order. We have not observed any facts that would seem to confirm Miss Leslie's supposition that the period of Rt is only a few months*.

IV. *Periods of Thorium Products.*

Since the trustworthiness of our results would depend in so large a measure upon the accuracy of the decay constants used in the calculations, we have made careful redeterminations of these constants for ThX, B, and C, and a less accurate determination for Ms₂. From experiments started several months ago we expect to get accurate data for Rt, the period of which is so long that an accurate determination of its constant will require two or three years. The period of ThX was found in connexion with the determination of the ratio x ; the others were the results of special experiments. Mesothorium-two was precipitated with aluminium hydroxide by means of ammonia, in the Ms₁ barium chloride preparation. The Ms₂ was then freed from traces of Ms₁ by reprecipitation of the aluminium hydroxide. Radiothorium was removed by precipitating a few milligrams of thorium chloride in the faintly acid solution of aluminium chloride by means of hydrogen peroxide. The thorium had just been several times reprecipitated with ammonia to remove Ms₁ and ThX, while B and C were removed from the aluminium as has been described under the preparation of pure Rt. Finally, a precipitation of barium sulphate was made in the acid solution of aluminium chloride. This barium sulphate-Ms₂ was made into thin films on metal disks. The beta-ray activity of Ms₂ was measured by placing the film in a brass box with a tightly-fitting lid, the top of which was a thin sheet of aluminium. Table III. gives the data obtained

TABLE III.—Period of Ms₂.

Interval, Hours.	Activity.	Period, Hours.
0.0	3.086
3.783	2.012	6.12
14.75	0.5842	6.14
23.73	0.2118	6.14

* *Le Radium*, viii. p. 356 (1911).

with such a film. Column one gives the interval in hours, column two the corresponding activities, in terms of the uranium oxide standard as unity. Column three gives the period. Hahn * had previously found as the period of Ms_2 6.20 hours.

Lerch † found the period of ThX to be 3.64 days. Levin ‡ found 3.65 days, and Elster and Geitel §, 3.6 days. From our measurements of the activity of the ThX barium sulphate films we have calculated the period of ThX. Observations through an interval of seven days on one film gave a value of 3.64 days; on a second, through an interval of six days, 3.63 days; on a third, through an interval of eleven days, 3.65 days. The average of these mean values, 3.64 days, agrees exactly with Lerch's value.

Lerch || found a value of 10.60 hours for the period B, and this remains the accepted value. In preparing B for measurements of its activity, a platinum plate charged to 110 volts was exposed to the emanation from a very active film consisting of a few milligrams of basic ferric carbonate containing Rt with its products. The excited activity so obtained amounted in 24 hours to about 100 times that of the uranium standard. After a plate so covered with B and C was removed from the presence of the emanation it was kept 10 or 12 hours before measurements were begun in order that the amounts of C and D should attain a fixed ratio to that of B present. Nevertheless the periods found from the rate of decay increased very noticeably toward the end of the measurements. Thus for an interval of 36 hours the period was found to be 10.71 hours, but after 76 hours it became 11.78 hours, 10 per cent. greater. This led us to think that ThX was also present with the B, a small quantity collecting on the platinum plate by recoil. This bears out the results obtained in the "blank" experiment reported in Part II. When the excited activity was obtained in a similar manner from a hundred grams of thorium hydroxide, the total amount of excited activity collected in the same time was only about one-sixth as great, but the decay of this excited activity gave a constant period, one film giving a mean value of 10.59 hours, for measurements extending over an interval of fifty hours. When the active Rt film was covered with a sheet of tissue paper during the collection of the excited activity the

* *Phys. Zeitschr.* ix. p. 246 (1908).

† *Wien. Ber.* (1905).

‡ *Phys. Zeitschr.* vii. p. 515 (1906).

§ *Phys. Zeitschr.* vii. p. 455 (1906).

|| *Wien. Sitz.-Ber.* cxvi. (II a) p. 1443 (1907).

period of the B obtained on the plate was found to be 10.65 hours, for measurements extending over an interval of forty-three hours. The first measurements were made on this film two days after it had been activated, so that only a thirteenth of the original activity was left. Had the film contained any ThX, this would have still been present to the extent of about 70 per cent. of its original amount. The period obtained shows that practically no ThX can penetrate the tissue paper. We have used as the period 10.6 hours in our calculations of the ratios x and y . The period of C has been variously given between 55 minutes* and about an hour†. Lerch‡ has given a value 60.4 minutes, in which he corrected his observed period owing to the supposed presence of a little B. Following the directions given by Schlundt and Moore§ for the separation of B and C by the use of fumaric acid, we found it possible to obtain C entirely free from B, as was shown by the activity measurements. Twenty c.c. of a very active solution of B and C in dilute nitric acid was made just neutral with dilute ammonia, using methyl orange as an indicator. The solution was then made faintly acid with dilute nitric acid; three drops of 10 per cent. ferric chloride solution was added, and the solution boiled. Then 10 c.c. of a hot 1 per cent. fumaric acid solution was added, and the iron fumarate which precipitated was filtered out. This contained the C with a little B. The precipitate and paper were boiled with 1 c.c. of six times normal hydrochloric acid to dissolve the iron fumarate, and then after diluting to 20 c.c. with water the solution was filtered. The filtrate was treated with an excess of ammonia to precipitate ferric hydroxide, which is readily soluble in dilute acid while the fumarate is not. The ferric hydroxide precipitate, which contained the C, was then dissolved in 1 c.c. of normal nitric acid, and to this was added enough ammonia solution to neutralize the acid. This solution was boiled and the iron precipitated as before by the addition of 10 c.c. of hot fumaric acid solution. This treatment was carried out four or five times, and then the iron fumarate precipitate containing the purified C was dried on the paper and its activity measured at frequent intervals during a period of about seven hours. It may be added that the measurements were not begun until sufficient time had

* Rutherford, Phil. Trans. Roy. Soc., London, A. cciv. p. 169 (1904).

† Pegran, Phys. Rev. xvii. p. 424 (1903). Lerch, *Ann. de Phys.* xii. p. 745 (1903).

‡ *Wien. Sitz.-Ber.* cxvi. (II a), p. 1443 (1907).

§ Trans. Am. Electrochem. Soc. viii. p. 269 (1905).

elapsed for D (period 3.1 minutes) to have accumulated in sufficient amount not to influence the results.

In one experiment in which 43 activity measurements were made, the mean value of the period was found to be 60.89 minutes, with an average deviation from the mean of .20 minutes for the individual measurements. The last three measurements of this series, made after the activity had fallen to about 5 per cent. of the initial value, indicated periods of 60.77, 60.94, and 60.86 minutes; thus showing that the sample was free from appreciable amounts of B. Two similar series of experiments, each made with a separate preparation of C, gave mean periods of 60.89 and 60.71 minutes. The most probable value, as indicated by our experiments, is 60.81 minutes, which is a little greater than the value found by Lerch, 60.4. We have used the period 60.8 minutes in our calculations of the ratios x and y .

V. *The Range of Thorium X.*

Prior to the appearance of the recent paper of Marsden and Barratt*, our knowledge of the existence of two alpha-ray products in the excited activity of thorium rested largely on the fact discovered by Hahn, that alpha rays of ranges 8.6 and 5.0 cm. respectively were found by Bragg's method. This fact did not seem to be in accord with the value $x=0.427$ if one assumes that each alpha-ray product produces per second the same number of alpha rays as does the equilibrium quantity of ThX. We therefore constructed a range apparatus of the type described by Geiger and Nuttall, using instead of a quadrant electrometer a gold-leaf electroscope. The active source was a circular aluminium disk 5 mm. in diameter, which had been exposed, on negative potential, to a source of thorium emanation until it had an alpha activity about fifteen times the uranium standard. It was then removed from the emanation and allowed to stand over night so that its decay would occur exponentially with the period of B. The activities (corrected for decay during the experiment) at various pressures between 88.21 and 21.82 cm. of mercury gave graphs which coincide essentially with those published by Marsden and Barratt, and show the existence of two alpha rays of range 8.6 and 4.8 cm.

The difficulty apparently caused by the proof of the existence of two alpha-ray products in the excited activity has been removed, however, by Marsden and Barratt's discovery that for each 100 alpha particles of Em there are

* Proc. Lond. Phys. Soc. xxiv. p. 50 (1912).

but 65 alpha particles of range 8.6 cm. and 35 of range 4.8 cm.*. The detailed discussion of this matter is given in Section VI.

Hahn † also determined the ranges of ThX and Em, finding 5.7 and 5.5 cm., and arbitrarily ascribed the 5.7 value to ThX. We now know that ThX must contain the very short-lived A as well as the emanation. Marsden and Barratt have found the ranges of Em and A to be 5.0 and 5.4 cm. respectively. Furthermore, if we calculate the range of ThX by the law relating ranges and periods, first suggested by Rutherford, and later tested by Geiger and Nuttall for the radium and actinium series, we find the value 4.1 cm. We have made range determinations of ThX which show very clearly the presence of an alpha-ray product of much shorter range than that of the emanation. The longer ranges correspond with those given by Marsden and Barratt for Em and A, namely 5.0 and 5.4 cm. (at 0° and 760 mm. pressure), while our lowest value is 4.1 cm. (at 0° and 760 mm.). The ThX was prepared as was described in Section II., special care being taken to have a very active preparation, obtained by the use of only one milligram of barium chloride, to precipitate the ThX. A part of the active barium sulphate was made into a very thin film 4 mm. in diameter on the centre of the brass disk of the silvered ionization flask, of internal radius 9.075 cm. Measurements of the activity were then made at pressures between 75 and 23 cm. of mercury. Table IV. gives the observed results, at a room temperature of 24°3.

TABLE IV.

Pressure	74.93	66.03	57.11	52.15	49.57	48.43	47.68	46.56
Activity	1.000	1.003	1.022	1.034	1.040	1.048	1.054	1.041
Pressure	45.40	44.41	43.12	42.38	41.40	40.13	39.06	38.26
Activity	1.028	1.023	1.014	1.006	.988	.969	.948	.930
Pressure	37.26	36.20	35.21	34.14	33.01	31.67	27.82	23.77
Activity914	.888	.864	.841	.804	.760	.647	.526

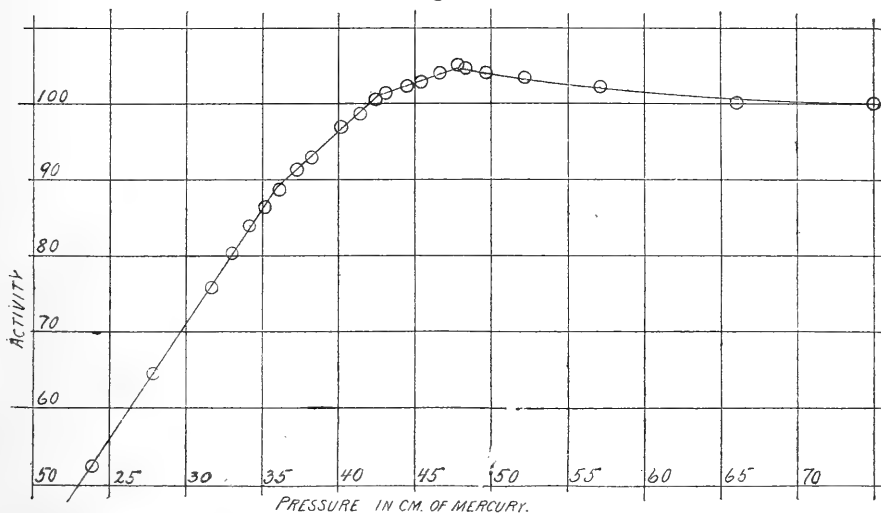
The graph obtained from these results (fig. 1) changes direction at points corresponding to pressures of 36.0, 42.7, and 47.6 cm. These points indicate ranges of 3.94, 4.68, and 5.22 cm. respectively at 0° and 76 cm. pressure. But these figures must be increased somewhat on account of a slight

* See also, Barratt, *Le Radium*, ix. p. 81 (1912).

† Phil. Mag. [6] xi. p. 792; xii. p. 82 (1906).

decrease of velocity of the alpha particles within the barium sulphate film. Although the latter was very thin, we estimate that its stopping power was equivalent to about 0.2 cm. of air. The ranges then become 4.14, 4.88, and 5.42 cm. for air at standard temperature and pressure. The

Fig. 1.



last two figures are close to the values found by Marsden and Barratt for Em and A ; namely 5.0 and 5.4 cm. respectively. Our lowest value must therefore represent the range of ThX. Three additional series of measurements gave results which agreed well with those represented by fig. 1. They all confirm Marsden and Barratt's values for Em and A and show, further, that the range of ThX is very close to 4.1 cm. at 0° and 76 cm. pressure. This value agrees with that calculated from the period of ThX and is also in good accord with that expected from its activity, as is shown in the following section.

VI. Relation of Activity to Range.

After the ranges of a number of the radio-products had been measured by Bragg, Boltwood* suggested that the ionization produced by equal numbers of alpha particles of various substances was proportional to their ranges. He found that the activity of radium plus the rapidly changing products of radium was 5.64 times the activity of radium alone, while the sum of the ranges was 5.60 times the range of the alpha particles of radium. Attempts to establish

* *Phys. Zeitschr.* vii. p. 489 (1906).

similar relationships in the thorium series have heretofore been unsatisfactory. There were reasons why this might be so. In the first place the activity ratios were not known with sufficient accuracy, as we pointed out in Section II. of this paper; secondly, Boltwood's assumption might not be correct; and finally, as is now known, the components of C are not successive, C₁ giving 65 per cent. and C₂ 35 per cent. as many alpha particles per second as the equilibrium amount of the emanation. We have made careful determinations of two activity ratios, x and y (Sections II. and III.), by means of which we can compare the activities of the respective substances with their ranges. The work of Bragg*, and Hahn †, Rutherford ‡, Geiger §, Taylor || and others has thrown much light on the nature of the ionization curve of an alpha particle. It is now quite certain that ionization is not uniform along the path of an alpha ray, but that it increases markedly toward the end of the range. It appears, however, that during the last two or three cm. of their ranges, the alpha particles of the various radio-bodies all behave exactly alike in respect to the number of ions produced in each corresponding element of the remainder of the path. This conclusion is wholly consistent with the fact that all alpha particles are atoms of helium, and differ from one body to another only in initial velocity. Bragg ¶ concluded that the ionization of an alpha particle was given by the expression

$$i = \frac{a}{\sqrt{R-Z} + 1.33},$$

where a is a constant, R is the range, and Z is the distance the particle has already travelled; $R-Z$ is then the remainder of the range to be traversed. More recent investigations by Geiger** have shown that

$$i = \sqrt[3]{\frac{a'}{R-Z}}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

where i is the ionization at any part of the path, and where R and Z have the same significance as before and a' is a constant. If we represent the total ionization of an alpha

* Phil. Mag. [6] xi. p. 617 (1906); xiii. p. 333 (1907).

† Phys. Zeitschr. vii. p. 412 (1906).

‡ Phil. Mag. [6] xii. p. 134 (1906).

§ Proc. Roy. Soc. A. lxxxiii. p. 505 (1910).

|| Phil. Mag. [6] xxiii. p. 670 (1912).

¶ Loc. cit.

** Loc. cit.

particle by I, then $dI=i dZ$, and therefore

$$I = \int_0^R \sqrt[3]{\frac{a'}{R-Z}} dZ = KR^{2/3} \dots \dots (14)$$

where K is a constant. The facts just considered indicate that the ionization of equal numbers of alpha particles is not directly proportional to the respective ranges, as Boltwood suggested. In a radioactive series if each atom of each alpha-ray product gives one and only one alpha particle upon disintegrating, then for equilibrium proportions of the products of the series, each product will give rise to equal numbers of alpha rays per second. In such a case the relative activities of various products will be proportional to the $\frac{2}{3}$ power of their ranges. In Table V., column three, are given values of $KR^{2/3}$, K being so chosen that the value of the expression is unity for Rt.

TABLE V.

Product.	Range.	$KR^{2/3}$.	Calculated Activity.	Observed Activity.	P.c. of total alpha-ray Activity.
Th	2.58	0.79	0.79	11.4
Rt	3.67	1.00	1.00	1.00	14.4
ThX	4.1	1.08	} 3.60	3.665	15.5
Em	5.0	1.23			17.6
A	5.4	1.29			18.6
C ₁	8.6	1.76	} 5.6	1.540	22.5
C ₂	4.8	1.20			
B+D	0.025	

Now we have found in Section II. that the activity of B + C₁ + C₂ + D compared with the equilibrium amounts of ThX + Em + A gave the value $x=0.427$; and in Section III. that the activity of ThX + Em + A + B + C₁ + C₂ + D compared with the equilibrium amount of Rt gave the value $y=5.23$. From these results it follows that the activity of B + C₁ + C₂ + D is 1.565 times that of Rt, and also that the activity of ThX + Em + A is 3.665 times that of Rt. A small correction must be made on account of the beta-ray activity of B and D. We found that this activity was 1.6 per cent. of the total activity of B + C₁ + C₂ + D for our electroscope. The alpha-ray activity of C₁ + C₂ is therefore 1.540 times that of Rt, while the beta-ray activity of B + D is 0.025. These observed

activities are recorded in column five of Table V. In column four are given the calculated activities of the two groups of products; for ThX + Em + A the calculated activity is taken as the sum of the values of $KR^{2/3}$ for the three products. For $C_1 + C_2$ the sum of the values of $KR^{2/3}$ would be 2.96 while the actual value is 1.54. The explanation of the apparent discrepancy is found in the fact, established by the work of Marsden and Barratt * and of Barratt †, that C_1 and C_2 together give per second the same number of alpha particles as the equilibrium amounts of each of the preceding substances, C_1 giving 65 per cent. and C_2 35 per cent. of the total. If we add together these fractions of the respective values of $KR^{2/3}$ for C_1 and C_2 we get 1.56, which is almost identical with the experimental value 1.54.

In the last column of Table V. are given the theoretical activities, calculated on the basis of the value under $KR^{2/3}$, excepting that for the activity of the components of C, $KR^{2/3}$ is taken as 1.56. The theoretical activity as calculated for thorium is 11.4 per cent. of the total activity of the series. Now Ashman ‡ has found 11 per cent. for this activity. The agreement is excellent, but the experimental result is probably not wholly trustworthy because of the probable presence of some ionium in the thorium; since Boltwood § has found that all the ionium in a mineral remains with the thorium. Ashman's thorite contained some uranium and must therefore have contained some ionium. However, we may expect that the activity of thorium will actually have just about the value Ashman found. The close agreement between the activities actually observed, as represented by the ratios x and y , and those calculated from the ranges, give further experimental evidence of the validity of the expression $I = KR^{2/3}$; they also lead us to believe that the uncertainty which up to the present time has existed in regard to the thorium series has at last been removed.

Summary.

1. Numerous chemical reactions of the radioactive products of thorium were studied. It was found that each product has its own characteristic chemical properties. From a knowledge of these properties, methods were worked out for the separations of the various products from inactive

* *Loc. cit.*

† *Le Radium*, ix. p. 81 (1912).

‡ *Am. Jour. Sci.* [4] xxvii. p. 65 (1909).

§ *Am. Jour. Sci.* [4] xxv. p. 292 (1908).

substances and from one another, and for the preparation of several of these products completely free from radio-active impurities.

2. The relative activities of thorium B + C + D and thorium X + Emanation + A was determined by preparing thorium X entirely free from B + C + D and determining its change of activity with time. Knowing the periods of each of the substances, the activity of B + C + D was found to be 0.427 of that of thorium X + Emanation + A.

3. By determining the initial activity of pure radio-thorium and its change of activity with time, it was found that the products of radiothorium are 5.23 times as active as the radiothorium itself.

4. In order to make the calculations of the results of 3 and 4, it was necessary to know the periods of the various radio-bodies accurately. As a result of new determinations, the accepted periods of thorium X and thorium B were confirmed as 3.64 days and 10.60 hours respectively. The period of thorium C was found to be 60.8 minutes instead of 60.4 minutes (Lerch).

5. It was shown that the accepted value of the range of thorium X 5.7 cm. was incorrect, and that the true value is 4.1 cm. This value is in good accord with that expected from the period of this substance.

6. It is shown to be theoretically probable that the total ionization of an alpha particle is proportional to the $\frac{2}{3}$ power of its range. It is then shown that the activities found in 3 and 4 are in excellent agreement with those expected from the ranges of the various active substances.

Kent Chemical Laboratory,
University of Chicago,
October, 1912.

XXXVIII. *Production of Fluorescent Röntgen Radiation.* By J. CROSBY CHAPMAN, B.Sc., Tutor in Mathematics at King's College, London, late Research Student of Gonville and Caius College, Cambridge*.

TO satisfy the corpuscular theory, Professor Bragg† has recently suggested that not only ionization is an indirect phenomenon due to β rays, but that in addition the fluorescent X-rays themselves are possibly due also to action of the β -rays. That is, the fluorescent X-radiation is a tertiary and not a secondary effect, being merely due to the expelled

* Communicated by Professor C. G. Barkla.

† Bragg and Porter, Proc. Roy. Soc. A. vol. lxxxv. p. 350.

electrons themselves colliding with other atoms, and in this way producing the peculiar type of radiation known as fluorescent X-rays.

This theory, that the secondary homogeneous radiation results from the bombardment of atoms by ejected corpuscles, has been discussed in a research published with Mr. Piper *, as well as in a later paper †. The object of the experiment, suggested by Professor Barkla, and described in the later paper, was to test this theory directly. Allowing X-rays to fall on bromine vapour (C_2H_5Br), it was found that the presence of CO_2 in the first case, and H_2 in the second case, as the gas separating the ethyl bromide molecules, made next to no difference in the amount of secondary radiation emitted by the bromine when excited by X-rays. Whereas on this theory, since the CO_2 , which is a heavy gas, must absorb many of the expelled corpuscles, while a light gas cannot do this, the CO_2 ought to interfere with the conversion of the cathode rays into bromine X-rays, and thus a greater intensity of secondary radiation be obtained in the second case than in the first. This was not found to be so.

The results obtained were :—

Secondary radiator C_2H_5Br .

$$\frac{\text{Intensity of secondary radiation with } H_2 \text{ separating } C_2H_5Br \text{ molecules}}{\text{Intensity of secondary radiation with } CO_2 \text{ separating } C_2H_5Br \text{ molecules}} = 1.01.$$

The calculations given in the paper show that, if the theory is correct that the expelled corpuscles from bromine do, by subsequently bombarding fresh bromine atoms, make the latter emit homogeneous radiation, there should be a noticeable difference in the intensity of the radiation in the two cases. From the fact that the radiations were of the same intensity, the conclusion naturally followed that this theory of the indirect action of the X-rays in producing fluorescent X-radiation is untenable.

This experiment, however, does not seem to Professor Bragg to be decisive. For in a recent paper published with Mr. Porter, he criticises the conclusion stated above, in the following way ‡:—"This does not seem to me conclusive. If the production of X-rays is a consequence of the encounters of cathode rays with bromine atoms, there will be an ample opportunity for the effect to take place even though the CO_2 molecules are scattered among the bromine atoms. If an electron meets a CO_2 molecule first it is not arrested there,

* Chapman and Piper, *Phil. Mag.* June 1910.

† Chapman, *Phil. Mag.* April 1911.

‡ *Loc. cit.* footnote on pp. 350 & 351.

but deflected, and may have hundreds of encounters before it; so that its chance of meeting a bromine atom is practically as great as ever. If it is argued that the cathode ray is 'absorbed' by the bromine and CO_2 in proportion to weight, it must be answered that whatever 'absorption' may mean, there is no clear evidence of the universality of Lenard's law."

Such a fundamental difference between the action of the CO_2 molecules and the Br atom on the electron, as Professor Bragg has been compelled to ascribe, is purely hypothetical, and until experimental evidence of its truth can be brought forward, it must be treated as an assumption which is merely a convenience when explaining the results of the above experiment from the point of view of the corpuscular theory.

With regard to Lenard's law, at the time when the paper was written, and in fact even now, the law is not completely established, but recently it has been shown to be an approximate representation of what actually takes place, even for slowly moving corpuscles, and Professor Bragg himself has published results from which he draws important conclusions which necessitate a far more accurate fulfilment of this law than was needed in the experiment referred to.

However, to settle the point as to whether the fluorescent X-rays are produced directly or indirectly, the following experiment was devised, so that in the case of one X-radiator the corpuscles were certainly absorbed in the radiating substance, while in the case of the other radiator, the corpuscles lost their energy in a substance in which it is impossible to produce measurable secondary fluorescent X-radiation. In constructing an experiment to meet this demand two difficulties have at once to be faced. In the first place, if any appreciable fraction of the total amount of corpuscular radiation produced in a sheet of metal is to escape from the metal, the latter must be exceedingly thin, of the order of 10^{-5} cm. Secondly, the method of separating the different parts of the radiator must be such as will readily allow of the whole serving as a convenient secondary radiator.

Recently, however, I have shown* that gold with other heavy elements is a most efficient secondary X-radiator; and that its type of radiation †, both in regard to the secondary X-radiation and the β -rays produced, differs in no respect from the type of radiation emitted by an element such as bromine of the more usual group K (elements Cr—I). Now gold in the form of leaf can be obtained in exceedingly thin

* Chapman, Proc. Roy. Soc. A. vol. lxxxvi. (1912).

† Chapman, Proc. Roy. Soc. A. vol. lxxxviii. (1913).

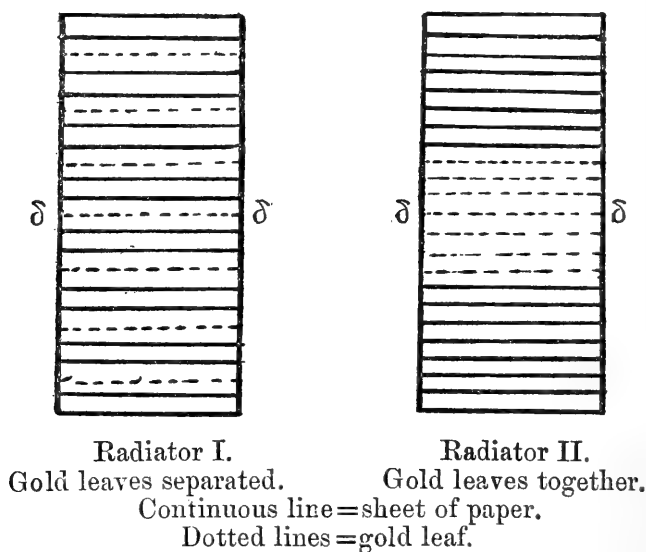
sheets of the order of thickness required by the experiment. In addition, it has often been proved that carbon is a most inefficient corpuscular radiator, so much so that in all experiments where this type of radiation from the walls of the ionization-chambers is to be minimised, carbon in the form of paper is used for this purpose. So that, instead of air or CO_2 separating the different portions of the radiator, which is in the form of gold leaves, it is possible to use thin paper.

Apparatus.—The apparatus, with a few modifications, was similar to that used in previous experiments.

Construction of Radiators.

The two radiators, the efficiency of which as fluorescent X-ray producers it was required to determine, were constructed as follows:—

Fig. 1.



The important point to notice is that both radiators consisted of the same mass of gold and paper, namely, seven gold leaves and sixteen paper sheets, the sole difference between the two radiators being the relative positions of the gold and the paper.

In radiator I. we have first two sheets of paper then a gold leaf, then again two sheets of paper and another gold leaf, and so on till the seven gold leaves and the sixteen paper sheets are all used. In radiator II., however, we take first eight sheets of paper, then seven gold leaves altogether,

followed by another eight sheets of paper. Each of these two arrangements of gold leaf and paper was mounted between thick aluminium frames. In this way the leaves and paper were gripped around their edges, and with a little care in fixing the outer paper sheets with shellac on to the frames, it was arranged so that the paper in each case was stretched tightly across the frame. The two aluminium frames were pressed together in a vice and melted wax was run around their edges, so that the two remained tightly pressed to one another. The thickness of the effective parts of each radiator, that is, in the centre, where the X-rays struck and where there was no aluminium, was such as could be accounted for by the presence of the paper sheets alone. The desirability of leaving no air-gaps will become apparent in the calculations. A third radiator was made in a similar manner containing only the sixteen paper sheets.

It may be added here, that alternate gold leaves, taken from the same book, were used to form the radiators I. and II. respectively. It will be noted that, owing to the arrangement of the paper and the gold leaves and their small absorption, the gold fluorescent radiation was absorbed to approximately the same extent in the two cases.

Object of this Construction.

Imagine now the same primary beam of X-rays to be passed through radiator I. and radiator II. successively. Consider, first, radiator I: suppose there is being produced in the central gold leaf δ a certain amount of corpuscular radiation. It will be shown later that the greater part of the energy of these corpuscles escapes from the leaf. This is the sole assumption made at the present, and it is proved by actual experiment later in the paper. Then in radiator I. the corpuscles which emerge from the central leaf δ will at once pass into paper, where they will be totally absorbed, so that their existence as regards acting on gold atoms is at an end. Whereas in radiator II. corpuscles produced at δ will have to spend practically the whole of their energy in the gold leaf itself. So that, while in the case of radiator I. the corpuscles spend a large part of their energy in the paper, in the case of radiator II. the corpuscles spend almost all their energy in the gold. So that, quite apart from any meaning "absorption" may have, we should expect, if the expelled electrons by bombarding other gold atoms produce secondary X-radiation, that the radiator II. would be more

efficient than radiator I. in producing such radiation. Two sheets of paper were used to separate the gold leaves in radiator I. so as to ensure in all parts a sufficient thickness to absorb the whole of the incident corpuscular energy.

The research resolves itself into three parts:—

- (1) to test the efficiency of the two X-radiators;
- (2) to determine the penetrating power of the exciting primary beam;
- (3) to investigate what fraction of the total corpuscular radiation produced in one gold leaf escapes from that leaf.

Efficiency of the two X-radiators.

The following were measured:—

- (a) the efficiency of radiator I. as a fluorescent X-ray producer;
- (b) the efficiency of radiator II. as a fluorescent X-ray producer;
- (c) the intensity of scattered radiation from the third radiator consisting only of paper.

Using the results so obtained, the ratio of the efficiencies of the radiators I. + II. was calculated. It only remained to show that the radiation which was being measured was actually the gold characteristic radiation. In order to prove this the absorption in aluminium of the radiations from the gold radiators was determined, allowance being made for the scattered radiation from the paper. No correction was applied for the scattered radiation from the gold itself; this correction is of such a small order that in the experiment it would have served no purpose. The absorption coefficient

$\left(\frac{\lambda}{\rho}\right)$ of these rays in aluminium was equal to 20.6, while the most accurate value of $\frac{\lambda}{\rho}$ for gold radiation in alumi-

nium = 21.6, and this is after somewhat tedious corrections have been applied. This near agreement of 20.6 and 21.6 showed that the radiation, the intensity of which was being determined, was actually the gold radiation.

The results obtained after subtraction of the scattered radiation from the paper are given below in tabular form. In each case the radiation when radiator I. was used is taken as the standard.

TABLE I.

Intensity of fluorescent X-radiation from radiator I. [gold leaves separated]. B.	Intensity of fluorescent X-radiation from radiator II. [gold leaves together]. A.	Ratio $\frac{A}{B}$.	Mean $\frac{\lambda}{\rho}$ in Al of primary.
100	100	1.00	1.8
100	104	1.04	0.8
100	96	.96	1.1
100	99	.99	4.1
100	99	.99	3.9
100	97	.97	7.5
100	100	1.00	4.8

Taking mean value

$$\frac{\text{Intensity of fluorescent X-radiation from radiator II.}}{\text{Intensity of fluorescent X-radiation from radiator I.}} = .99$$

$$\frac{\lambda}{\rho} \text{ in Al of gold characteristic radiation experimental} = 20.6$$

$$\text{Standard value} = 21.6$$

Penetrating Power of the Primary Radiation.

The X-ray bulb furnishing the exciting primary radiation was fitted with a palladium side tube, which enabled the rays leaving the bulb to be made of any desired degree of hardness. The value of the mean penetrating power of the radiation was obtained by finding the absorbability of the radiation scattered by a thin carbon sheet, the scattered radiation from carbon being almost identical with that of the primary radiation. In order to obtain the very hard rays, not only was the bulb worked at its maximum hardness, but in addition thick aluminium (.19 cm.) was placed in the path of the primary beam so as to absorb all but the hardest rays from the bulb. The values for the absorption coefficient $\left(\frac{\lambda}{\rho}\right)$ in aluminium of the primary beam are given in column 4 of Table I.

The importance of knowing the order of the penetrating power of the primary beam is clear from the work of Cooksey*, Innes†, Sadler‡, and Beatty§, which shows that the velocity

* Cooksey, Amer. Journ. Sci. (4) xxiv. (1907).

† Innes, Proc. Roy. Soc. lxxxix. (1907).

‡ Sadler, Phil. Mag. March 1910.

§ Beatty, Phil. Mag. Aug. 1910.

with which the corpuscles are ejected varies directly with the penetrating power of the exciting radiations. Suppose in this experiment it had been possible to use a very soft radiation, say $\frac{\lambda}{\rho}$ in aluminium = 60, the corpuscles ejected by this primary would have had relatively low velocities, and would be rapidly stopped, and few would be able to emerge from the gold leaf, so that the total effect would have been that practically all the corpuscular radiation would have been absorbed in the gold leaf, whether radiator I. or radiator II. was used. In this case the experiment as a test of the two theories breaks down. If now instead of a soft radiation the hard primary beam is employed, it can be shown that as large a fraction as 70 per cent. of the total corpuscular energy produced in a gold leaf escapes from the metal.

As the only assumption underlying the experiment depends on the fact that a reasonable fraction of corpuscles which have still sufficient velocity to excite the characteristic radiation from the gold shall escape, it was thought advisable to determine this fraction experimentally, though the penetrating power of the corpuscular radiation could easily have been calculated from the figures of Beatty or Sadler.

*Corpuscular Radiation produced in Gold by the
Tin Radiation.*

Tin serves as a convenient secondary radiator, for it emits in moderate quantity a very hard radiation the absorption coefficient $\left(\frac{\lambda}{\rho}\right)$ of which in aluminium = 1.5, a hardness of the order of the primary beam used in this experiment (see Table I. column 4). The object of this part of the research was to determine what fraction of the total energy of the corpuscles produced in a gold leaf by tin radiation is able to escape from the metal itself.

This was accomplished in the following manner:—An ionization-chamber (1 cm. thick), kindly lent me by Mr. Philpot, was fitted with an electrode made of fine aluminium wire mounted on an aluminium frame, and this electrode was connected to an electroscope. The back and front of this chamber were made of carbon. Initially when rays passed through the chamber, the ionization, which was small, was almost wholly due to the ionization of the air by the tin

radiation. Supposing now on the internal incidence face of this ionization-chamber a single gold leaf is affixed; and the tin rays again passed through the chamber. There is then superimposed on the original effect due to the air, the ionization produced by that fraction of the corpuscular rays produced by the tin radiation which is able to escape from the gold and produce ionization in the air. If now a second leaf be added, and if it happens that corpuscles are able to penetrate more than one thickness of leaf, there should be an increase in the ionization due to that fraction of the corpuscular rays from the first leaf which is able to penetrate the second leaf, and thus ionize the air in the chamber. In this way leaf after leaf was added until further leaves produced no increase in the intensity of ionization. At this point the layer of gold on the internal incidence face could be considered infinitely thick from the point of view of corpuscular rays.

In the following table the values of the ionization corresponding to the various numbers of radiating leaves are given.

TABLE II.

Metal acting as corpuscular radiator—Gold.

Exciting radiation—Tin.

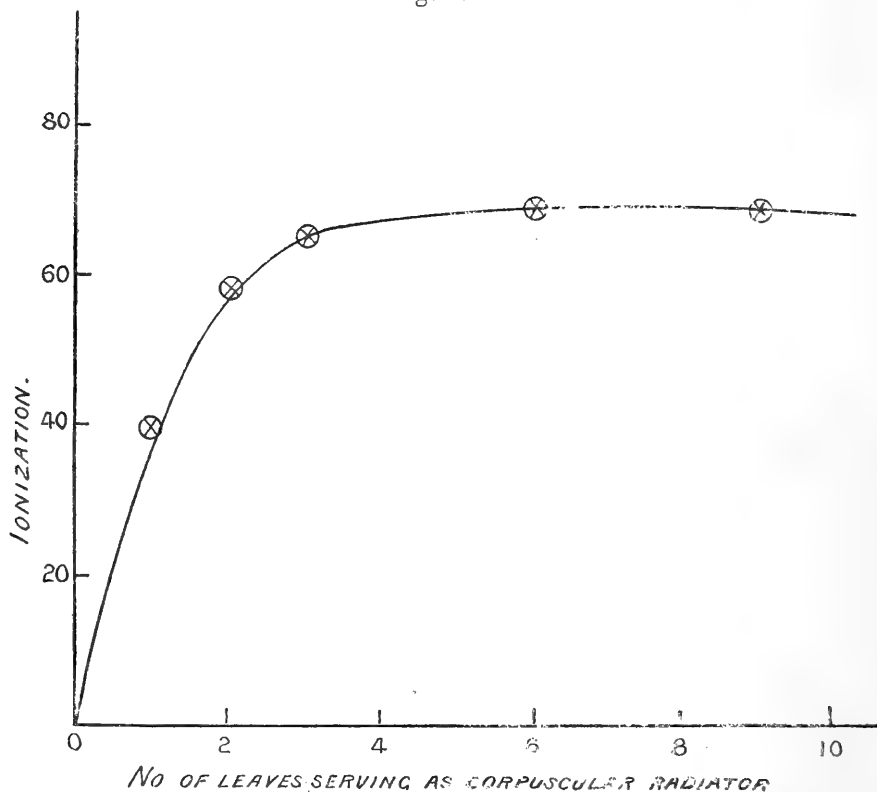
Thickness of gold = 9.9 to 10.1×10^{-6} cm.

No. of gold leaves serving as corpuscular radiator.	Intensity of Ionization due to :— (I.) Direct air effect. (II.) Corpuscles expelled from gold.	Intensity of corpuscular radiation.
0	2.0	0
1	6.0	4.0
2	7.9	5.9
3	8.6	6.6
6	9.0	7.0
9	8.9	6.9

From these results a curve (p. 368) is plotted showing the relation between ionization due to corpuscular radiation, and the number of leaves which served as corpuscular radiator.

From measurements of this curve it can be shown at once that the total energy of the radiation produced in the gold leaf by the tin radiation is absorbed to the extent of 52 per cent. (approximately), when it passes through a thickness of gold

Fig. 2.



equivalent to one leaf. Since the absorption of corpuscular rays in one gold leaf is 52 per cent., this means that half that thickness will absorb something of the order of 30 per cent.

Arithmetical calculation gives the following figures when one gold leaf is considered.

Gold leaf thickness = 9.9 to 10.1×10^{-6} cm.

Corpuscular radiation produced by tin characteristic rays.

$$\frac{\text{Energy of corpuscular radiation emerging from gold leaf}}{\text{Total energy of corpuscular radiation produced in gold leaf}} = .3.$$

And this was the fraction it was required to determine.

The following results should be stated as showing the smallness of error due to absorption of the gold X-radiation by the paper and gold leaf.

Percentage absorption of gold fluorescent radiation by:—

- (1) A single thickness of paper = .7 per cent.
- (2) A single thickness of gold leaf = 2.0 „

It is now possible to calculate as completely as the experiment demands what should be the difference in the efficiencies of the two radiators I. and II., supposing that the bombardment theory to be an accurate representation of fact.

From Whiddington's* results, assuming the general law, velocity of ejection of corpuscles by tin radiation

$$= 119 \times 10^8 \frac{\text{cm.}}{\text{sec.}}$$

Now velocity of corpuscles when they no longer have the power of producing gold X-rays $\left(\frac{\lambda}{\rho} \text{ in Al} = 21.6\right)$

$$= 74 \times 10^8 \frac{\text{cm.}}{\text{sec.}}$$

Therefore the minimum fraction of energy which they must lose before they cease to produce gold X-rays is

$$\frac{(119)^2 - (74)^2}{(119)^2} = 61 \text{ per cent.}$$

But it is experimentally found that they lose only 30 per cent. of their energy before they emerge from the gold; that is, they must still possess the power of producing an intense X-radiation from the gold. The experiment shows, however, that the X-radiation is just as intense when this corpuscular energy is absorbed in paper as when it is absorbed in gold.

If the X-radiation produced in gold be taken as proportional to the diminution in energy of the corpuscles in the gold, the ratio of the X-ray efficiencies of the two radiators would be

$$\frac{\text{Efficiency of radiator II.}}{\text{Efficiency of radiator I.}} = 2.1.$$

Correcting for the surface effect in radiator II., this ratio works out at

$$\frac{\text{Efficiency of radiator II.}}{\text{Efficiency of radiator I.}} = 1.9.$$

The experimental ratio of the two efficiencies is

$$\frac{\text{Efficiency of radiator II.}}{\text{Efficiency of radiator I.}} = .99.$$

No conceivable hypothesis as to the relative efficiencies of corpuscles of varying velocities in producing X-rays can explain this difference between the theoretical and the experimental ratio. So that this experiment seems clearly to

* Proc. Roy. Soc. A. lxxxvi. p. 376 (1912).

prove that the bombardment theory does not represent even to a small extent what takes place when secondary fluorescent radiation is produced. That is, fluorescent radiation cannot be an indirect effect of β -ray activity.

In addition, it will be noticed that in the case of radiator I. there is much less ionization in the gold than is the case in radiator II. So that this experiment seems to negative those theories which assume that it is on recombination of the gold atoms that the fluorescent X-radiation is produced.

The evidence of this paper strengthens the theory put forward by Professor Barkla*, and supported by later papers, namely, that the atom from which the electron is ejected is the seat of production of the radiation.

Summary.

The paper deals with Professor Bragg's theory that the fluorescent X-radiation is produced indirectly by the action of the expelled β -rays, and not by the direct action of the primary beam.

His criticisms of a previous paper in which an experiment is described to test this theory have been discussed.

Another experiment has been performed, in which the theoretical objections he raised have been obviated. The results obtained agree precisely with those given previously, and indicate that Professor Bragg's bombardment theory does not represent even to a small extent the process of production of the fluorescent Röntgen radiation.

In conclusion, I wish to express my thanks to Professor Barkla for his continued help and advice.

Wheatstone Laboratory,
King's College.

XXXIX. *The Ionization produced by Heated Salts.* By CHARLES SHEARD, M.A., Assistant Professor of Physics, Ohio State University, and Fellow in Physics, Princeton University†.

INVESTIGATIONS have been made in recent years upon the existence of positive and negative emissions from heated salts and upon the values of e/m of the emitted ions. Many substances have been examined as to their ionizing

* *Jahrbuch der Radioaktivität und Elektronik*, iii. (1908).

† Communicated by Professor O. W. Richardson. Read before the American Physical Society, New York Meeting, March 2nd, 1912. See Abstract, *Phys. Rev.* xxxv. pp. 234-236, 1912.

powers * and certain conclusions drawn which are indicated below. The relation † between the values of the currents and the temperature is generally that given by Richardson's ‡ formula

$$i = A\theta^{\frac{5}{2}}e^{-\frac{b}{\theta}}.$$

It seems likely that this formula always holds good, provided the chemical nature of the source of the ionization is unaffected by the temperature changes. The positive current-time relations show a rise to a maximum value of the current followed by decay with time, and are satisfactorily represented by a formula § of the type

$$i = A(e^{-\lambda_2 t} - e^{-\lambda_1 t}).$$

The only exceptions to this statement of which the writer is aware are the results of Schmidt's || experiments with haloids of cadmium. Some substances apparently give copious positive and others abnormally large negative ionizations ¶. Most of these experiments have been made with salts in contact with metallic plates, usually platinum. Garrett and Willows **, in repeating the work of Beattie †† upon the conductivity produced by heating common salt and iodine on an insulated zinc plate, concluded "that the metal is a necessary part to the changes causing the conduction." This is likewise the view held by W. Wilson ‡‡ in some recent investigations with aluminium phosphate. Furthermore, Horton §§ has advanced the view that molecules of CO gas, liberated from the glass walls of the containing vessel and diffusing into the surface of the metal, finally emerge in an ionized condition. It is important, then, that the ionization

* Some of the substances which have been found to produce ionization at temperatures of about 400° C. are listed in papers by Garrett (Phil. Mag. [6] xiii. p. 729, 1907) and Schmidt (*Ann. der Phys.* [4] xxxv. p. 404, 1911).

† Garrett & Willows (Phil. Mag. [6] viii. p. 437, 1904); A. E. Garrett (Phil. Mag. [6] xiii. p. 728, 1907).

‡ Proc. Camb. Phil. Soc. xi. p. 286, 1902, and Phil. Trans. 201, p. 516, 1903.

§ *Loc. cit.* under † and also A. E. Garrett (Phil. Mag. [6] xx. pp. 573-591, 1910).

|| *Ann. der Phys.* [4] xxxv. p. 401 (1911).

¶ A. Wehnelt (Phil. Mag. [6] x. p. 80, 1905). J. J. Thomson (Camb. Phil. Soc. Proc. xiv. p. 105, 1907).

** *Loc. cit.*

†† Phil. Mag. [5] xlvi. p. 97 (1899) and [6] i. p. 442 (1901).

‡‡ Phil. Mag. [6] xxi. p. 634 (1911).

§§ Proc. Roy. Soc. ser. A. vol. lxxxiv. p. 433 (1910); Camb. Phil. Soc. Proc. xvi. p. 89 (1911).

effects from heated salts be examined, using apparatus which does not involve the heating of the salt in contact with metal.

The nature of the ionization process or processes has not been adequately investigated. Richardson* examined the positive ionization from several sulphates and phosphates by the "strip" and "tube" methods. The tube method gave no such diminution in the ionization at low pressures as was observed when the salts were heated on the platinum strip. These results are explicable if the ionization arises in part or in whole from the decomposition, not of the salt itself, but of an intermediate product. The results presented in this article will show that there is both an ionization of the salt vapour and an emission of ions from the salt.

Determinations of the specific charge† of the emissions from heated salts have shown positive ions characteristic of the base of the salts and electrons only. In this paper it will be shown that with fresh samples of cadmium iodide there is a large emission of negative ions when it is first heated. In general, the current-E.M.F. curves for the negative ionization are very similar to those for the positive. This indicates that the negative ions are comparable in mass with the positive ions. This point of view is confirmed by measurements, carried out about the same time by Professor Richardson‡, of the value of e/m for the negative ions given out by the iodides of the alkaline earth-metals. The values found agreed with the view that the ions were atoms of iodine carrying a single electronic charge. I have not yet had an opportunity to investigate the effect of a magnetic field on the initial negative emission from cadmium iodide.

Apparatus and Methods of Experimentation.

Fig. 1 represents a form of apparatus used in the earlier experiments. It consisted of hard glass tubes, each 30 cm. long and 2.5 cm. internal diameter, joined by a cross-connexion of glass 2 cm. long and 1.5 cm. diameter. Each tube was closed with a ground-glass stopper, into which were sealed the electrodes. The outer electrodes were cylinders of platinum gauze each 6 cm. in length. When in place they fitted closely against the surfaces of the containing tubes. This ensured the heated tube and salt being at the potential of the gauze, and also prevented the passage

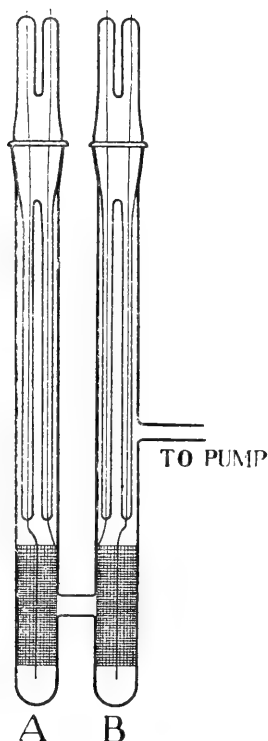
* Phil. Mag. [6] xxii. p. 669 (1911).

† Richardson (Phil. Mag. xx. p. 981, 1910). Davisson (Phil. Mag. xxiii. p. 121, 1912).

‡ Phys. Rev. xxxiv. p. 386 (1912).

of salt vapour between the outer glass walls and the gauze. The inner electrodes, centralized with respect to the outer ones, were of platinum wire 0.2 mm. in diameter. Each wire was sealed in glass; the lower 6 cm. only were left exposed.

Fig. 1.



The double-tube apparatus was heated in an electric oven, and was inserted into it some 10 centimetres above the electrodes. The furnace was first heated some 50°C . higher than the temperature desired, the tube was then introduced and the required temperature obtained in 3–5 minutes. This is important, particularly in determining the initial stages of the rise or decay of the ionization with time. By means of control resistances it was possible to keep the temperature constant within 5 degrees over several hours of experimentation.

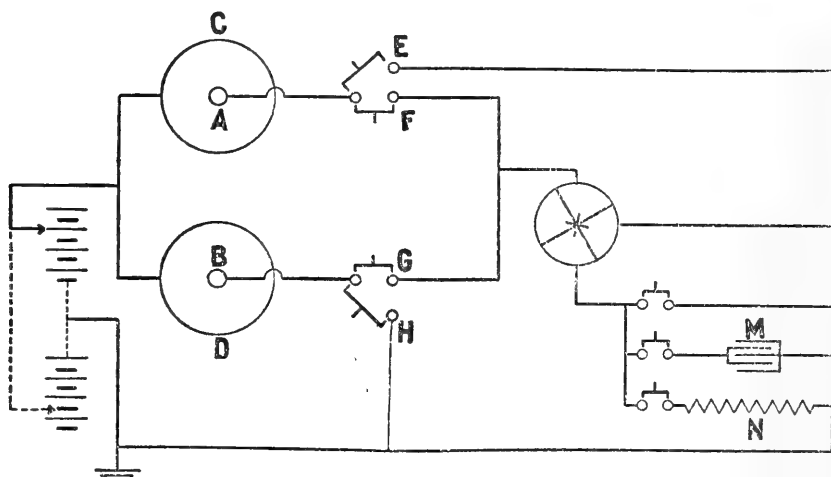
Before each test the main tubes and the electrodes were thoroughly cleansed with nitric acid, sulphuric acid, alcohol and ether mixture and distilled water, and then slowly dried. At temperatures between 350°C . and 500°C . and with potential of ± 200 volts applied at the outer electrodes, leakage currents were obtained which ranged in value from 1×10^{-13} to 1×10^{-11} ampere. These currents

were in general negligible in comparison with those obtained after the introduction of the salts.

The samples of salt investigated were inserted in the same half of the double-tube arrangement. In the presentation of results, the tube carrying the salt will be referred to as A and the "unsalted" one as B.

The connexions and method of operation are outlined in fig. 2. The outer electrodes, C and D, were connected to

Fig 2.



a source of high potential. The inner electrodes, A and B, were connected in turn to one pair of quadrants of the electrometer, or earthed, by means of suitable keys represented as E, F, G, and H. For currents less than 10^{-8} ampere, the time rate of deflexion method was used, a one-microfarad subdivided condenser M being connected in parallel with the insulated quadrants. For larger currents the electrometer was shunted with a resistance of a megohm N, or any fraction thereof, and the steady deflexions observed.

Experiments showing that the Ionization is partly an Ionization of the Vapour.

Current-E.M.F. curves were obtained for both the positive and negative ionization from samples of cadmium iodide under different conditions of pressure and temperature. Table I. contains a representative set of data given under a pressure of 9 cm. and at a temperature of $450-5^{\circ}$ C. Approximate saturation of currents in both tubes was obtained at a potential of ± 160 to ± 200 volts. The currents remained fairly constant under potentials ranging from 160

to 320 volts when ionization by collision occurred. The above remarks are applicable to positive and negative current-E. M. F. relations obtained at pressures of 9, 7, 3, 1, and 0.4 cm. In general it was impossible to obtain, during the first ten or fifteen minutes' heating, current readings which were of any value in determining the saturating potential. The very rapid initial rise or decay of the ionization, as exhibited in the curves in fig. 3, explains the difficulty. It was expedient, therefore, to determine the relations between current and potential in the regions of steady or slow decay with time effects.

TABLE I.

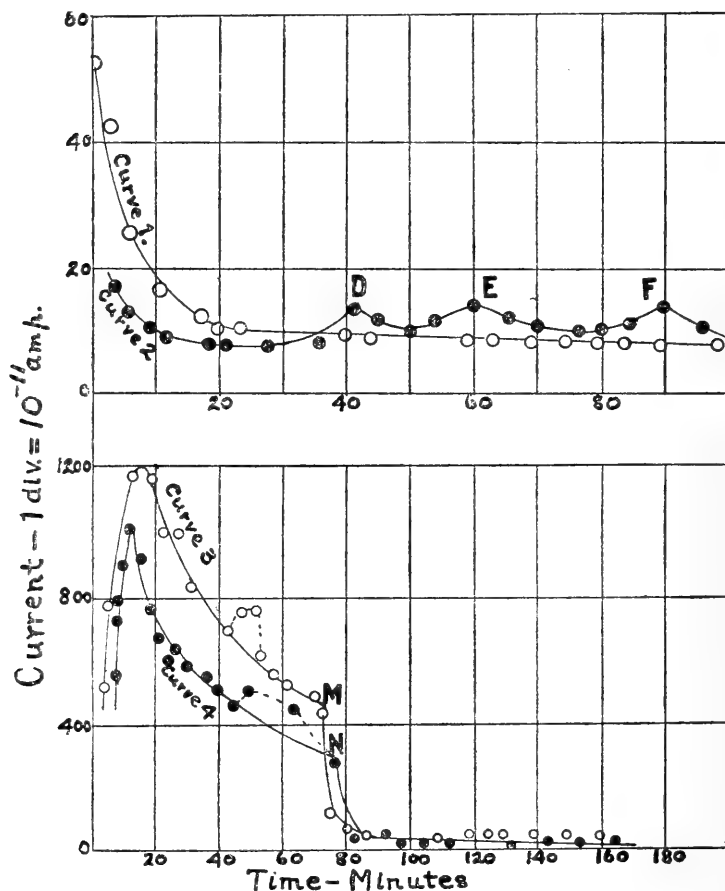
P = 9 cm. Hg. T = 450–5° C. 1 div. = 1×10^{-10} amp.

POTENTIAL. (Volts.)	CURRENT.	
	(Tube A.)	(Tube B.)
+40	25.8	4.6
+80	46.9	11.7
+120	64.0	18.3
+160	80.0	22.5
+200	82.5	22.1
+240	85.0	26.8
—40	22.0	2.0
—80	41.5	2.9
—120	60.3	4.4
—160	70.8	5.4
—200	70.0	5.3
—240	73.2	6.7

The positive ionization was examined under a constant pressure of 1.3 cm. and at temperatures which ranged from 345° C. to 465° C. 300 mgms. of cadmium iodide were used in each case. Two sets of results are given in fig. 3; curves 1 and 2 show the current-time relations at a temperature of 385° C., curves 3 and 4 at 465° C., under the saturating potential of 200 volts. Curves 1 and 3 pertain to the ionization effects in the salted tube A. Curves 2 and 4, obtained with the unsalted tube B, show that *there can be an ionization in B when uncharged matter only enters it*. In fact the ionization in B may equal or exceed that of the salted tube. The current-time relations at 415° C. showed that the currents in B, initially equal to those in A, were after two hours' time twice or thrice as large. The ionization produced in both tubes when the temperature was below the

melting-point of CdI_2 (402°C . at atmospheric pressure) showed decay with time from initial maximum values. In contrast, curves 3 and 4, obtained at a temperature of 465°C ., show a rise of current to a maximum value after

Fig. 3.



15–20 minutes' heating followed by values falling off asymptotically with the time. Also, the current-time relations, determined at a temperature of 415°C . and a pressure of 1.3 cm., showed a rapid rise in five minutes' heating to a maximum value of the current which was maintained for about twenty minutes and then decayed with time to a steady value after an hour's heating. These results at temperatures above 400°C . are not in accord with Schmidt's conclusion that the cadmium salts differ from other salts used in not exhibiting an initial rise, and that the products of decomposition, the active and inactive, have rates of decay, λ_1 and λ_2 , which are nearly equal to each other. The results may be made to fit this explanation if λ_1 and λ_2 have about

equal values at the lower temperatures, but vary with the temperatures at different rates.

The maximum positive currents in the salted tube increased in the ratio of 20:1 in passing from a temperature of 350° C. to 415° C. at a pressure of 1.3 cm., the same quantity of salt being used in the two cases.

The ionization in tube B exhibited several maxima during the period of slow decay or steady valued currents in tube A. Points D, E, and F in curve 2 of figure 3 indicate such maxima. Also, at 415° C. it was found that the currents in A decayed asymptotically with the time from a value of 105×10^{-10} ampere at the thirty-minute point, to a steady value of 22×10^{-10} ampere after an hour's further heating. In the same interval of time the maxima and minima given below occurred in B:—

Time (min.)	50	60	73	80	92	120
Current	88	40	71	44	63	36

1 div. = 10^{-10} ampere.

These secondary maxima appeared under different conditions of pressure and temperature. It is not likely that they were due to salt which had condensed on the cooler portions of the tube and fallen back, for these maxima did not occur in tube A which carried the salt and, moreover, they did not occur in the emission from the original salt, but were found in the ionization effects from the first distillate as tested by the air-cooled electrode method (see page 386). Professor Richardson * has recently reported work in which he was unable to obtain with cadmium iodide the specific charge characteristic of the cadmium atom. Values were obtained, however, showing the presence of sodium, potassium, and zinc. Complex chemical changes may, then, have taken place, causing these maxima and minima in the positive ionization, or else several substances present as impurities and having different decay constants may have been the sources.

A rapid fall in current values is shown in curves 3 and 4, figure 3, at the points M and N, followed immediately by a practically steady current condition of $5-10 \times 10^{-11}$ ampere covering a period of over an hour. These end effects indicate the disappearance of the salt and the rapid ionization of the salt vapour present in the tubes. The steady current stage may be attributed to the ionization from the platinum alone, or to the ionization from the products formed at the electrodes due to the interaction of the vapour and the platinum.

* Physical Review, xxxiv. p. 386 (1912).

When the temperatures were below 400° C., the melting-point of cadmium iodide, the greater portion of the salt inserted in A remained after the experiments had been made.

The effect of changing potential from positive to negative values, and *vice versa*, on the ionization in tubes A and B, was investigated at a temperature of 345–350° C. and a pressure of 1.3 cm. The positive current-time relations during the first twenty minutes of heating were identical with those represented in curves 1 and 2, figure 3. The steady current state, reached after 30–40 minutes' heating, furnished an excellent opportunity of studying the effects produced by a reversal of the electric field.

TABLE II.

1 div. = 1×10^{-11} ampere.

TUBE A.			TUBE B.		
Time. (Min.)	Volts.	Current.	Time. (Min.)	Volts.	Current.
25	+120	46.0	26	+120	9.6
27		43.2	28		9.6
31	–120	6.8	29	–120	46.0
33	+120	55.3	32		31.0
35		39.2	36	+120	8.9
37		34.3	39		7.3
42	–120	7.2	41	–120	33.0
44		3.4	43		12.3
46		2.6	45		7.6
48	+120	41.5	49	+120	9.5
52		25.0	53		6.2
55		18.2	57		5.2
59		15.3	60		4.7

An inspection of the results given in Table II. shows that a reversal of potential in tube A from positive to negative voltages gave negative current readings of about one-fifth to one-tenth the positive values immediately preceding. When the potential was again reversed, the positive readings were temporarily increased, but fell off asymptotically with the time and ultimately assumed values fitting upon a curve indicating the general decay with time of the positive ionization. The corresponding treatment of B showed the exact counterpart to the phenomena in A; since, for example, the reversal from a positive to a negative potential gave a current about five times as great as the previous positive

potential reading. Schmidt* investigated in detail the effects produced by a reversal of the electric field, using cadmium iodide at temperatures of 260°C . and 332°C . and a pressure of 3.7 mm. The results recorded in Table II. agree in general with those of Schmidt in the case of the effects observed in tube B. The results, however, in the salted tube A (which should be compared with Schmidt's results) are quite different.

The ionization produced by cadmium iodide under positive and negative potentials was further investigated by making use of a modification of the apparatus shown in fig. 1. The glass portions were similar in form to those previously described; the tubes were 15 cm. in length and 1 cm. in diameter. The arrangement of electrodes in tube B was the same as shown in figure 1. The inner electrode, however, of the tube carrying the salt consisted of a closed platinum cylinder fitted in symmetrically with respect to the outer platinum gauze. The distance between these two electrodes was 2 mm. It was thus possible to obtain saturation with greater surety, allowing the passage of uncharged matter only into B. The experiments with this apparatus were made at a temperature of $353\text{--}360^{\circ}\text{C}$. and at a pressure of 1 cm. Saturation was obtained in A for both positive and negative potential currents with 80–120 volts. Table III. contains data for representative current-E.M.F. curves.

TABLE III.

TUBE A.			TUBE B.	
V	+	—	+	—
10	3.6	3.4
20	5.0	4.8
40	6.3	5.6	16.0	2.0
80	9.8	5.8	26.3	3.4
120	10.2	6.2	29.0	5.1
160	10.8	7.0	30.1	5.3
200	13.7	8.3	32.0	7.0

The current-time effects were examined in both tubes under the saturating potential of ± 120 volts. The pressure was 1 cm. and the temperature $358\text{--}363^{\circ}\text{C}$. The ionization in the salted tube, under either a positive or negative potential, fell off from an initial maximum and reached the steady state after forty minutes' heating. This constancy

 * *Loc. cit.*

and practical equality of positive and negative potential currents continued for two hours or more. Plenty of salt remained in A at the end of the experiment. The positive and negative current-time relations for A were identical in form with those given in curve 1, fig. 3. The values given for tube A in Table IV. are in excellent agreement with Schmidt's results. The ionization effects in the unsalted tube, however, showed marked contrasts with those obtained in the salted tube. The magnitude of both negative and positive potential currents in B in comparison with those in A (see Table IV.) is a most noticeable feature. Both currents in A had about the same value at corresponding times; in the unsalted tube the ratio of the initial negative maximum to the initial positive maximum was 7:1. These experiments fully confirm the statement that the ionization is partly an ionization of the vapour.

TABLE IV.

P = 1 cm. T = 358–363° C. 1 division = 10^{-10} ampere.

Time. (Min.)	Tube A.		Time. (Min.)	Tube B.	
	+	–		+	–
5.....	65		6.....	2347	
7.....		101	10.....		17745
11.....	13.3		12.....	1547	
13.....		30.3	14.....		16198
16.....	2.8		17.....	1183	
19.....		5.7	20.....		12103
22.....	1.26		23.....	819	
25.....		1.83	26.....		9100
28.....	0.61		29.....	637	
32.....		0.83	31.....		7462
37.....	0.43		35.....	455	
43.....		0.47	38.....		5187
53.....	0.38		48.....	192	
57.....		0.39	50.....		2366
			60.....	57	
			62.....		910
			67.....	27	
71.....	0.31		69.....		544
77.....		0.37	86.....	3.1	
			90.....		83
			98.....	2.3	
100.....	0.35		102.....		48
104.....		0.35	121.....	0.78	
			123.....		7.4
155.....	0.42		166.....	0.7	
157.....		0.41	169.....		1.4

Several attempts were made to carry out similar experiments with this form of apparatus at temperatures above the melting-point of cadmium iodide. Enormous irregularities

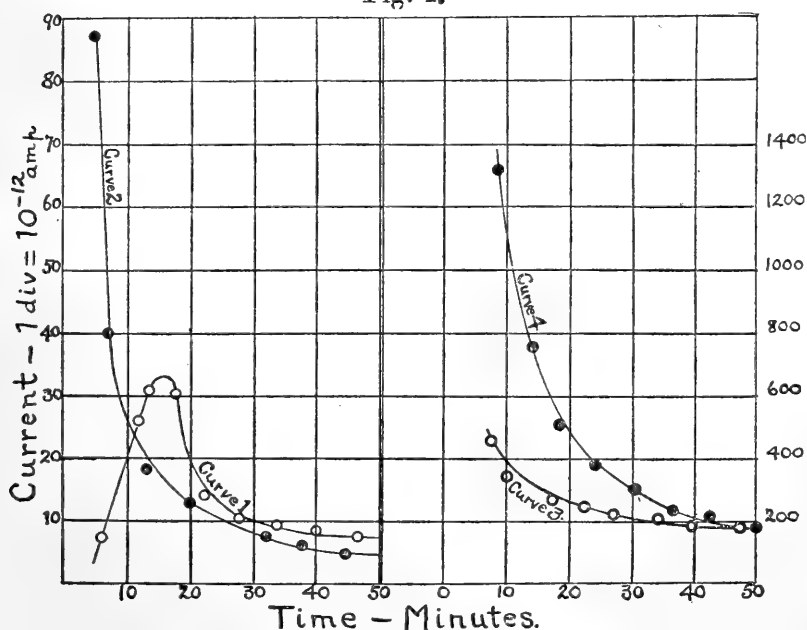
superimposed upon a rapid growth of current with time appeared soon after the heating had been commenced. Observation showed that the vaporized salt condensed on the cooler glass portions of the electrodes and finally bridged across, forming an increasingly better conductor as time went on.

Ionization Effects with Iodine and a Comparison with those given by Cadmium Iodide.

Shortly after the experiments just described (Table IV.) had been commenced, a heavy cloud of what seemed to be iodine vapour appeared in the unsalted tube B. There was little indication of its presence in other portions of the apparatus. This vapour condensed upon the cooler parts of the tube and electrodes and partially disappeared with time. The tube had a strong odour of iodine when opened. Similar phenomena were observed in other experiments.

These observations suggested that the liberation and ionization of the iodine constituent might play an important role in the current-time relations, especially in the effects observed in the unsalted tube. A considerable quantity of iodine was, therefore, inserted in A, and the conditions of the previous experiment, using cadmium iodide, as to temperature, pressure, and potential were duplicated. The current-time relations in the tube containing the iodine are

Fig. 4.



given in fig. 4, (o) indicating positive readings and (●) negative values. Curves 3 and 4 of this figure show the corresponding relations in tube B. These curves show that

the maximum currents obtained in both tubes under negative potentials exceeded the maximum positive currents in the ratio of 3 to 1. This is in agreement with results published by A. Campetti*, in which he showed that the electric dispersion in iodine with platinum electrodes and for temperatures up to 500° C. was greater for negative than for positive potentials.

The positive ionization with iodine in A rose to a maximum value in twenty minutes and then decayed with time. There is no similarity between the positive time-current relations in A, using iodine and cadmium iodide under similar conditions of pressure and temperature. The negative current curves are, however, comparable in form. The positive and negative current relations in tube B are similar in the two cases. The following ratios were found in the case of iodine (fig. 4) and cadmium iodide (Table IV.).

	RATIO.	I.	CdI ₂ .
(1)	$\frac{\text{Max. Negative in B}}{\text{Max. Negative in A}} =$	13	17
(2)	$\frac{\text{Max. Negative in B}}{\text{Max. Positive in B}} =$	3	6
(3)	$\frac{\text{Max. Positive in B}}{\text{Max. Positive in A}} =$	20	25

Considering the experimental difficulties involved, especially in getting the initial, and hence the maximum, current readings, it is fairly definitely proven that there is a *true negative ionization from cadmium iodide due to the iodine constituent*.

Emission of Ions from the Salt.—The Existence of Negative Ions.

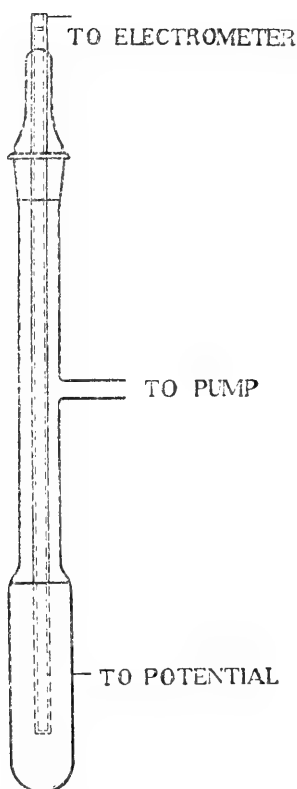
The existence of a current when the salt-covered plate, usually of platinum, is negatively charged, has been taken to indicate the emission of negative ions from the salt or volume ionization of the vapours given off from the salt. However, it might equally well arise from the vapour or the sublimed salt at the opposite electrode giving an emission of positive ions which would then saturate to the negatively charged electrode. For this reason the results with a hot detecting electrode, such as was used in the foregoing experiments and also by Schmidt in his work, may be equivocal. Furthermore,

* *Sci. Torino, Atti*, 40, 1, pp. 55-64 (1904-5).

chemical reaction* between the vapours and the heated electrodes may vitiate the true ionization effects.

In order, then, to obtain decisive tests as to the presence of a true negative ionization and to eliminate effects due to chemical action, the containing vessel was provided with an *inner air-cooled metallic electrode* and an *outer hot non-metallic electrode*. The apparatus used is shown in fig. 5.

Fig. 5.



It consisted of a glass tube 40 cm. long by 4.5 cm. diameter. The inner electrode was a quarter-inch brass tube sealed into the glass stopper with sealing-wax, and so adjusted that its lower end, closed air-tight with a brass plug, came about 1.5 cm. from the salt in the bottom of the main tube. It was kept cool by passing dry air under pressure through a glass tube slipped into the metallic tube. The temperature of this electrode rarely exceeded 50–75° C. after

* There was evidence of chemical action in the blackish appearance of the platinum electrodes. Hot aqua regia dissolved these films, but hot or cold acids or cold aqua regia had little effect. Ammonia readily removed them. Chemical tests, made after several experiments, showed traces of zinc, cadmium and a subiodide of platinum. The lower ends of the electrodes, which rested above the heated salt, became permanently black in colour and brittle after considerable usage.

the whole system had been heated for over an hour at 460°C . The glass vessel, the lower 15–20 cm. of which were inserted in the furnace, served as the outer heated non-metallic electrode. Auxiliary experiments showed that the glass was a good conductor of electricity in the vicinity of 300°C ., the currents varying linearly with the applied voltages. Aluminium foil wrapped tightly about the outside of the tube and baked to the glass furnished a convenient method of connecting with the source of potential.

The *modus operandi*, connexions of the tube with the remainder of the testing system, &c., were essentially the same as those described in connexion with fig. 2. The empty tube, properly cleaned, when heated to 500°C . at low pressure gave currents of the order of 1×10^{-12} to 1×10^{-11} ampere.

Table V. contains a set of data for positive and negative current-E.M.F. relations obtained at 460°C . and 1 cm. pressure. These values were obtained in the steady current regions reached after an hour's heating under potential.

TABLE V.

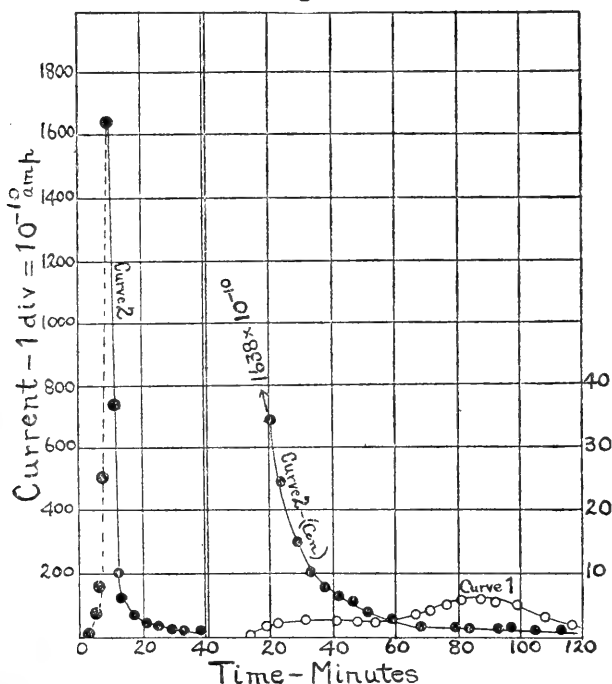
1 div. = 10^{-11} ampere.

Potential.	+ Currents.	– Currents.
0	0.1	0.05
10	2.1	
20	3.3	0.13
40	6.0	0.22
80	9.2	0.32
120	10.4	0.43
160	10.4	0.45
200	10.8	0.46

Two grams of cadmium iodide were heated at a temperature of 465 – 475°C . and at a pressure of 1.8–2 cm. under potentials of ± 200 volts. The current-time relations obtained are exhibited in fig. 6. Curve 1 (O) shows the positive and curve 2 (●) the negative current readings. The most noticeable feature is the quantitative relation existing between the maximum values of the negative and positive ionizations, for the former is over three hundred times as great as the latter. The negative current decayed from a value of 1638×10^{-10} ampere to 118×10^{-10} ampere during the first ten minutes. This was followed by the slow decay with time period for the succeeding forty minutes, after which

the current remained practically constant at a value of 2.1×10^{-10} ampere for over an hour. The dotted portion of curve 2, fig. 6, shows a rise of current to a maximum

Fig. 6.



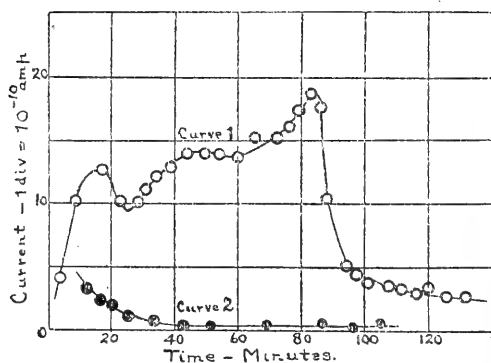
value after ten minutes' heating. This was not as definitely indicated in some similar experiments. It is difficult to say whether or not such a relation exists, since it is quite likely that there is a considerable temperature lag in the glass. To overcome this difficulty the furnace was heated about fifty degrees higher than the temperature required, the tube was then inserted and the currents in the heating apparatus regulated to values which experience had shown would give the desired constant temperature. The positive ionization increased slowly with time from a value of 1×10^{-10} ampere to a maximum value of 5.8×10^{-10} ampere after 80-100 minutes, followed by a slow decay period. It is of interest to note the dissimilarity in the positive current-time relations shown in curve 1, fig. 6, and curve 3, fig. 3. The temperature and pressure conditions were nearly identical in the two cases; the testing vessels were entirely different. The negative ionization effects are, however, in good accord with those recorded in Table IV., tube B. Other experiments similar to those described above were made at the same temperature and with the same quantity of salt, but at a pressure of 5-8 mm. The negative current fell initially

from a maximum value of 800×10^{-10} ampere to 8×10^{-10} ampere in seven minutes; the positive current increased with time from a value of 1.7×10^{-10} ampere to 12.2×10^{-10} ampere after 45–60 minutes' heating. These experiments, in toto, show conclusively that *there is an emission of ions from the salt, and that there are negative as well as positive ions.*

The Ionization Effects from the Distillates.

Various distillates collected on the cool inner electrode were re-run at the same temperature and pressure as the original sample of salt. The first distillate from the original salt at a pressure of 2 cm. and a temperature of $465^{\circ}\text{C}.$, showed a negative ionization falling off with time from a maximum value of 260×10^{-10} ampere in a manner analogous to curve 2, fig. 6. The positive current-time relations, however, differed considerably from those shown in curve 1, fig. 6. Three distinct current maxima were exhibited after 20, 40–45, and 80–90 minutes' heating; this third maximum, the greatest of the three, had a value of 22×10^{-10} ampere in comparison with 5.8×10^{-10} ampere shown by the original salt. The positive ionization curve for the second distillate is given in curve 1, fig. 7, and is practically the duplicate of

Fig. 7.



that given by the first distillate. The negative current (curve 2, fig. 7) had an initial maximum value of 3.2×10^{-10} ampere. These curves show that the ratio

$$\frac{\text{Maximum Negative Emission, Original Salt}}{\text{Maximum Negative Emission, Second Distillate}} = 500 \text{ (roughly),}$$

and that

$$\frac{\text{Maximum Positive Emission, Original Salt}}{\text{Maximum Positive Emission, Second Distillate}} = 0.33.$$

Two grams of cadmium iodide were originally used, and 750 mgms. of the second distillate were recovered and used as described above. Ten distillates from this original sample of salt were re-tested; alternations of greater negative or positive emission occurred. The power which the distillates had of producing negative ionization was in no wise comparable to that of the original salt; on the other hand, the positive ionization was considerably greater in certain of the distillates.

The results showing the maximum values of the positive and negative currents at a temperature of 465°C . and a pressure of 0.8 cm. are given in Table VI.

TABLE VI.

$P=0.8$ cm. Hg. $T=465^{\circ}\text{C}$. 1 div. = 1×10^{-10} ampere.

Substance.	Maximum Negative.	Maximum Positive.
Original CdI_2	800.0	10.5
1st distillate	0.9	30.0
2nd distillate.....	92.0	3.2
3rd distillate	1.2	16.6
4th distillate	54.2	5.1

These figures show that the ratio of

$$\frac{\text{Maximum Negative Emission, Original Salt}}{\text{Maximum Negative Emission, First Distillate}} = 900 \text{ (roughly),}$$

and that the

$$\frac{\text{Maximum Positive Emission, Original Salt}}{\text{Maximum Positive Emission, First Distillate}} = 0.34.$$

No explanation can, as yet, be offered why these distillates exhibit such alternations in their powers of negative and positive emission. No visible differences existed in the colour or general appearance of the distillates and the original salt. It seemed possible that the presence or absence of moisture might account in part for the marked dissimilarities in the ionization from the distillates. To this end the sixth and seventh distillates in the experiments at 2 cm. pressure were, in turn, treated with about a gram of water, and the negative and positive current-time relations determined.

No effects were observed in contradiction to the facts already set forth. *Nor can the large negative emission from the original salt be attributed to moisture.* A thick paste of fresh salt of about 3 grams weight was made and the ionization effects determined at a pressure of 1.8 cm. and a temperature of 480–90° C. The negative current fell off asymptotically with the time from a maximum of 200×10^{-10} ampere, a value about one-eighth of that shown in curve 2, fig. 6. The positive ionization, however, from the moistened salt was increased tenfold. When the distillate was removed from the inner electrode it was found coated on the inside with a thin blackish coloured film, a phenomenon which was not observed in other experiments.

Chemical Analyses of the Distillates.

Chemical analyses were made as to the percentage of iodine in (1) a sample of the cadmium iodide (Einer and Amend) used, (2) of the fifth distillate obtained at 1 cm., and (3) of the tenth distillate at 2 cm. pressure. The following percentages of iodine were found: (1) 72.14, (2) 70.27, and (3) 65.85. Hence *continued distillation diminishes the percentage of iodine.* This fact lends further support to the view that *the negative ionization consists in large part of the iodine constituent.*

Conclusions.

The following points have been fairly definitely established:—

(1) There can be an ionization in the secondary chamber B when only uncharged matter enters B, since there is a saturating potential in A. Thus the ionization is partially an *ionization of the vapour*. This may arise from the action of the vapour on the electrodes or it may be a volume ionization, or both.

(2) In addition there is an *emission of ions from the salt*, as shown by the experiments with the air-cooled electrode apparatus. Furthermore, the presence of *negative ions* is definitely proven. There is a large initial negative emission and practically no positive on heating a sample of the original salt. As the heating continues the positive ionization increases to a maximum and then falls away; the negative continually diminishes.

(3) The ionization in the unsalted tube B may equal or

exceed that in A, and the currents change in a different way when the direction of the applied field is reversed. The fact that the ionization in the tube B can be greater than that in the salted tube A seems to indicate that a great deal of the ionization arises from a substance which takes some time to form. Thus there may be more of this substance in the vapour by the time it has diffused into the tube B than there was when it was first given off by the salt.

(4) At temperatures below 402°C ., the melting-point of CdI_2 , the positive ionization effects in both tubes decay asymptotically with the time from an initial maximum value; when the temperature is above this point the positive ionization increases with time to a maximum followed by decay with time.

(5) Iodine alone gives quite large currents. A comparative study of cadmium iodide and iodine shows that some, at least, of the negative ionization effects are probably due to the subsequent ionization of the iodine vapour which is liberated by chemical dissociation in visible quantities.

(6) The distilled salt is less active than the undistilled. The successive distillates exhibit alternations in their power of negative and positive emission. Those distillates which show a comparatively large negative emission exhibit a small positive ionization and *vice versa*. In the case of the distillates in which the negative emission is small the positive emission exceeds that of the original salt.

(7) Continued distillation diminishes the percentage of iodine in the salt, but does not produce much, if any, change in its appearance.

Several points suggested by these results are being tested by further experiments.

In closing this paper the writer expresses his thanks to Professor O. W. Richardson, who suggested this line of research, and to whom he is indebted for many suggestions during its progress. He also wishes to thank Mr. C. Bol for the construction of the various pieces of glass apparatus used.

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XL. The Valency of the Radioelements. By G. VON HEVESY, Ph.D., Hon. Research Fellow in Physics, Manchester University.*

§ 1. *Introduction.*

THERE is at present no recognized intimate relation between the processes that occur inside an atom and the processes that take place outside it, that is to say, between the radioactive and the chemical properties of an atom. It may be said, however, that there is some connexion between atomic weight and radioactive phenomena, for only elements of atomic weight greater than 200 disintegrate with evolution of helium. Rubidium and potassium, elements of low atomic weight, however, appear to be radioactive, emitting β -rays.

In the search for a relation between radioactive and chemical properties, the most likely line of attack seemed to be to investigate the connexion between the nature of the radiation accompanying the disintegration of an element, and the difference in valency between the resultant and the parent product. Since the discovery of Faraday's law of electrolysis, valency has become more and more to be considered from an electrochemical point of view. When an α -particle is expelled from an atom, the atom loses positive electricity, and when a β -particle is expelled, it loses negative electricity. It is therefore to be expected that this loss of positive and negative electricity, as the case may be, would have a definite influence on the valency of the resultant atom. To investigate this point, the valency of a great many radioelements has been determined. Apart altogether from the interest of this problem, it is important to know what are the valencies of the various radioelements, as very little is known of the chemical properties of many of these bodies, especially of those which follow the emanations in the disintegration series.

The two chief methods of determining the valency of an element are the stoichiometrical and the electrochemical. In the former method, the valency is obtained from an analysis of various compounds of the element under consideration; in the latter method, it is obtained from the ratio of the number of coulombs passing during electrolysis and the quantity of metal deposited from, or passing into solution. The amount of radioactive bodies at one's disposal, however, is so small that neither of these methods can be applied to

* Communicated by Prof. E. Rutherford, F.R.S.

them. It will be shown in the present paper that it is possible to deduce the number of charges borne by the cation, *i. e.* its valency, from the velocity with which it diffuses in presence of a large excess of the anion. The diffusion constant of a cation has also been determined by measuring its mobility in an electric field. This second method acts as a check on the first one. Before proceeding to describe the methods employed in this research, the subject of diffusion of electrolytes will be discussed from a general point of view.

§ 2. Diffusion of Electrolytes.

When dilute hydrochloric acid diffuses in pure water, the H and Cl ions are borne from points of higher to points of lower osmotic pressure by the osmotic forces. The smaller the frictional resistance offered to the migrating ion, the more rapidly does it move. Now a hydrogen ion has to overcome a frictional resistance which is only about 1/5 of that to be overcome by the chlorine atom. It is therefore to be expected that the rapidly moving H ion, when allowed to diffuse, would soon leave the slowly moving Cl ion, and be completely separated from it. This, however, does not take place. The polar ions are not capable of being separated by diffusion, for as Nernst showed in his fundamental theory of diffusion of electrolytes, the foremost hydrogen ion gives a positive charge to the water layer, and a negative charge to the residual ion. A compensating potential difference is thus produced, which accelerates the motion of the Cl ions, so that the resultant velocity of diffusion of the Cl ions is the same as that of the H ions. For this reason the diffusion of an electrolyte depends both on the mobility of the cation and of the anion.

The numerical relation between the diffusion constant and the mobility of an n -valent electrolyte may be derived as follows.

The effect of the osmotic forces is that in unit time

$$N'_K = -U \frac{dP}{dx} \text{ cations}$$

and

$$N'_A = -V \frac{dP}{dx} \text{ anions}$$

pass unit cross-section*. U and V are proportional to the mobilities of the cation and the anion respectively, c is the concentration, and n the valency.

* Nernst, *Zeit. phys. Chem.* vol. ii. p. 614 (1888).

Since the osmotic pressure P is $\frac{RTc}{n}$, we obtain, therefore,

$$N'_K = -\frac{1}{n} URT \frac{dc}{dx}$$

and

$$N'_A = -\frac{1}{n} VRT \frac{dc}{dx}.$$

The effect of the compensating electric forces is that

$$N''_K = -Uc\epsilon \frac{d\psi}{dx} \text{ cations}$$

and

$$N''_A = +Vc\epsilon \frac{d\psi}{dx} \text{ anions}$$

traverse unit cross-section in unit time. $\frac{d\psi}{dx}$ is the P.D. accelerating the slow ions, and retarding the fast ones, and ϵ is the charge borne by the gram-ion.

The total number of cations and anions passing unit cross-section in unit time are N_K and N_A respectively, where

$$N_K = N'_K + N''_K = -U \left[\frac{RT}{n} \frac{dc}{dx} + \epsilon c \frac{d\psi}{dx} \right],$$

and

$$N_A = N'_A + N''_A = -V \left[\frac{RT}{n} \frac{dc}{dx} - \epsilon c \frac{d\psi}{dx} \right].$$

Since the same number of anions and cations traverse the cross-section, we get

$$N_K = N_A,$$

and therefore

$$\frac{d\psi}{dx} = \frac{U - V}{U + V} \frac{RT}{n\epsilon c} \frac{dc}{dx}$$

and

$$N_K = N_A = -\frac{2UV}{n(U+V)} RT \frac{dc}{dx}.$$

Now

$$U = 1.036 \text{ } u \cdot 10^{-5},$$

$$V = 1.036 \text{ } v \cdot 10^{-5}$$

$$RT = 8.61 \cdot 10^{13} \text{ } T,$$

and

$$D = N_K / \frac{dc}{dx},$$

where u and v are the absolute velocities of the ions in cm. per sec., and D the diffusion coefficient. If this last constant

be expressed in days, the right-hand side of the equation must be multiplied by $8.64 \cdot 10^4$.

We therefore obtain the expression

$$D_{180} = \frac{0.04485 uv}{n(u+v)} \cdot \cdot \cdot \cdot (1)$$

Equation (1) was tested by Nernst* for the special case of monovalent electrolytes ($n=1$), and found to be in good agreement with experimental results. The general equation was not tested, however, owing probably to the absence of experimental data, and to lack of knowledge of the conditions under which multivalent electrolytes dissociate. Nernst's view is based on the assumption that dissociation is complete, that is for instance, that NaCl dissociates into Na' and Cl' ions only. In a solution of the bivalent BaCl₂, however, not only are Ba'' and Cl' ions present, but also BaCl' ions, the last named being monovalent and of unknown mobility. Although the validity of the general equation cannot be tested strictly on account of this difficulty, its truth is rendered very probable by the results tabulated in Table I. In this table are given the relative number of molecules of various substances diffusing in equal times †.

TABLE I.

KCl	803	} monovalent.
NH ₄ Cl	689	
NaCl	600	
BaCl ₂	450	} divalent.
CaCl ₂	429	
SrCl ₂	432	
MgCl ₂	392	

The mobilities of Ba, Ca, Sr, and Mg are approximately the same as those of K and Na. The essentially slower diffusion of these bivalent halogen compounds must therefore be ascribed to their greater valency.

§ 3. *Connexion between the Diffusion Constant of a Salt and the Mobility of the Cation. Diffusion in excess of the Anion.*

In equation (1) a relation between the valency and the mobility either of the cation or of the anion of the salt is given. A direct relation between the diffusion velocity of a salt, such as for instance BaCl₂, and the mobility and valency of the radium cation, may be obtained by allowing the

* Nernst, *Zeit. phys. Chem.* vol. ii. p. 616 (1888).

† Long, *Wied. Ann.* vol. ix. p. 613 (1880).

radium chloride to diffuse in excess of some chloride, *e. g.* in hydrochloric acid. The electrical forces act on the ions so that their velocity is proportional to their concentration. Since, however, the concentration of the chlorine ions is much greater than that of the radium ions, the rate of diffusion of the RaCl_2 will depend only on the mobility of the radium ion. It follows from this that dilute hydrochloric acid in a concentrated solution of potassium chloride diffuses much more rapidly than it does in pure water, because in the second case the slow motion of the Cl ions hinders that of the H ions. Experiments on this particular point have been made by Abegg and Bose*.

The relation between the diffusion velocity of RaCl_2 in an excess of hydrochloric acid, the velocity of the ions, and the valency of the radium ion will be next derived.

If c be the concentration of the RaCl_2 diffusing, γ that of the hydrochloric acid, and U and V be constants proportional to the mobilities of the radium ion and the chlorine ion respectively, then under the action of the osmotic forces

$$N'_{\bar{K}} = -\frac{1}{n} URT \frac{dc}{dx} \text{ cations}$$

and

$$N'_{\bar{A}} = -\frac{1}{n} VRT \frac{dc}{dx} \text{ anions}$$

pass unit cross-section in unit time.

Under the action of the compensating electric forces also,

$$N''_{\bar{K}'} = -Uc\epsilon \frac{d\psi}{dx} \text{ cations}$$

and

$$N''_{\bar{A}'} = +Vc\epsilon \frac{d\psi}{dx} \text{ anions}$$

pass unit cross-section in unit time.

The total number of cations migrating is

$$N_K = N'_{\bar{K}'} + N''_{\bar{K}'} + N_{K'}$$

where

$$N_K = 0 - U'\epsilon\gamma \frac{d\psi}{dx}$$

is the number of H cations diffusing.

* *Zeit. phys. Chem.* vol. xxx. p. 545 (1895).

The total number N_A of anions migrating is

$$N'_A + N''_A,$$

and since $N_A = N_K$ we get

$$\frac{d\psi}{dx} = \frac{RT(U-V)}{n\epsilon[c(U+V) + \gamma(U'+V)]} \frac{dc}{dx}.$$

Hence the total number of cations migrating is

$$N_K = - \frac{URT}{n} \frac{dc}{dx} \left(\frac{2V + (U' + V)\gamma/c}{U + V + (U' + V)\gamma/c} \right),$$

and the total number of anions migrating is

$$N_A = - \frac{VRT}{n} \frac{dc}{dx} \left(\frac{2U + (U' + U)\gamma/c}{U + V + (U' + V)\gamma/c} \right).$$

The diffusion constant of the cation D' in excess of the anion is

$$N_K \bigg/ \frac{dc}{dx}.$$

From equation (1) the usual diffusion coefficient D is

$$- \frac{2UV}{U+V} RT \frac{dc}{dx},$$

and therefore we get

$$\frac{D'}{D} = \frac{c/\gamma + \frac{U'+V}{2V}}{c/\gamma + \frac{U'+V}{U+V}},$$

and for the case $\gamma = \infty$,

$$\frac{D'}{D} = \frac{U+V}{2V} \dots \dots \dots (2)$$

For the particular case of RaCl_2 diffusing in an excess of hydrochloric acid, we have

$$U = 1.036 \ u \cdot 10^{-5} = 0.00059,$$

$$V = 1.036 \ v \cdot 10^{-5} = 0.00068,$$

$$U' = 1.036 \ u' \cdot 10^{-5} = 0.00329,$$

where u , v , and u' are the absolute mobilities of the ions of radium, chlorine, and hydrogen, respectively.

$$\text{Now} \quad \frac{U' + V}{2V} = 2.92$$

$$\text{and} \quad \frac{U' + V}{U + V} = 3.12,$$

and when $\gamma/c = 100$ $D' = D'_\infty (1 + 0.002)$.

When hydrochloric acid is present with the body diffusing, 100 times in excess, the value of the diffusion coefficient found differs from the theoretical value by less than 0.2 per cent. In our experiment with RaCl_2 γ/c was greater than 10^5 , and in the experiments carried out with the short-lived radio-elements it was even greater than 10^{15} .

From equation (2) we deduce that, in the case of diffusion of the cation in excess of the anion, *e. g.* the diffusion of radium chloride in hydrochloric acid, the diffusion constant is given by the expression

$$D = 0.02242 \frac{u}{n} \dots \dots \dots (3)$$

Equation (3) is a linear relation connecting the diffusion coefficient of radium chloride, the velocity of the radium ion, and the valency of radium. This equation is a general one, and is free from any hypothetical assumptions.

§ 4. *Relation between the Magnitude of the Diffusion Constant, and the Valency of the Cation.*

Since, when diffusion takes place in excess of the anion, the diffusion constant depends only on the mobility and the valency of the cation, and since, also, the mobility of the cation varies only within somewhat narrow limits, the magnitude of the diffusion constant can be obtained immediately from the valency of the diffusing ion. The limits referred to extend from the value of the mobility of sodium 44 to that of caesium 68. The mobility of lithium, however, is exceptionally low, and this is due to the fact that the ion is strongly hydrated.

In Table II. are given the mobilities of cations so far as they are known.

TABLE II.

Metal.	Mobility.	Metal.	Mobility.
Na	43.6	Ba	55.1
Mg	45.9	Ra	57.4
Zn	46.6	Pb	61.1
Cu	47.2	NH ₄	64.4
Cd	47.4	K	64.7
Ca	51.4	Tl	66.6
Sr	51.5	Rb	67.6
Ag	54.0	Cæ	68.2

The mean value of the mobility of a cation is 55.7. The mean value of the diffusion constant calculated from this value is $\frac{1.25}{n}$ cm.² per day. For monovalent ions, therefore, the most probable diffusion coefficient is 1.25, for divalent ions it is 0.63 and so on. The mobility of sodium, and especially that of lithium, is exceptionally low. The diffusion coefficient of sodium is 0.98 when the NaCl diffuses in excess of chlorine ions. Sodium is therefore monovalent. The diffusion constant of lithium, however, is 0.75. Lithium may therefore be either mono- or divalent. This element has a very low atomic weight, and it is not to be expected that this uncertainty regarding its valency will apply to elements of high atomic weight like the radioelements. It is therefore legitimate to calculate the number of charges borne by the cation from the velocity with which a salt diffuses in excess of its anion.

There is another method of determining the valency, and that consists in determining the mobility of the ion, and calculating n from the equation

$$n = 0.02242 \frac{u}{D}.$$

Both these methods have been used in this research and both have yielded similar results. The validity of the method of obtaining the valency of the diffusing cation from its diffusion constant in excess of the anion has therefore been confirmed.

§ 5. *Analogy between Diffusion of Ions in Gases and in Liquids.*

Equation (1) holds also for diffusion of gaseous ions. If k be the mobility of the gaseous cation and k' that of the anion, then

$$D = \frac{0.04483 k k'}{n(k + k')}.$$

The experiments of Townsend* and others have shown that this equation holds as accurately for gas ions as it does for liquid ions. The well-known equation of Townsend connecting the diffusion coefficient of a gas ion with its mobility

$$D = \frac{u\Pi}{Ne} = K \frac{u}{n}$$

(Π being the pressure of the gas, N the number of molecules

* *Phys. Zeits.* vol. i. p. 313 (1900). Nernst, *Theoret. Chem.* 6 edit. p. 404.

per cm., and K a constant) is analogous to equation (3) given above, namely,

$$D = 0.02232 \frac{u}{n}.$$

The older measurements of the valency of gas ions invariably gave a value of 1. According to more recent experiments by Townsend* and by Frank and Westphal†, however, some bivalent ions are produced when air is ionized by X-rays. By allowing the ions to diffuse partially, the last named authors were able to separate the bivalent ions partially from the monovalent. This affords a proof, of great importance to the theory given here, that the mobility of the ions is independent of the charge of the ion. Since, however, the velocity of diffusion is inversely proportional to the charge, it is at once apparent that by comparing the two quantities, the charge, and therefore the valency, can be obtained.

Gaseous ions of higher valency than two have not been isolated. Consequently it is not possible to test the equation for higher values of n .

§ 6. *Determination of the Diffusion Constants of the Radioelements.*

The method employed in these experiments was that of Graham and Stephan. This method consists in placing the solution, the diffusion of which is under investigation, under a vertical column of water, and after a certain time has elapsed and diffusion has taken place, removing different layers and analysing them. From the ratio of the concentration of the layer which initially contained all the substance to that of another layer, and from the height of this layer, the diffusion constant in sq. cm. per day is calculated from the equation

$$D = \left(\frac{h}{2}\right)^2 / TK,$$

where h is the height of the layer in cm., T the time in days, and K a function of the ratio of the concentrations, obtained from Stephan's table.

As is well known, this method assumes only the validity of Fick's differential equation of diffusion, that is to say, it assumes that the velocity of diffusion is independent of the absolute concentration, and depends only on the fall of concentration. This condition has always been fulfilled strictly

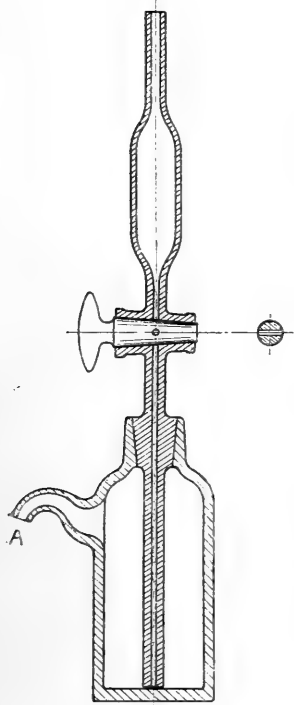
* Proc. Roy. Soc. vol. lxxx. p. 207 (1908).

† Ber. deut. phys. Ges. vol. xi. p. 152 (1909).

in the experiments with the extremely dilute solutions dealt with in the work to be described, since no difficulty on account of incomplete dissociation could arise.

The apparatus shown in fig. 1 is essentially a copy of Scheffer's. The lower part is filled with 3×16.05 c.c. of water, and the liquid under examination is allowed to flow into it from a pipette 16.05 c.c. in volume. Experiments with KMnO_4 solution showed that a sharply defined surface formed between the heavy liquid which had flowed in from the pipette, and the light liquid already contained in the vessel.

Fig. 1.



When diffusion has taken place and the experiment is finished, the pipette is filled with some heavy liquid such as chloroform, or a saturated solution of calcium chloride, and the liquid allowed to flow in very slowly while an equal volume of the diffused liquid is forced out of the apparatus at A. This gives layer I. By repeating this operation, layers II., III., and IV. are obtained, and then analysed. As a rule only layers I. and II. were investigated. The height of the layers was measured with a cathetometer, and found to be 1.510 cm.

A heavy block of lead was attached to the glass apparatus and the whole immersed in a large water-bath in an underground room, the temperature of which did not vary more than about 0.1°C . during an experiment. The diffusion coefficient of normal hydrochloric acid solution determined with the apparatus described above was at 15.2° , 2.29 sq. cm. per day, which by calculation gives at 18° , 2.48 . The values obtained by Arrhenius and Scheffer are 2.40 and 2.48 at 18° respectively. All values determined in these experiments were reduced to 18° , a temperature coefficient of 2.6 per cent. per degree being assumed. This is the value obtained theoretically by Nernst*, and experimentally by Schuhmeister†, Long‡, Weber§, and others.

* *Zeit. phys. Chem.* vol. ii. p. 624 (1888).

† *Wien. Ber.* vol. lxxix. p. 603 (1879).

‡ *Wied. Ann.* vol. ix. p. 613 (1880).

§ *Wied. Ann.* vol. vii. p. 469 (1879)

(a) *The diffusion constant of Radium.*

Radium chloride dissolved in 1/100 normal HCl solution diffused in a solution of 1/100 normal HCl. The concentration of radium in the solution was in one experiment $4.51 \cdot 10^{-7}$, and in another $4.72 \cdot 10^{-8}$ gram per c.c., so that practically an infinite excess of chlorine ions was present with the radium ions. The radium content of the different layers was determined by the emanation method. The emanation was completely removed from the solution by boiling. It was allowed to accumulate for a definite time, then completely removed by boiling, collected over a saturated solution of calcium chloride, and transferred to the ionization-chamber of the electroscope. The reason for using a saturated solution of calcium chloride is that in this liquid the emanation is very insoluble. In this respect it is nearly as good as mercury, and is besides much more easy to work with.

The following values of the diffusion constant were obtained. The signs I. and II. indicate the layers which were examined.

$$(1) \quad D_{15^{\circ}8}^{\text{I}} = \frac{0.57}{2.53 \times 0.318} = 0.632 \quad . \quad D_{18^{\circ}} = 0.669$$

$$D_{15^{\circ}8}^{\text{II}} = \frac{0.57}{2.83 \times 0.316} = 0.639 \quad . \quad D_{18^{\circ}} = 0.675$$

$$(2) \quad D_{15^{\circ}4}^{\text{I}} = \frac{0.57}{3.12 \times 0.286} = 0.634 \quad . \quad D_{18^{\circ}} = 0.669$$

$$D_{15^{\circ}4}^{\text{II}} = \frac{0.57}{3.12 \times 0.285} = 0.635 \quad . \quad D_{18^{\circ}} = 0.670$$

$$(3) \quad D_{15^{\circ}4}^{\text{I}} = \frac{0.57}{1.82 \times 0.495} = 0.637 \quad . \quad D_{18^{\circ}} = 0.672$$

$$D_{15^{\circ}4}^{\text{II}} = \frac{0.57}{1.82 \times 0.492} = 0.640 \quad . \quad D_{18^{\circ}} = 0.675.$$

Mean value $D_{18^{\circ}} = 0.667$ sq. cm. per day.

Since the mean value of the diffusion coefficient is $\frac{1.25}{n}$, it follows that the valency of radium is 2.

(b) *Diffusion constants of ThX and ActX.*

In these experiments also the radioactive substances were dissolved in 1/100 normal HCl and diffused in 1/100 normal HCl. At this dilution the cation (*i. e.* the ThX⁺⁺ or the

ActX^{..}) diffuses in practically infinite excess of the anion Cl[']. The acidity of the solution prevents also any possible precipitation of these substances which might easily take place if the solutions were neutral. The ThX was prepared by the usual method. Some thorium nitrate was dissolved in water, from this solution the thorium was precipitated as hydroxide by ammonia, and the filtrate which contained the ThX evaporated to dryness. The solution used contained initially 10^{-12} gm. ThX per c.c. 1 c.c. of this solution was diluted to 10 c.c. and evaporated to dryness on a watch-glass. This was done with 10 c.c. of each of the layers on completion of diffusion. About six days later when ThX, ThB, and ThC were formed in equilibrium amounts, the activities of the watch-glasses were determined, and from these measurements the quantities of ThX present were obtained.

The following are the values of the diffusion constant obtained for ThX :—

$$(1) \quad D_{14^{\circ}2}^I = \frac{0.57}{1.90 \times 0.500} = 0.600$$

$$D_{14^{\circ}2}^{II} = \frac{0.57}{1.92 \times 0.492} = 0.604$$

$$(2) \quad D_{14^{\circ}0}^I = \frac{0.57}{2.31 \times 0.412} = 0.599$$

$$D_{14^{\circ}0}^{II} = \frac{0.57}{2.32 \times 0.409} = 0.602.$$

Mean value of $D_{18^{\circ}} = 0.659$ sq. cm. per day.

The valency of ThX is therefore 2.

G. Hoffman* investigated the diffusion velocity of $\text{ThX}(\text{NO}_3)_2$ in water by Weber's method, which consists in determining the change in concentration with time at the free surface of a system consisting of two layers of liquids of different concentration. In his experiment Hoffman determined the ThX by means of the emanation it produced, by passing a current of air over the free surface. He found $D_{10^{\circ}} = 0.504$, from which by calculation we get $D_{18^{\circ}} = 0.608$ sq. cm. per day.

The diffusion velocity of ActX was determined by the same methods as used for ThX, and the following results obtained. Each c.c. of the solution used contained 1.5×10^{-12} gm. ActX.

* *Ann. der Phys.* vol. xxi. p. 239 (1906).

$$(1) \quad D_{15^{\circ}9}^I = \frac{0.57}{2.0 \times 0.455} = 0.626$$

$$D_{15^{\circ}9}^{II} = \frac{0.57}{2.0 \times 0.452} = 0.629$$

$$(2) \quad D_{16^{\circ}0}^I = \frac{0.57}{3.21 \times 0.282} = 0.631$$

$$D_{16^{\circ}0}^{II} = \frac{0.57}{3.22 \times 0.280} = 0.634.$$

The mean value of $D_{18^{\circ}} = 0.664$ sq. cm. per day, and therefore the valency of ActX is 2.

(c) *Diffusion velocity of ThB and ThC.*

In these experiments the active deposit of thorium was dissolved in 1/100 normal HCl, the solution was allowed to stand 10 hours in order to allow ThC to be formed in equilibrium amount, and then placed in the diffusion apparatus surmounted by a 1/100 normal HCl solution. One c.c. of the active solution contained 10^{-13} gm. ThB. Each layer of active material after removal from the apparatus was evaporated to dryness, and 10 hours later its activity was measured. From the activities of the different layers, the diffusion constant of ThB was calculated. The following results were obtained:—

$$(1) \quad D_{14^{\circ}}^I = \frac{0.57}{1.0 \times 0.541} = 1.06$$

$$D_{14^{\circ}}^{II} = \frac{0.57}{1.02 \times 0.530} = 1.06$$

$$(2) \quad D_{14^{\circ}2}^I = \frac{0.57}{1.82 \times 0.297} = 1.05$$

$$D_{14^{\circ}2}^{II} = \frac{0.57}{1.84 \times 0.289} = 1.07.$$

Mean value $D_{18^{\circ}} = 1.21$ sq. cm. per day.

The valency of ThB is therefore 1.

A shorter diffusion apparatus was used in determining the diffusion constant of ThC owing to the rapidity with which this body decays. We had at our disposal the active deposit from a preparation of mesothorium 1 which equalled in activity 2 milligrams of radium, and also that from a preparation of radiothorium equal to 4 milligrams of radium. The duration of an experiment must not of course exceed 8 to 10 hours, for at the end of this time the ThC originally

present has decayed to 1/1000 of its original amount. It is much more difficult to prepare pure ThC than it is the corresponding products of the other two series. Perfectly pure ThC cannot be obtained by von Lerch's method of depositing it on nickel, nor by the author's method*, which consists in depositing it on silver from a neutral solution of a silver salt. Prepared by these methods the ThC was found to contain 1 to 5 per cent. of the equilibrium amount of ThB. Since ThB decays to half value in 10·6 hours, and ThC in 1 hour, at the end of 10·6 hours one half of the disturbing ThB is present with only 1/1000 of the ThC. It is thus impossible to determine the diffusion constant of the ThC prepared in this way. The author has shown in a previous paper* that the ratio of the amounts of ThB and ThC deposited on a metal plate from a solution is a function of the potential difference metal/solution, and that the more electronegative the latter is, the purer is the ThC deposited. We succeeded in depositing very pure ThC by the following method. A solution of NiCl_2 was added to the active HCl solution, and in it was immersed a plate of nickel which had been previously rendered passive by polarizing it in a solution of caustic soda. After the plate was removed from the solution, the ThC deposited on it was found to be very pure, the amount of ThB present with it being only from ·006 to ·02 per cent.

The diffusion experiment occupied 0·313 days. The concentration of ThC in layer I was ·00418 of that of the original solution, and in layer II ·056. Since, however, a portion of the ThC did not diffuse as ThC but resulted from the ThB diffusing with it, it was found, that in spite of the very great purity of the ThC used, a not inconsiderable correction had to be applied. When this was done the values of the concentrations given above become ·0035 and ·048 respectively. The following are the results obtained:—

$$D_{14^{\circ}2}^{\text{I}} = \frac{0\cdot119}{0\cdot313 \times 0\cdot662} = 0\cdot58$$

$$D_{14^{\circ}2}^{\text{II}} = \frac{0\cdot119}{0\cdot314 \times 0\cdot680} = 0\cdot56$$

$$D_{14^{\circ}0}^{\text{I}} = \frac{0\cdot119}{0\cdot282 \times 0\cdot724} = 0\cdot57$$

$$D_{14^{\circ}0}^{\text{II}} = \frac{0\cdot119}{0\cdot283 \times 0\cdot710} = 0\cdot58.$$

The mean value $D_{18^{\circ}} = 0\cdot625$ sq. cm. per day.

The valency of ThC is therefore 2.

* Phil. Mag. vol. xxiii. p. 628 (1912).

(d) *The diffusion constants of RaD, RaE, and RaF.*

A solution of these substances was obtained by dissolving in acid the active deposit formed in a glass tube in which a large quantity of radium emanation had disintegrated. One c.c. of the solution used contained 2×10^{-7} gm. RaD and 2×10^{-10} gm. RaF. The same experiment serves to determine the diffusion constants of both RaD and RaE. The β -ray activities of the layers were compared immediately after the experiment had been stopped, and from these results, the diffusion constant of RaE was obtained. After an interval of forty days the β -ray activities of the same layers were compared, and from these results the diffusion constant of RaD was obtained. It was found that the constants of both bodies were very similar.

The following results were obtained:—

RaD.

$$(1) \quad D_{15^{\circ}6}^I = 0.654$$

$$D_{15^{\circ}6}^{II} = 0.648$$

$$(2) \quad D_{15^{\circ}6}^I = 0.651$$

$$D_{15^{\circ}6}^{II} = 0.646.$$

Mean value $D_{18^{\circ}} = 0.651$ sq. cm. per day.

The valency of RaD is therefore 2.

RaE.

The value of $D_{18^{\circ}} = 0.646$ sq. cm. per day.

The valency of RaE is therefore 2.

RaF.

$$(1) \quad D_{15^{\circ}8}^I = 0.700$$

$$D_{15^{\circ}8}^{II} = 0.712$$

$$(2) \quad D_{15^{\circ}6}^I = 0.702$$

$$D_{15^{\circ}6}^{II} = 0.711.$$

Mean value $D_{18^{\circ}} = 0.760$ sq. cm. per day.

The valency of radium F is therefore 2.

(e) *The diffusion velocity of Radiothorium.*

From comparison of the activities of the different layers immediately after the experiment had been stopped, a diffusion constant of about 0.7 was deduced. In the course of a month the ratio of the activities fell to a value corresponding to the diffusion constant given below. One gram of the solution used contained 4×10^{-10} gm. radiothorium.

The following results were obtained:—

$$(1) \quad D_{17^{\circ}6}^I = \frac{0.57}{0.796 \times 2.17} = 0.329 \quad . \quad D_{18^{\circ}} = 0.332$$

$$D_{17^{\circ}6}^{II} = \frac{0.57}{0.780 \times 2.19} = 0.332 \quad . \quad D_{18^{\circ}} = 0.335$$

$$(2) \quad D_{17^{\circ}7}^I = \frac{0.57}{0.479 \times 3.64} = 0.327 \quad . \quad D_{18^{\circ}} = 0.330$$

$$D_{17^{\circ}7}^{II} = \frac{0.57}{0.469 \times 3.66} = 0.332 \quad . \quad D_{18^{\circ}} = 0.335.$$

Mean value $D_{18^{\circ}} = 0.333$ sq. cm. per day.

The valency of radiothorium is therefore 4.

It is apparent from this result, and the results given above, that ThX diffuses twice as quickly as radiothorium, and ThB four times as quickly. The upper layers after diffusion have therefore proportionately more ThB than ThX, and more ThX than radiothorium. In one experiment, for example, after diffusion had taken place for two days the ratios of the equilibrium amounts of radiothorium, ThX, and ThB in the topmost layer were 1 : 18 : 81.

(f) *The diffusion constant of Ionium.*

A preparation of ionium containing thorium dissolved in normal HCl was allowed to diffuse in the usual manner. The activities of the different layers were measured in an α -ray electroscope. The following results were obtained:—

$$D_{16^{\circ}}^I = \frac{0.57}{0.475 \times 3.64} = 0.308 \quad . \quad D_{18^{\circ}} = 0.331$$

$$D_{16^{\circ}}^{II} = \frac{0.57}{0.462 \times 3.66} = 0.315 \quad . \quad D_{18^{\circ}} = 0.327.$$

Mean value $D_{18^{\circ}} = 0.327$ sq. cm. per day.

The valency of ionium is therefore 4.

(g) *The diffusion constant of Thorium.*

The solution used contained 24 mg. per c.c. ThCl_4 in normal HCl. The amounts of thorium in the different layers were obtained by igniting the thorium, and weighing it as oxide. The following results were obtained:—

$$D_{16^{\circ}}^I = \frac{0.57}{0.460 \times 3.90} = 0.318 \quad . \quad D_{18^{\circ}} = 0.333$$

$$D_{16^{\circ}}^{II} = \frac{0.57}{0.470 \times 3.92} = 0.310 \quad . \quad D_{18^{\circ}} = 0.325.$$

Mean value $D_{18^{\circ}} = 0.329$ sq. cm. per day.

The valency of thorium is therefore 4.

(h) *The diffusion velocity of Uranium X.*

The uranium X used was separated from uranyl nitrate by precipitating it with iron as hydroxide in presence of excess of ammonium carbonate. The iron itself was not separated from the uranium X, and therefore constituted an impurity. The amount of the uranium X in the layers was obtained by comparing their β -ray activities. Owing to the presence of the impurity, the accuracy with which the measurements were carried out was not so great as in most of the other experiments. One c.c. of the solution used contained 2×10^{-10} gm. uranium X. The following were the results obtained:—

$$D_{16^{\circ}9}^I = \frac{0.57}{2.77 \times 0.525} = 0.392$$

$$D_{16^{\circ}9}^{II} = \frac{0.57}{2.77 \times 0.530} = 0.389.$$

Therefore $D_{18^{\circ}} = 0.400$ sq. cm. per day.

The valency of uranium X is 4.

The value of n is either 3 or 4. The latter value is preferred for reasons to be given later, and also because, in accordance with the law of mass action, the Cl ions due to the ferric chloride tend to prevent the dissociation of the UrX Cl_4 . This, possibly gives rise to too low a value of the charge carried.

TABLE III.

Diffusion constants of the radioelements at 18° ,
diffusion taking place in an excess of the anion.

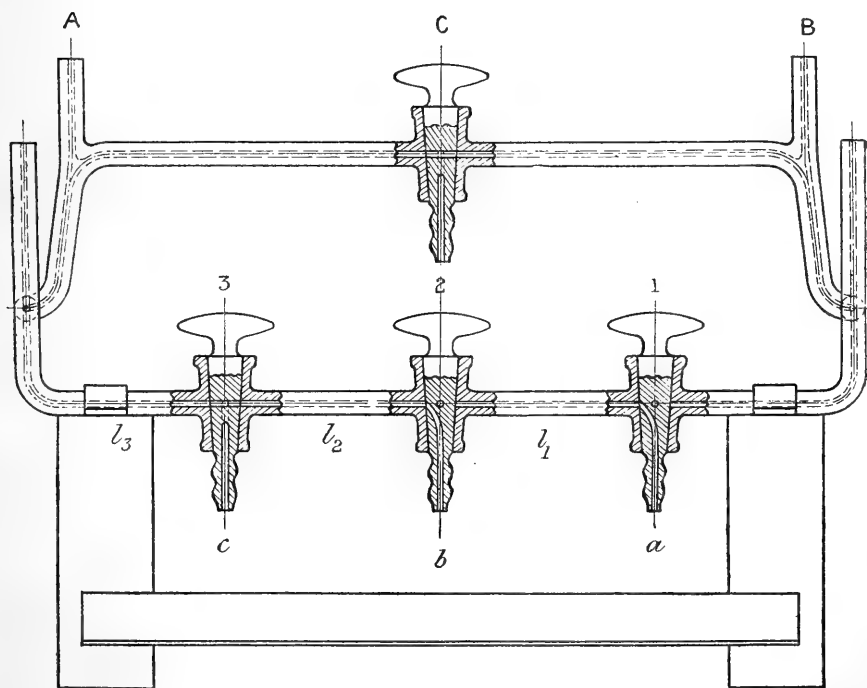
Substance.	Diffusion Constant (sq. cm. per day)
UrX.....	0.400
Io.....	0.327
Ra ..	0.667
RaD ..	0.651
RaE ..	0.646
RaF ..	0.760
Th.....	0.329
Radiothorium.....	0.333
ThX ..	0.659
ThB · (RaB ·, ActB ·) ...	1.21
ThC·· (RaC··, ActC··) .	0.625
ActX··	0.664

§ 7. Ion mobility of the Radio-ions.

The mobility of ions may be calculated, either from the coefficient of migration or the conductivity as the case may be, or may be directly determined. The first method, which is that most generally used, is not applicable to the case of most radio-ions, owing to their small concentration. The conductivity of a solution of radium bromide has been determined, however, by Kohlrausch and Henning*, and from their result the mobility of the radium ion was found to be 57.4.

The mobilities of the radio-ions must therefore be determined directly. The methods in common use for determining the mobility of an ion directly may be divided into two classes. The first of these may be called the volume method, and the second the surface method. In the volume method the apparatus (see fig. 2) is filled with an indifferent electrolyte as far as the tube l_1 . This tube itself is filled with a

Fig. 2.



solution say of RaBr_2 of the same conductivity as the indifferent electrolyte. After electrolysis has taken place for a given time t seconds, the concentration c of the radium

* *Verh. d. Phys. Ges.* vol. vi. p. 144 (1904).

bromide has fallen to $\frac{c}{2}$. The radium bromide of concentration $\frac{c}{2}$ not present in l_1 must be in the cathodic branch l_2 .

If we assume, as Kohlrausch has done, that as soon as the field is applied the ions move all together as a column, the path traversed by the ions in the time t will be $\frac{l_1}{2} = \frac{l_2}{2}$. If

after time t there is still radium bromide of concentration $\frac{c}{n}$ present in l_1 , the displacement of the ion column is

$\frac{n-1}{n}l$ and the mobility of the cation U is $\frac{n-1}{n} \frac{l}{tV}$, where

V is the potential gradient. It was by this method that G. Hoffman * determined the mobility of the ThX ion. The disadvantage of it is that the precipitation of a portion of the dissolved active substance may easily take place, and this makes results uncertain. We tried this method but were unable to obtain consistent results with it. In the surface method, on the other hand, the displacement of the end of the ion column is measured. In this case also the ions move in a column, but the distance traversed by the whole column is much greater, and by this method there is no difficulty in obtaining consistent results. So far when this method has been used the displacement of the ions has been observed optically. The apparatus shown in fig. 2 enables the displacement of the ions to be measured without, if necessary, using optical means. The apparatus is filled, for example, with a solution of copper sulphate. Copper electrodes are inserted at A and at B. The tap C is closed, and then the taps 1 and 2. This enables the copper sulphate in l_1 to flow out through a and b without disturbing the remainder of the system. Copper sulphate of the same strength as the last, but containing now some active body, say $\text{RaF}(\text{SO}_4)_2$, is drawn in through a , and the taps 1 and 2 turned as they had been before. After the field has been applied for a definite time, the three-way tap 3 is turned so that the tubes to the right of the tap are shut off from the rest of the apparatus, and at the same time tube l_3 is open to the air. This enables the contents of l_3 to flow out through c . This amount of solution is tested for activity. The time t is varied until it is just possible to trace the activity of the solution in l_3 . The mobility of the radio-cation is then calculated from the formula

$$U = \frac{l}{Vt}.$$

* *Phys. Zeit.* vol. viii. p. 553 (1907)

The value of the mobility of the H ion of HCl, obtained by this method, phenolphthalein being used as an indicator, was 0.0027 cm. per second. The value found by Lodge under the same conditions, but with a different arrangement, was 0.0026; that calculated from Kohlrausch's formula is 0.0028 cm. per second. Whetham* has shown that in the range of potential gradients employed in these experiments the velocity of the ions is strictly proportional to the potential gradient.

(a) *The velocity of the ions of Radium.*

In this experiment the indifferent electrolyte used was a 1/50 normal HCl solution. Palladium electrodes were used in order to obviate disturbances due to the generation of gas. When l was 10.6 cm. and V , 2.12 volts, the values of t found in four different experiments were 9180, 9270, 9140, and 9220 seconds respectively at 16°. From these results the mobility of the radium ion at 18° is calculated to be 56.6 cm. per sec. When V was 1.49 volts the value was 55.9, and when V was 3.30 volts it was 56.2. The potential gradient was measured by a compensation method. 2.2 per cent. per degree was taken as the temperature coefficient of the mobility, a value which has been obtained in previous investigations of ion mobility. As mentioned above, the value obtained by Kohlrausch and Henning from the conductivity of the radium bromide was 57.3, a value similar to that obtained by us directly.

We prefer to accept Kohlrausch's as the more correct value, and all our results are calculated on this value. Any alteration in the value obtained by Kohlrausch will therefore necessitate a corresponding change in the values given in this paper.

By inserting the values $D=0.667$, and $u=57.3$ in the equation

$$D=0.02232 \frac{u}{n},$$

we obtain

n for radium 1.91.

This value of the valency is in good agreement with the value calculated from the diffusion coefficient alone. It is of course also the value to be expected from the chemical behaviour of radium.

(b) *Ion mobilities of ThX, ActX, RaC, ThB, ThC, RaD, RaE, and RaF.*

The ion mobilities of these radio-ions were also determined by the method described above. The results are tabulated

* Proc. Roy. Soc. vol. lii. p. 289 (1892).

in column 3 of Table IV. In column 2 are placed the values of the diffusion constants, and in column 4 the calculated values of the valency.

TABLE IV.

	D in sq. cm. per day.	u in 10^5 cm. per sec.	n .
Ra	0.667	57.3	1.91
ThX	0.659	58.0	1.96
ActX	0.664	56.1	1.88
ThB	1.21	55.4	1.11
ThC	0.625	54.0	1.93
RaC	0.625	54.5	1.95
RaD	0.651	61.9	2.11
RaE	0.646	61.9	2.13
RaF	0.760	68.8	2.02

As is to be expected from the fact that they have similar electrochemical properties, ThC, RaC, and ActC have very similar ion mobilities.

The ions of ThB, however, move more rapidly than those of ThC, and in this way it is possible to separate ThB from ThC. It is impossible by this method to separate RaD from lead, as these bodies have very similar ion mobilities, namely, 61.0 and 61.9 respectively. RaF may be easily separated from both RaE and RaD on account of its greater mobility.

§ 8. *Relation between the mobility of the Ions and their position in the Periodic Table.*

Bredig* was the first to show that the mobility of an ion in an infinitely dilute solution is a function of its weight. The mobility of the ions of elements belonging to any particular group in the periodic system increases as the atomic weight of the element increases. By means of this rule, it is possible to indicate the position of the elements ThB, RaB, and ActB in the periodic system. These elements are monovalent, and therefore belong either to the group of alkaline metals or to the group containing Ag, monovalent Hg, and monovalent Tl.

From Table V., however, it is seen that if ThB belonged to the alkaline metal group, it would possess a greater mobility than that of cæsium, namely 68.2. Its mobility is, however, less than this amount. ThB is therefore most likely a member of the second group, and since it has a greater atomic weight than silver, and therefore is more

* *Zeit. phys. Chem.* vol. xiii. p. 191 (1904).

electronegative, its most probable position is between thallium and lead. This conclusion is supported by the electrochemical and the chemical behaviour of the substance, as shown by the recent work of the author *, and by Fleck † respectively.

TABLE V.
Mobility of the cations.

Lithium	33.44	Silver.....	54.02
Sodium	43.55	{ Radium B ... }	55.4
Potassium.....	64.67	{ Thorium B ... }	
Rubidium.....	67.60	{ Actinium B ... }	
Cæsium	68.20		
Magnesium ...	49.0		
Calcium.....	53.0		
Strontium.....	54.0		
Barium	57.3	Zinc	47.5
{ Radium	57.6	Copper	49.0
{ Thorium X ...	58.0		
{ Actinium X ...	56.1		

§ 9. *Expulsion of an α -particle or a β -particle from a disintegrating atom, and the difference in valency between the parent and the resultant atom.*

The valencies of no less than 22 radioelements are now known. They are given in Table VI. (p. 412). It now remains to discuss with these data how far the difference in valency between the parent and the resultant atom is due to the expulsion of an α - or a β -particle. For two reasons, however, it is necessary to be cautious in drawing conclusions. The first is that the valency of an element is not an invariable quantity like its atomic weight, but depends on various factors such as, for instance, the nature of the element with which the element is combined. In all our experiments, the radioelements were present as chlorides in a weakly acid solution, and there is no reason therefore for believing that the valencies found are not the chief valencies. The second reason is that all the elements in a disintegration series may not yet be discovered, and the discovery of new elements intermediate between known elements in the series may profoundly modify our conclusions. In this connexion the recent work of Marsden and Darwin ‡ on the complexity of thorium C, and of Fajans § on radium C, is of considerable

* Phil. Mag. vol. xxiii. p. 628 (1912).

† British Assoc. Reports, Dundee, 1912.

‡ Marsden & Darwin, Proc. Roy. Soc. A. vol. lxxxvii. p. 17 (1912).

§ Fajans, Phys. Zeit. vol. xiii. p. 699 (1912).

importance. It may be said that the properties of radium C given in this paper do not refer to the product called radium C' by Fajans, but to its mother substance, namely the product which has a period of 19.5 minutes, and is called radium C₁. There is thus between radium C₁ of known valency, and radium D of known valency, a product radium C' of unknown valency.

TABLE VI.

Radioelement.	Period.	Valency.	Ratio of the difference in valency between parent and resultant product, and the number of positive charges emitted by the parent atom.
Uranium 1	5×10^9 years	6	—
Uranium X	24.5 days	4	$\frac{2}{2} = 1$
Uranium 2	2×10^6 years	6	β
Ionium	10^4 years(?)	4	$\frac{2}{2} = 1$
Radium	1760 years	2	$\frac{2}{2} = 1$
Radium emanation ...	3.85 days	0	$\frac{2}{2} = 1$
Radium A	3.15 mins.	probably 2	?
Radium B	26.7 mins.		?
Radium C ₁	19.5 mins.	2	β
Radium C'	?	?	β
Radium D	16.5 years	2	?
Radium E	5 days	2	β
Radium F	136 days	2	β
Thorium	3×10^{10} years	4	—
Mesothorium 1	5.5 years	2	$\frac{2}{2} = 1$
Mesothorium 2	6.2 hours	?	?
Radiothorium	737 days	4	β
Thorium X	3.67 days	2	$\frac{2}{2} = 1$
Thorium emanation ...	54 seconds	0	$\frac{2}{2} = 1$
Thorium A	1/7 second	probably 2	?
Thorium B	10.6 hours		?
Thorium C	1 hour	2	β
Radioactinium	19.6 days	4	—
Actinium X	10.5 days	2	$\frac{2}{2} = 1$
Actinium emanation...	3.9 seconds	0	$\frac{2}{2} = 1$
Actinium A	1/450 second	probably 2	?
Actinium B	36 mins.		?
Actinium C	2.2 mins.	2	β

Similarly, the properties of thorium C given in this paper refer to the product called thorium C by Marsden and Darwin. This is the parent substance of thorium C₂, a quick changing product of unknown valency. In both these cases, therefore, it is obvious that the connexion between change of valency and expulsion of an α -particle must remain at present unsettled.

β in the fourth column of the table means that the parent substance of the element is a β -ray body. The electrochemical behaviour of radium A renders it very probable that radium A, and therefore very probably thorium A and actinium A, are divalent. It would be extremely difficult to settle this point with certainty.

It is seen from the above table that expulsion of a β -particle seems to affect the valency in a direction opposite to that affected by the α -ray change. In the case of expulsion of an α -particle, the relation is much more obvious. There are nine cases in which the valency of the resultant atom is two units different from that of the parent atom after the latter has expelled an α -particle. These are the transformations of ionium into radium, radium into emanation, thorium into mesothorium 1, radiothorium into thorium X, thorium X into emanation, radioactinium into actinium X, and actinium X into emanation. The case of uranium 1 and 2 is rather a complex one, and will be dealt with in the paper that follows. In ten further cases it is impossible to say whether or not this rule holds, owing to want of complete data, but there is at present no reason to assume that it is not fulfilled. Whether the rule be shown to hold strictly or not by subsequent research, there can be no doubt that the change of valency with expulsion of an α -particle is not simply fortuitous.

After the present work was finished the author's attention was directed to a view, practically the same as that given above, put forward by F. Soddy in his recent book *. It is there pointed out that all long-lived radioelements are elements of even valency, and that the valency suffers a change of two units when an α -particle is expelled. In addition to the nine cases cited above, the change of radium D into radium F, and of the latter into lead, are cited as obeying the rule. Each of these three bodies has a valency of 2. Radium D and lead, however, belong to group IV. of the periodic system, and radium F very probably to group VI. In the present state of our knowledge, therefore, the rule holds better, if instead of saying that the valency of an element suffers a change of two units, we say that the number of the

* 'Chemistry of the Radioelements,' p. 29.

group in the periodic system to which it belongs is changed by two units, after an α -particle has been expelled. Of course when Soddy put forward this view, the valencies of most of the radioelements had not been directly determined, but had been simply assumed to be those of the common elements, to which they are chemically most akin.

SUMMARY.

From the velocity with which a cation diffuses in great excess of its anion, it is shown that it is possible to determine the number of charges borne by the cation, and therefore its valency. The diffusion constants of radium, thorium X, actinium X, uranium X, radiothorium, thorium B, thorium C, radium D, radium E, radium F, ionium, and thorium have been determined, and from these results the valencies of these bodies have been obtained.

By measuring the mobilities and the diffusion constants of radioactive bodies their valencies can also be obtained. This second method may therefore be used to check the results obtained by the first. The mobilities of radium, thorium X, actinium X, thorium B, thorium C, radium C, radium D, radium E, and radium F have been determined, and from these results the valencies of these bodies have been calculated. The values obtained by the second method are in good agreement with those obtained by the first.

Nernst's theory of the diffusion of electrolytes, which was derived and proved to hold for monovalent electrolytes, is shown to be applicable for electrolytes of any valency.

From the relation between the mobilities of ions and their position in the periodic system, light has been thrown on the chemical nature of thorium B. The three B bodies are monovalent, but do not belong to the alkaline metal group of bodies. Their chemical properties lie most probably between those of thallium and lead.

In nine cases after the expulsion of an α -particle by a parent substance, the valency of the resultant product differs from that of its parent by two units. It is at present impossible to say if this rule holds strictly in all cases owing to absence of complete data. The relation is certainly more than a mere fortuitous one.

I wish to thank Professor Rutherford very much not only for the continued interest he has taken in the research, but also for the valuable radioactive preparations he has placed at my disposal.

Physical Laboratories,
Manchester University,
November 1912.

XLI. *The Diffusion of Uranium.* By G. VON HEVESY, Ph.D., Hon. Research Fellow of the University of Manchester, and L. VON PUTNOKY*.

BOLTWOOD found that uranium in disintegrating emits twice as many α -particles as the other bodies in the uranium-radium series, each of which emits one α -particle only. To explain this result we may assume, either that a uranium atom expels two α -particles on disintegrating, or that there is present with the uranium a second long-lived body which also expels an α -particle. Geiger and Nuttall† have shown recently that there are two different α -particles emitted by uranium, one having a range about 4 mm. greater than the other. The emission of an α -particle of definite range is a characteristic property of a radioelement. The obvious deduction, therefore, from Geiger and Nuttall's experiments is that ordinary uranium consists of two bodies, uranium 1 and uranium 2, each of which expels one α -particle. The same authors have shown further that there is a linear relation between the logarithm of the range of the α -particle in air and the logarithm of the transformation constant. From this relation they have deduced that the period of uranium 1 is 5×10^9 years, and that of uranium 2 2×10^6 years. Hence in 2500 parts of commercial uranium, there is one part of uranium 2, and the activity of this body, weight for weight, is 1250 times that of the uranium. The isolation of uranium 2, therefore, would be of considerable practical interest.

In the preceding paper it is shown that after expulsion of an α -particle, the resultant product in many cases has a valency which differs by two from that of the disintegrating atom. It is of interest, therefore, to ascertain whether uranium 2 differs in valency from uranium 1. If it does it would diffuse at a different rate, and should therefore be capable of being partially separated from it.

With this object in view the diffusion rates of the complex bivalent ion UO_2^{++} and the quadrivalent ion U^{++++} have been compared. The bivalent ions are produced by dissolving uranyl salts in water, and the quadrivalent ions by dissolving the urano-salts.

The diffusion constant either of the uranyl ion or of the urano ion may be obtained in two different ways:—

- (1) By determining the weight of uranium in equal volumes of the solution in the various layers.
- (2) By determining the activity of the uranium in equal volumes of the solution in the various layers.

* Communicated by Prof. E. Rutherford, F.R.S.

† Phil. Mag. vol. xxiii. p. 439 (1912).

If uranium 1 diffuses at a different rate from that of uranium 2, some of the layers will be more active, weight for weight of uranium, than others, and the diffusion constant obtained by the second way will be very different from that obtained by the first.

The diffusion apparatus employed in this experiment is described in the preceding paper.

The amount of uranium in a layer of the liquid was determined gravimetrically by evaporating the solution to dryness, igniting first in air and then in hydrogen, and weighing as UO_2 . The activity was determined by rubbing a small quantity of the oxide in a finely powdered condition on a ground-glass disk, and measuring it in an α -ray electroscope. The amount of uranium oxide per sq. cm. exceeded in no case more than $1/3$ mg., as with thicker layers the absorption of the rays by the material becomes of consequence.

The uranyl nitrate used was purified by crystallization. The urano salt was prepared by reducing a uranyl salt electrolytically at a lead cathode surrounded by a diaphragm. The current density employed was 0.15 amp. per sq. cm. Reduction took place in an atmosphere of CO_2 . During the diffusion of the urano salt also, the diffusion apparatus was filled with CO_2 .

The following are the results of the experiments made:—

(1) Diffusion velocity of $\text{UO}_2(\text{NO}_3)_2$ from a $1/5$ molar solution of uranyl nitrate and an 8 molar nitric acid solution in 8 mol. HNO_3 .

Diffusion constant at 18° calculated from the weight of the material used

0.442 sq. cm. per day.

Same calculated from the activity

0.438 ± 0.005 sq. cm. per day.

In this experiment the diffusion of the UO_2 ion takes place in an excess of the anion (NO_3). In this case, as is shown in the foregoing paper, differences in the nature of the migrating cation are more pronounced than in the case when it diffuses in water. The diffusion velocity of the cation in water depends to the same extent on both ions.

(2) Diffusion velocity of $1/5$ molar $\text{UO}_2(\text{NO}_3)_2$ in water. Diffusion constant calculated from the weight of material,

0.576 sq. cm. per day.

Same calculated from the activity,

0.581 ± 0.006 sq. cm. per day.

(3) Diffusion velocity of 1/6 molar $\text{U}(\text{SO}_4)_2$ in water.
Diffusion constant calculated from the weight of material,

0.480 sq. cm. per day.

Same calculated from the activity,

0.480 ± 0.004 sq. cm. per day.

In these experiments diffusion was allowed to take place for periods of from two to eight days.

The results show clearly that the differences in the diffusion constant calculated from the amount of material used and from the activity lie wholly within the error of experiment. If uranium 2 differs in valency from uranium 1 by two units, the diffusion constants calculated from the two sets of data should show a difference of about 30 per cent.

The fact that the diffusion constant of the quadrivalent urano salts is only about 20 per cent. lower than that of the bivalent uranyl salts may seem to contradict the conclusions of the preceding paper. In these experiments, however, not only does diffusion take place in excess of the anion, but the solution used is so concentrated (1/6 molar) that the dissociation of the $\text{U}(\text{SO}_4)_2$ into its quadrivalent ions is incomplete, and it is to be expected therefore that it has a correspondingly greater diffusion constant.

It is difficult at present to say whether or not the results of these experiments contradict the hypothesis that loss of an α -particle from an atom causes the valency of the resultant atom to differ by two from the parent one. The existence of uranium 2, though rendered probable by the work of Geiger and Nuttall* and of Marsden and Barrett†, is not established with certainty. Again, its position in the disintegration series is at present uncertain. It may lie either between uranium 1 and uranium X, or between uranium X and ionium. The experiments of Soddy on the growth of radium from uranium X indicate that it comes after uranium X, though naturally these results are capable of another interpretation. If this were so, uranium (hexavalent) produces uranium X (quadrivalent), and the latter, uranium 2 (hexavalent). The transformation of uranium 1 into uranium X, and that of uranium X into uranium 2, would then result in the valency changing by two units in each case. It is not improbable that this is really what takes place, for the expulsion of an α -ray should change the nature

* *Loc. cit.*

† Proc. Phys. Soc. 1911, vol. xxiii. p. 367.

of an atom so much, that it is unlikely that the parent and the resultant products would differ in no way chemically.

Experiments have been made to separate uranium 1 from uranium 2 by depositing the oxide on electrodes at different potentials. The results have been negative. This agrees with the previous work of Boltwood, and of Soddy, on the same problem.

Summary.

The existence of uranium 2 cannot be shown chemically. Uranium 1 cannot be separated or concentrated from uranium 2 by diffusion. If uranium 2 really exists, a fact rendered very probable by the experiments of Geiger and Nuttall, it is not only very similar chemically to uranium 1, but has also the same valency.

Physical Laboratories,
The University, Manchester.
November 1912.

XLII. *On an Anomalous Variation of the Rigidity of Phosphor Bronze.* By H. PEALING, M.Sc., late Oliver Lodge Fellow, University of Liverpool*.

PHOSPHOR-BRONZE strip is used in many delicate physical instruments, and has largely displaced silk fibre for the suspension of light magnetic and electric systems such as are needed in a vibration electrometer and in quadrant electrometers. The strips are very strong, will stand a good deal of rough usage, are readily manufactured, are very uniform in cross-section, and the ratio of the breadth to the thickness is considerable. The last property is particularly useful when the strips are used in a vibrating magnetometer, where great strength is needed and a very feeble resistance to twisting wanted. De St. Venant calculated that a given couple will produce in a strip whose cross-section is a very elongated ellipse having semiaxes of length a and b , $\frac{a}{2b}$ times the twist it produces in a circular wire of the same cross-sectional area and length, and a similar relationship holds for a strip of rectangular cross-section. As a set off against these advantages the strips have one very serious disadvantage which does not appear to have been noticed before, viz. the restoring couple per unit angle of twist varies considerably with the load which is supported,

* Communicated by Prof. L. R. Wilberforce.

being much greater for a heavy load than for a light one. This discrepancy was noticed during experiments with a vibration magnetometer for which it was necessary to measure the restoring couple per unit angle of twist, which, though small, was appreciable, by means of brass bars of the same dimensions as the magnets whose magnetic moments are being measured; and it was found that the rigidity was much less when the stirrup only was supported than when the brass was held in the stirrup. The discrepancy observed was so large that the following experiments were made to determine the cause of it.

The experiments were made chiefly with phosphor-bronze strips of the following dimensions: (1) 0.0010 cm. thick, 0.022 cm. wide, and 25 cm. long; and (2) 0.0043 cm. thick, 0.48 cm. wide, and 25 cm. long. The dynamical method was used to measure the coefficients of torsion of the strips. One end of the strip was soldered to a piece of brass which was rigidly held in a torsion-head, and the other end was soldered to a light copper stirrup, which supported in a horizontal position circular brass rods of weights varying from .1 gr. to 25 gr. and each about 9 cm. in length. The whole was enclosed in a glass case. When a rod of a given weight had been placed in the stirrup the time of a convenient number of swings was observed. The moments of inertia of the rods and stirrup were then calculated from a knowledge of their measurements and weights. It is easy to see that a knowledge of these and of the time of swing for each of them will give the values of the restoring couple per unit angle of twist. In practice relative values of the restoring couples for the various weights supported were obtained in the following manner:—

Let τ_1 and τ_2 be the restoring couples, T_1 and T_2 the times of swing when the first and second rods were respectively placed on the stirrup, and let I_1 , I_2 , and I_s be the moments of inertia of the first and second rods and stirrup respectively.

Then

$$T_1 = 2\pi \sqrt{\frac{I_1 + I_s}{\tau_1}},$$

and

$$T_2 = 2\pi \sqrt{\frac{I_2 + I_s}{\tau_2}}.$$

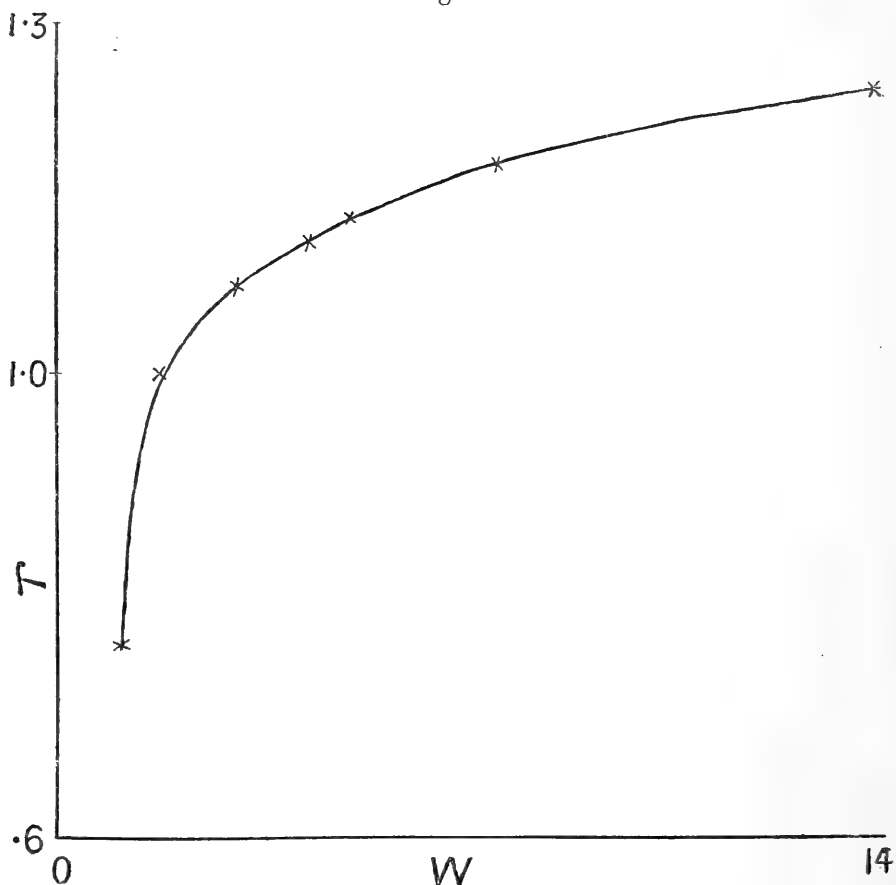
Hence

$$\frac{\tau_2}{\tau_1} = \frac{T_1^2}{T_2^2} \div \left(\frac{I_1 + I_s}{I_2 + I_s} \right).$$

Similarly the ratios of τ_3 , $\tau_4 \dots \tau_n$ to τ_1 were determined.

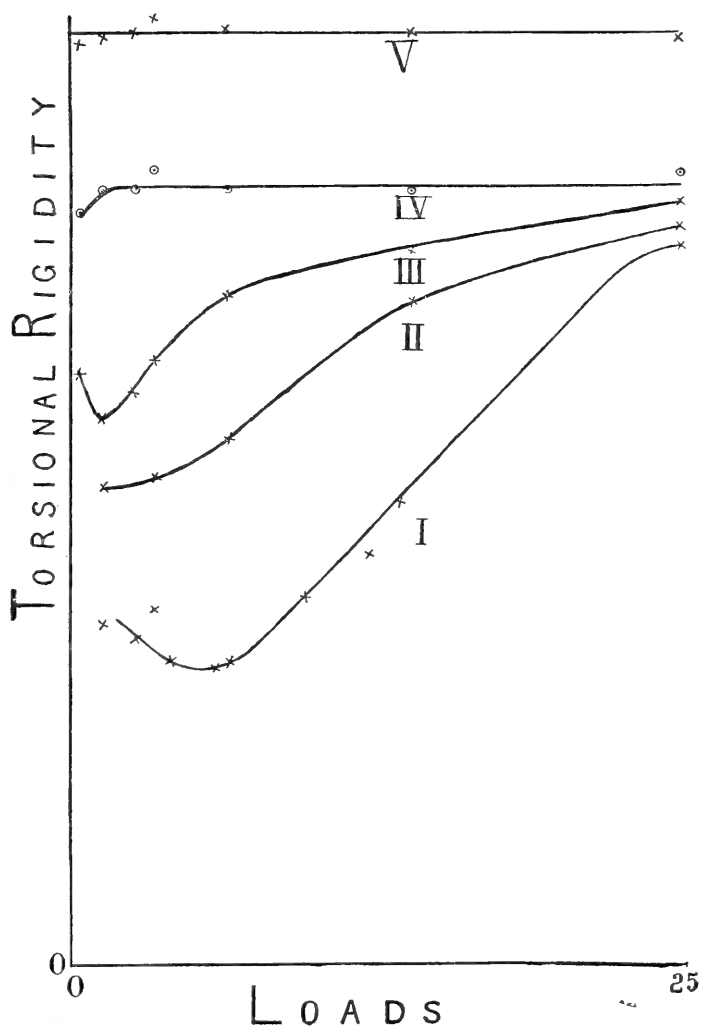
Fig. 1 and fig. 2 curve 1 give typical graphs obtained by plotting the relative values of the rigidity as ordinates and

Fig. 1.



the weights supported as abscissæ. Fig. 1 was for a phosphor-bronze strip 0.0010 cm. thick, and fig. 2 for a strip 0.0043 cm. thick. In fig. 2 it will be noticed that the restoring couple per unit angle of twist for a small load is only one third of that for a heavy load. With the thin strips the rigidity varied very rapidly for small loads, as is shown in fig. 1, decreasing as the load is decreased, but for very small loads increasing again. The discrepancy was different for different strips of the same thickness even when they were cut off the same length, but the maximum ratio of $\frac{\tau_n}{\tau_1}$ was about 3. In general fig. 1 is typical of the behaviour of all the thin strips and fig. 2 of the thick strips, though the amount of variation was different in different specimens.

Fig. 2.



*(I.) Behaviour of strip on first test.

(II.) " " two days later.

(III.) " " fortnight later.

†(IV.) " " after overstraining it by bending.

(V.) " " after annealing it.

* Curve I. became level for heavier loads than those shown in diagram and the maximum value obtained was much less than those in curve V.

† This was tested a month later and to a close approximation the same values were obtained.

Influence of the Thickness of the Strip.

When thicker strips than these were tried variations in the coefficients of torsion were observed, but these were not more than 5 per cent., and were very irregular, the irregularities being much greater for small loads than for large ones.

Some of the specimens of strip 0.0043 cm. thick showed quite as much variation of the torsional rigidity as those only 0.0010 cm. thick, but as a rule this was not so, and the thicker specimens showed less variation. Phosphor-bronze wire 6 mm. diameter showed no variation in the torsional rigidity, although loads of up to 4 kilograms were tried.

Diminution of the Discrepancy with Time.

The graphs obtained were the same no matter in what order the readings were taken, and the values obtained were not appreciably different when the readings were repeated if that was done so at once; but the values obtained when a strip was newly set up differed considerably from those obtained a few days later, the strip having been under a tension of 25 grams weight in the interval. This alteration in rigidity continues for a few days. This is shown in fig. 2, curves I., II., & III. It must be concluded that the strips when under tension gradually alter in structure, and that this alteration is of a permanent nature and makes the strip have a greater restoring couple when supporting small loads than formerly. Other strips which were tried did not show such a pronounced initial difference between the torsion for a slight and for a heavy load, and also showed a much smaller alteration with time, but the alterations that were observed were always in the same direction, and were most pronounced for the small loads.

Influence of Amplitude on the Effect.

A few preliminary experiments showed that the time of swing altered very little if at all with increase of amplitude. The rod which was held in the stirrup was displaced from its equilibrium position about 180° , and the time of the first 20 swings was found to be very little different from the time of any 20 swings subsequent to these, which were of course necessarily of much smaller amplitude. In all the observations mentioned in this communication an initial amplitude of 180° was made; but whenever this was not done it was never found that the time of swing was appreciably different.

Influence of Damping on the Effect.

The damping of the oscillation in all these experiments, although it was not very large, was still very noticeable. The damping was due to two causes, the resistance of the air and the viscosity of the strip. The first may be dismissed from consideration, as it can have only a negligible effect on the period of the rod, but the second is certain to have

an effect on the period especially when the period is small, as the viscosity causes the zero to move periodically. In the case of phosphor-bronze the viscosity could not have been very great as the logarithmic decrement was never very large. To test what effect altering the period (and hence the damping) had on the rigidity the following experiment was made. Two brass circular nuts of total weight 19.5 grams moved on a brass screw 9 cm. long and 6.1 grams in mass. The moment of inertia of the system could then be varied very readily without varying the weight. By this means the time of swing was made to vary in the ratio of 2:1. This alteration in period was not accompanied by any appreciable alteration in the rigidity. For a light load a slightly different procedure was adopted. A rod was soldered to the strip, and then to vary the moment of inertia it was bent into the shape of an inverted V. Again the rigidity did not vary for the same weight. It was concluded that the rigidity does not depend on the damping. In further proof of this it may be mentioned that the strips which had had the discrepancy removed from them by annealing showed no change in the damping of their oscillations.

Influence of Temperature on the Discrepancy.

To test whether raising the temperature of the strip for a short time and then allowing it to cool influenced the variation of rigidity the following experiment was tried. The strip was placed in a glass tube which was then closed and put in a steam-jacket and steam was allowed to flow through briskly for about an hour. When taken out the behaviour of the strip was found to be exactly the same as before. It was therefore concluded that temperature had no influence on the result. In later experiments this view was found to be erroneous, as when the strips were heated strongly enough and sufficiently long to anneal them the effect was largely removed. This will be considered in more detail when an explanation of the discrepancy is given.

The experiments described above were made to discover the properties of this discrepancy between fact and theory; those described below were made to test possible explanations of it.

1. It is well known that in a bifilar suspension the restoring couple per unit angle of twist is proportional to the weight supported. It is possible that a strip of metal will show a bifilar property. To test this a steel strip was set up 67 cm. long, .64 cm. wide, and .04 cm. thick. It was gripped firmly at the top by a pin-vice, and supported in a horizontal position a light rectangular wooden platform provided with

a paper millimetre-scale fastened on it in the direction of its length, and also with a pin-vice through its centre to grip the steel strip. Two equal weights were then placed on the platform at equal distances (say R_1) from the axis of suspension and T_1 the time of a hundred swings noted. These two weights were then placed at a distance R_2 from the axis of suspension and T_2 observed. This was done for a number of weights varying from 100 grams to 1000 grams. When the results were plotted as a graph it was found that $T_1^2 - T_2^2$ was accurately proportional to the weight supported, showing conclusively that the restoring couple per unit angle did not depend upon the weight supported. It will be noticed that the method of experimenting eliminates the effect of the platform and of the finite size of the weights. As the steel strip is much broader than the phosphor-bronze strip, the experiment clearly negatives the view that in the phosphor-bronze strip we have any bifilar property.

2. Most of the specimens examined had small kinks in them, though some seemed to the eye to be perfectly smooth. Now the presence of a kink means that the strip is both bent and twisted at that point. The bending and twisting will have an effect upon the times of swing of the rods, and of these that of the twist will be the greater. As more weight is added the twist of the strip will be increased, hence the effect of the kink will be greater the greater the load supported. The effect of the twist will be to shorten the time of swing, and so the time of swing for the heavy loads will be shorter than it ought to be, and the restoring couple will appear to be bigger for the heavy loads than for the light loads. That is, a twist in the strip will produce an effect of the nature of the one we are investigating. Experiments with the strips did not support this view. Some of the strips were smooth and free from kinks to begin with, but showed the effect just as distinctly as those which had kinks, and when they had kinks made in them either by design or accident, no difference in behaviour was noted. The effect of a twist was tested in a more definite manner by an experiment on the same steel strip described above. The strip was deformed in such a way that it received a twist of about 180° but still hung perpendicularly. The time of swing was altered by only a small amount; but when $T_1^2 - T_2^2$ was plotted as ordinate and the weight supported as abscissæ a straight line was obtained as before. It was concluded that the effect of kinks was negligible.

3. It also occurred to me that as well as overstrains such as kinks, the strips may have overstrains in them owing to the method of manufacture, although the strips may be of

uniform cross-section and perfectly straight. It is well known that metal manufactured in sheets is subject to such overstrains, especially when it is rolled at too low a temperature—as is shown by the fact that a perfectly plane sheet of metal may be made convex by a very small force, and cannot be made plane again unless manipulated by skilful hands. That such overstrains existed in the phosphor-bronze strip seems to be proved by the following experiments.

I thought it possible that if the observed discrepancy was due to such an overstrain it would disappear if the strip was annealed; and on making a trial found that it did so. The method finally adopted for the purpose of annealing the strip was to place it, after carefully straightening it out, on the plane surface of a brass bar 2 cm. square and 28 cm. long, and then to place on the top of the strip a similar bar of brass, care being taken to keep the strip straight during the operation. The whole was then placed on a tripod and gently heated with a blowpipe-flame. When a suitable temperature was reached, the bar was kept approximately at that temperature for about 10 minutes and then allowed to cool. It was not necessary to wait until the rods had completely cooled and the strip could be taken out when fairly hot. It was then found to be very soft, and the restoring couple per unit angle of twist was now the same for all loads. Fig. 2 curve V. shows the results obtained with one strip. It will be noticed that although the annealing has made the strip softer, yet the restoring couple per unit angle of twist has been substantially increased. In the process of annealing care must be taken not to make the strip too hot nor to keep it hot too long, as if either is done the strip becomes “short,” its strength is much diminished, and the restoring couple per unit angle of twist becomes much less. It is difficult to avoid this when using very thin strips; but even in this case the discrepancy was very largely removed, and this alteration was permanent in character. These experiments therefore afford strong proof that the discrepancy is due to an overstrain in the strip. This view was further confirmed by another experiment. It was thought that if the discrepancy was due to such an overstrain, then if it was overstrained in another manner the effect would be altered. It is obvious that it would be better to overstrain it in such a way that the outside layers were treated differently from the interior portions, as the overstrain due to the method of manufacture will be chiefly on the outer layers. Such a method of overstraining is that of wrapping the strip round a narrow cylinder. This method was adopted. When taken off the cylinder it was in the form of a spiral of permanent form,

about 4 mm. in diameter. It was then straightened out as far as possible by hand, and its behaviour tested. The discrepancy was found to have almost disappeared, and when the strip was left standing for four weeks it did not alter perceptibly, so that the disappearance of the effect seemed to be permanent. This is shown in fig. 2, graphs I. and IV. It is seen that the rigidity for the heavy loads has scarcely altered, but that for the light loads has been greatly increased. Other specimens gave similar results. It was not found possible to treat the very thin strips in this manner as they invariably broke in the process. The conclusion drawn was that the bending overstrain removed the discrepancy. A later experiment threw a little doubt on this; for when an attempt was made to straighten the strip a little more it went back to the form of a spiral such as it had been into before; thus proving that the bending overstrain had not been removed by the straightening, but had superposed on it another overstrain largely of the nature of a twist which could be more easily removed. We have, therefore, the alternative explanation that the original effect remains unaltered, but that we have now in addition an opposite effect nearly neutralizing the other owing to the overstrain we have added. This, however, appears to be very unlikely, as the twist we have given to the strip in overstraining it will not produce a contrary effect, but would increase the amount of the original effect. The explanation that the discrepancy is due to overstrains given to the strips during the process of manufacture thus receives ample proof from experiments on bending overstrain, and more particularly on the annealing of the strips.

Sir William Roberts-Austen found that the addition of 2 per cent. of potassium to gold diminished the greatest pull it would sustain without breaking to $\frac{1}{1\frac{1}{2}}$ of its former value. If the presence of a small amount of foreign substance has such a large influence on the strength of a material, it would seem to be very likely that when the relationship of the foreign ingredient, which in the case of phosphor bronze is phosphorus, is altered with regard to the metal, such as would occur with an overstrain, then a large alteration in the elasticity will take place.

Summary.

1. When phosphor-bronze strip is very hard, in which condition it usually is when sent out from the manufacturer, it shows an anomalous variation of its coefficient of rigidity, the rigidity for small loads being much less than for heavy loads.

(a) The variation is greatest in the thin strips, is very small with thick strips, and is entirely absent in phosphor-bronze wire.

(b) It is not present owing to any variation of amplitude or of damping, and disappears partially though very slowly when under tension.

2. The effect was found to be practically removed when the strip was annealed, and was partially removed when it was overstrained by bending it.

3. The explanation given is that the effect is due to overstrains given to the strips during the process of manufacture.

In conclusion it is with great pleasure I express my thanks to Professor Wilberforce, who suggested the investigation to me and who first noticed this anomalous effect.

George Holt Physics Laboratory,
University of Liverpool.
Dec. 7, 1912.

XLIII. The Electrical Vibrations associated with thin terminated Conducting Rods. By Professor H. M. MACDONALD, F.R.S.*

IN a paper, "The correction to the length of terminated rods in Electrical Problems" † Lord Rayleigh concludes, from comparison with the corresponding electrostatic problem, that the difference between the half-wave length of the gravest vibration and the length of the rod tends to zero when the radius of the rod tends to zero. The result is also involved that the radiation from the rod tends to zero as the radius does. The rod is assumed to be perfectly conducting and the medium surrounding it to be such that electrical discharge does not take place from the end of the rod.

The question at issue is whether these assumptions represent the actual circumstances when the medium surrounding the rod is such that electrical discharge, and therefore radiation, can take place from the free end, as, for example, in the case of Marconi's antennæ ‡. The distribution of electric force in the neighbourhood of a terminated rod or wire in air, on which there are electrical oscillations, appears to have been first investigated by Sarasin and Birkeland §, and they conclude that there is direct radiation from the free

* Communicated by the Author.

† Phil. Mag. vol. xxv. p. 1 (1913).

‡ Cf. Phil. Mag. vol. viii. p. 276 (1904).

§ *Comptes Rendus*, vol. cxvii. p. 618 (1893); Phil. Mag. vol. xxxvii. p. 241 (1894).

end of the wire. The disturbance in the immediate neighbourhood of the free end that gives rise to this radiation appears to be of the same kind as in the electrical discharge from a conductor which has a sharp point on it. It would follow from this that the mechanism by which energy is radiated from the extremity of a Marconi antenna is the same as that by which the electric charge of a conductor is discharged from a sharp point on it, and that it receives energy in the same way as a lightning-conductor discharges a thundercloud. These considerations appeared to me to lead to the conclusion that the radiation from the free end was the important factor both in the case of the Hertz resonator and of the electrical oscillations associated with a terminated wire. The mathematical representation of this radiation when the oscillations are not maintained steady presents difficulties which so far have not been overcome; but when the oscillations are maintained the representation can be effected by some distribution of Hertzian oscillators. The radiation from a resonator is the same as that from a Hertzian oscillator whose axis coincides with the straight line joining the free ends of the resonator, and therefore the radiation from a free end is the same as the radiation from an end of the oscillator. In the case of a terminated wire the radiation from the free end may also be assumed to be approximately the same as from an end of an oscillator, and the solutions of both problems obtained on this hypothesis are in agreement with the results of observation on resonators and terminated wires in air.

XLIV. *Notices respecting New Books.*

Annuaire pour l'an 1913. Publié par le Bureau des Longitudes.
Paris : Gauthier-Villars. Price 1 fr. 50 c.

THIS Annual, following out the alternating programme which it has adopted in recent years, contains this year, besides the usual astronomical tables, various tables relating to Metrology, Exchange Geography, Statistics, and Meteorology.

The special technical articles to which the reader will naturally turn at first are by Commandant Ferrié on the application of wireless telegraphy to the transmission of time signals, and by M. Bigourdan on the eclipse of the sun on the 17th April, 1912. But this volume contains also articles of more melancholy interest. These are the memorial discourses of M. Deslandres and M. Henri Poincaré on the astronomer Radau; and alas! the orations of MM. J. Claretie, Lippmann, Painlevé, Appell, Bigourdan, and General Cornille on M. Henri Poincaré himself! "De quelle immense proie la mort vient de se saisir!"

The Theory of Determinants in the Historical Order of Development.

By THOMAS MUIR, C.M.G., LL.D., F.R.S. Vol. II. The Period 1841 to 1860. Macmillan & Co. Limited; London, 1911.

THE care and thoroughness which characterized the earlier volume of this important history of Determinants is evidenced also in the second volume, which brings the history down to the year 1860. Of the many writers whose works are discussed, Cayley, Sylvester, and Brioschi are the most frequently cited; and of these Cayley was the one who gave the great impetus to the study of determinants, due, as Dr. Muir expresses it, to "the choice of an exceedingly apt notation and the masterly manner in which he put the functions to use." The method adopted in the first volume of treating special kinds of determinants in appropriate chapters is followed also here, there being fifteen chapters devoted to General Determinants, Axisymmetric Determinants, Alternants, Recurrents, Wronskians, Jacobians, Skew Determinants, Hessians, Circulants, and so on; while in chapter xvi. some less common special forms are considered. Apart from the value of the book as indicating the historic lines along which the subject developed, Dr. Muir's own critical and explanatory remarks are always most interesting and elucidating. The book should be in every mathematical library, and students should be encouraged to read it along with their more systematic studies of the method. They will learn a great deal else besides.

High Temperature Gas Thermometry. By ARTHUR L. DAY and R. B. SOSMAN; with an investigation of the metals, by E. T. ALLEN. Carnegie Institution of Washington.

THIS is a valuable summary of a series of investigations intended to extend the absolute determinations of temperatures above 1200° , using a constant volume nitrogen thermometer with a platinum-rhodium bulb. The conditions of the success of the investigation are very thoroughly detailed. The book should be in the hands of all those engaged in high temperature work.

Tables Annuelles de Constantes et Données numériques de Chimie, de Physique et de Technologie. Published by the International Committee nominated by the VIIth Congress of Applied Chemistry held in London. Vol. I.; pp. xxix+727. Paris: Gauthier-Villars, 1912.

THIS fine volume of data comprises those only which were published during the year 1910. It is intended to issue a volume yearly, each volume to contain only one year's data. To carry out this great scheme it has been necessary to enrol a large number of compilers, who have reduced to order the data obtained for them by a still larger number of abstractors. The general editor is Dr. Charles Marie of Paris; we must congratulate him on the successful way in which the first fruits of his labours, as presented here, have been reached.

The issue of such a work as this is bound to facilitate the search *Phil. Mag.* S. 6. Vol. 25. No. 147. March 1913. 2 G

by investigators for work done by others cognate with their own. No research institute should be without it.

The work is not intended to be self-paying, at any rate at the beginning. Very substantial monetary aid has been received from numerous Governments, Academies, Scientific Societies, and private individuals. The need for aid still exists we believe, and we venture, in this brief notice, to urge the great claims this enterprise possesses to all the support that can be given it.

Theoretische Astronomie von Dr. W. KLINKERFUES. Third Edition, revised and enlarged. By Dr. H. BUCHHOLZ. Pp. xxxviii + 1070. Quarto, with 67 figures. Brunswick: Fr. Vieweg & Son, 1912. Price 50 Marks bound.

THOSE who are familiar with the second edition of Klinkerfues' 'Theoretical Astronomy,' produced in 1899 by Dr. H. Buchholz, will have a cordial welcome for the third edition of the same work which has recently appeared.

The former edition differed in several important respects from Klinkerfues' original work on which it was based. The earlier lectures of the series, dealing with the fundamental principles on which the determination of the orbit of a heavenly body depends, were developed at much greater length and with more completeness than in the original treatise. The value of the work was also much enhanced by the addition of an elaborate exposition of Gibbs' *Vector Method of Determining an Elliptic Orbit from Three Complete Observations*, and of tables designed to facilitate the labour of computing orbits, which, with one exception, were wanting in the original.

The third edition now before us marks another step in advance, and affords the reader a comprehensive knowledge of the various devices most frequently employed by the astronomer of the present day in determining the orbits of heavenly bodies. It is composed mainly with an eye to practical utility, and the aim of the editor appears to have been, not so much the attainment of mathematical elegance or uniformity of treatment, as to enable the astronomical computer to reach in the most advantageous way the best result deducible from the observational data at his disposal.

Prefixed to the work is a long introduction in which, *inter alia*, the writer discusses at considerable length the reasons for an important change in the first lecture. Towards the end of that lecture as it appeared in the second edition, in describing the general problems of planetary motion, it was stated that Gylden's "Theorie der absoluten Bahn" afforded a satisfactory solution of the perturbation problem and represented the motion for an indefinite time. As is well known, however, Gylden's "horistic" method has been called in question by Poincaré and has given rise to a lively controversy, in view of which the references to the subject in the first lecture of the new edition have been entirely modified.

Amongst the more recent methods of computing the orbit of a planet those of Gibbs, Harzer, and Leuschner are deserving of special mention; and just as the second edition of this work was

distinguished from other textbooks on the same subject by containing an exposition of Gibbs' *Vector Method*, so the third edition offers a special attraction in the lecture (No. 82) dealing with Leuschner's method, and an appendix of 69 pages containing a collection of the formulæ to be applied in different cases, and a series of seven numerical examples fully worked out in detail. Of the last two methods—Harzer's and Leuschner's—the late M. Poincaré has said “MM. Harzer et Leuschner paraissent avoir réalisé un progrès notable sur les méthodes usuelles”; and of those who are familiar with Prof. Harzer's contribution to the *Astronomische Nachrichten*, No. 3371, “Ueber eine allgemeine Methode der Bahnbestimmung,” some may be inclined to regret that room was not found in this volume for a lecture on his method as well as that of the American astronomer. But, indeed, it might well appear unreasonable to complain of omissions in a work containing so much that is new and valuable, and the writer explains at length in his introduction the reasons which guided him in the selection of his material.

The objections to be urged against Harzer's method are chiefly of a practical kind. It presupposes in the most advantageous case five complete observations of the planet, and the amount of labour entailed in the computations is large in proportion to the increased accuracy to be gained. It seemed, however, to Leuschner that, if freed from its practical disadvantages, Harzer's method would permit of the determination of an orbit, without previous hypothesis as to the eccentricity, more readily even than Olber's classical method for determining parabolic elements in the case of comets.

The improvements aimed at by Leuschner were:—

- I. The restriction of the number of the observations to three, the minimum number necessary for the solution of the problem.
- II. The reduction of the fundamental data to be approximated. These are (a) two observed geocentric coordinates, their velocities and accelerations; (b) the rectangular heliocentric coordinates and their velocities—all for the normal date.
- III. A short method of obtaining preliminary values of these quantities which will do away with the solution of simultaneous equations, as in Harzer's method.
- IV. A short method of solving Harzer's equation of the seventh degree for the geocentric distance.
- V. A short method of determining the final values of the fundamental quantities (b) from which the elements are computed.

To ascertain how these improvements are effected reference must be made to the volume itself. Suffice it to say here that the solution of the equation of the seventh degree is accomplished by showing that it reduces to the form of an expression on which Oppolzer bases Table XIIIa of his *Lehrbuch zur Bahnbestimmung*. In the work before us Oppolzer's table has been extended to six places of decimals by Prof. Leuschner. It appears there as Table XVI, covering 42 pages, and by means of it the necessity for solving Harzer's equation by trial is avoided, and the geocentric distance can be found directly by interpolation.

The chief advantages claimed for Leuschner's method in its latest form are:—

The orbit can be computed with or without any assumption as to the eccentricity.

The influence of aberration and parallax can be completely eliminated in the first approximation.

Criteria are given by means of which the correctness of the assumption of a parabolic or of a circular orbit can be decided as the computation proceeds.

It is easy to pass from a parabolic or a circular path to an orbit of a general character in the course of the computation.

By the introduction of expressions of a closed form the correction of the orbit can be extended to time intervals of any length.

The limits of the possible periodic time may be easily determined and thus the degree of certainty attaching to the computed orbit may be estimated.

For much disturbed bodies the perturbations may be considered in the first approximation and so osculating elements obtained.

The generality of the method permits its application without change to comets, planets, or satellites.

It may perhaps be of interest to state here that about the time this book was passing through the press a striking illustration of the capabilities of Leuschner's method was afforded in the case of the minor planet MT 1911. This planet was discovered by Palisa at Vienna on Oct. 3, 1911, and was observed again by him on the 4th. It was also observed later on the same day by Pechüle at Copenhagen. After an interval of bad weather all efforts to recover it failed; and as it seemed to be moving in an orbit of high eccentricity, it was feared that the object was definitely lost.

The problem of finding the orbit from three observations so close together appeared well nigh hopeless; but two of Prof. Leuschner's assistants at the Berkeley Observatory, California, attacking the problem by his powerful method, succeeded in finding an orbit and computed an ephemeris by the aid of which a faint image of the planet, previously overlooked, was detected on some of the Greenwich photographic plates taken on Oct. 11. The planet was subsequently picked up in the same way at Heidelberg and other places.

For the rest Prof. Buchholz's new volume is very similar to the second edition, with the exception that the application of Gibbs' method to the interesting case of Swift's comet of 1880, and Lecture 94 on Mechanical Quadrature, have been omitted to make room for Leuschner's method. But Prof. Buchholz has taken the opportunity afforded by the appearance of a new edition to correct many errors in the mathematical formulæ and numerical computations which had escaped notice in the previous edition; and further he has published, in the form of a separate *brochure* supplied with each copy of his work, a long list of *errata* found in Bauschinger's textbook *Die Bahnbestimmung der Himmelskörper*, and in Oppolzer's *Lehrbuch zur Bahnbestimmung*, which will be much appreciated by computers of orbits who have occasion to consult those important works.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1913.

XLV. *The Selective Dispersion of Mercury Vapour at the 2536 Absorption Line.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University* *.

[Plate III.]

UP to the present time no quantitative determinations have been made of the selective dispersion of non-luminous absorbing gases. About ten years ago I made a somewhat detailed study of the dispersion of sodium vapour, and a good deal of work has been done since by other observers, working along similar lines, but in the case of this vapour no one has succeeded in working under conditions of known density, for the vapour cannot be bounded by transparent solid surfaces on account of the chemical action which it exerts. Ladenburg and Loria's determinations of the dispersion of hydrogen at the α and β lines are not open to this objection, but in this case the absorption and dispersion results from the circumstance that the gas is ionized and rendered luminous by the electric discharge, and the conditions are consequently a little more complicated.

A number of years ago I made some observations of the anomalous or selective dispersion of mercury vapour at the ultra-violet absorption line, the wave-length of which is 2536. This vapour appeared to be an ideal medium for a quantitative investigation of the phenomenon, since it can be contained in transparent vessels of fused quartz, and its vapour density

* Communicated by the Author.

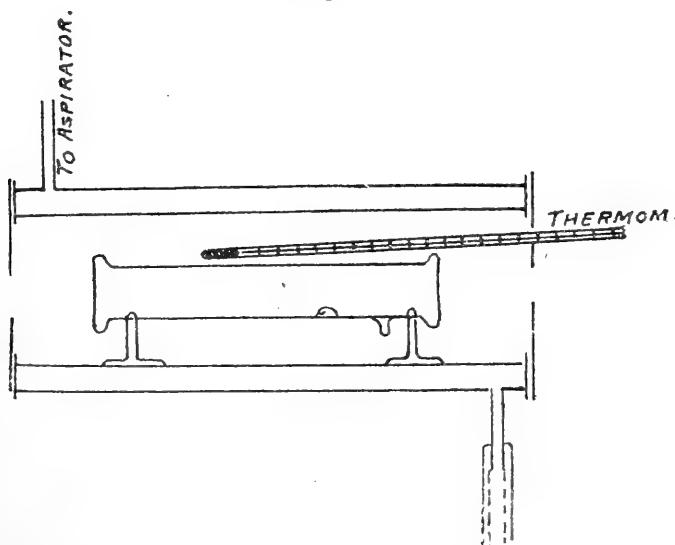
at various temperatures is very accurately known. As it seemed desirable to work with very low vapour densities, the interferometer method was the only one well adapted to the work, and I ordered from Heræus a tube of fused quartz 10 cm. in length, terminated with end plates of the same material, which had been ground and polished, and were fused to the ends of the tubes. This tube is shown in fig. 1 of my paper on the selective scattering, &c. of resonating gas molecules (Phil. Mag. 1912, vol. xxiii. p. 689). It contained a drop of mercury and was very highly exhausted and sealed.

For the ultra-violet interferometer I had Mr. Petitdidier, of Chicago, prepare for me a plane-parallel plate of white fluorite, as it was feared that the double refraction of quartz would give trouble. Fused quartz would perhaps answer the purpose if it could be obtained free from striæ, but as it was my intention to carry on other investigations with the instrument in the remote ultra-violet, I decided upon fluorite. Some difficulty was found in getting a good deposit of silver on the plate, and a cathode deposit of gold was accordingly used. The back mirrors of the Michelson interferometer were of speculum metal, and no compensating plate was used. The quartz tube was introduced into the optical path of the instrument in which the compensator is usually placed, and the two end plates which closed it very nearly equalized the two paths, as their combined thickness was very nearly equal to that of the fluorite plate. It proved to be quite a problem to heat the tube, without at the same time heating the instrument, or the air in its vicinity, for the former would have caused a slow drift of the fringes, and the latter a fluttering confusion of them, either of which would have made photography impossible. The sodium tubes in the earlier work gave very little trouble, as it was necessary to heat only the central portion of the tube, which was done by an electric current. In the present case it was of course necessary to have every part of the tube, including the end windows, at the same temperature, and it seemed at first impossible to do this and at the same time keep currents of warm air out of the optical paths of the instrument. The problem was finally solved in a very simple manner. An air-bath was constructed of the form shown in fig. 1, out of two large brass tubes, one fitting within the other with a clearance of about a centimetre all around. Two small tubes were soldered into the ends of the outer tube, one of which was put in communication with an aspirator pump, and the other with a glass tube which was heated by a Bunsen burner turned down low. The temperature of the inner chamber

could be very nicely controlled by varying the height of the burner and the rate of flow of the water in the aspirator. For higher temperatures the flame was placed just below the aperture of the glass tube, so that the hot products of combustion were drawn through the air-bath.

It was found that the temperature could be held constant, or rather within half a degree, for fifteen minutes or more, and as exposures of two or three minutes were all that were necessary, this arrangement gave entire satisfaction. The

Fig. 1.



air-bath was wrapped up in cotton, and disks of black paper, each perforated with a hole 1 cm. in diameter, were placed over the ends. The beam of light passed through these holes, traversing the quartz tube, which was mounted at the centre of the air-bath. As I do not remember to have seen any account of interferometer work in the ultra-violet, brief mention of some of the difficulties may be helpful to others taking up work along similar lines. The source of light was the iron arc, which was rendered parallel or slightly convergent for the ultra-violet, by means of a quartz lens. The fringes were first found with sodium light and the centre of the system found in the usual manner with a small gas flame. The mirrors of the instrument were adjusted so as to give a system of four or five horizontal fringes across the field of the instrument, which was of course somewhat constricted by the perforated screens of black paper, used to prevent as much as possible the escape of currents of hot air from the air-bath. The iron arc was now placed in position behind the sodium flame and its light focussed upon the back mirrors

of the instrument by means of a quartz lens. An image of the fringe system was now projected upon the slit of a quartz spectrograph by means of a quartz fluorite achromatic lens. This gives us a spectrum of the arc traversed by horizontal black lines (the interference fringes), and if we have perfect compensation of the optical paths, and are at the centre of the system, the fringes will run in a horizontal direction throughout the entire spectrum. As a matter of fact it was found that no fringes at all were visible in the ultra-violet region, and that they sloped in a very oblique direction in the violet, the slope increasing with a decrease of wave-length. This circumstance is due to the use of the two quartz end plates as a compensator for the fluorite plate: the dispersion of the two substances is quite different, and the thickness traversed is not the same. The movable mirror of the instrument was now moved back a little and a second photograph taken. Matters were now worse than before, so the mirror was advanced a little ahead of the position which it occupied (perhaps 200 wave-lengths) when the coloured fringes were visible with white light. The fringes could now be followed through the entire spectrum, though they were very oblique at the extreme ultra-violet end. A further advance of the mirror brought them approximately horizontal in the region of the 2536 line of mercury, where all of the work in the present case was to be done. Viewed with an eyepiece the spectrum now showed nearly vertical fringes in the red and orange, and very oblique ones in the yellow and green.

A rather poor photograph of the entire spectrum is reproduced on Pl. III. fig. 9, which, however, gives a fair idea of the change in the slope of the fringes with change of spectral range. At the right-hand end of the picture (blue) the fringes slope down to the right at an angle of about 45° . In the middle (upper ultra-violet) they are horizontal, while at the left (lower ultra-violet) they slope down to the left. This method of studying dispersion was first used by Puccianti in his study of the vapours in metallic arcs. It has the advantage of giving us a photographic record of the retardations or accelerations, as we may for convenience term them, of waves of various lengths in the vicinity of absorption bands. In the present case we are dealing with a single absorption band only, the 2536 line of mercury, which fortunately falls in the middle of a group of strong iron lines. When mercury vapour is formed in the quartz tube, the fringe systems in the various iron lines are shifted by different amounts, and in different directions. A photograph of the iron spectrum in coincidence with that of the quartz mercury arc, in the

region under investigation, is reproduced on Pl. III. fig. 7. The mercury line which gives rise to the selective dispersion is indicated by a long arrow, and the fainter companion line which borders it on the short wave-length side by a short one. Curiously enough, this faint companion line does not show any evidence of its existence in the absorption spectrum, though there is a faint absorption line on the other side of the main line at about the same distance from it, which I have found represented by a bright line in the fluorescence spectrum of the vapour excited by the light of the cadmium spark. A photograph of this spectrum will be found in the second edition of my 'Physical Optics,' on p. 580, in which the 2536 fluorescent line will be seen to be accompanied by a faint companion on the long wave-length side. The negative, of which fig. 7 is a sixfold enlargement, was made with a large quartz spectrograph by Fuess, which was placed at my disposal by Professor Trowbridge, of Princeton University. It has lost much in the process of enlarging, for on the original the iron line immediately to the right of the mercury line is a beautifully resolved double line. The wave-lengths of the two mercury lines were measured with reference to Rowland's values given for the iron lines, the main line being 2536.5, and the faint companion 2534.8.

The wave-lengths of the iron lines immediately to the left and right of the main mercury line, which are the lines in which the greatest displacement of the interference fringes occur, are 2535.6 and 2536.9. Inasmuch as the mercury line is much nearer the latter, it is in this line that we should expect to observe the greatest displacement of the fringes, for a given vapour density. Over 100 plates were exposed with the tube at various temperatures between 23° and 60°. It was found impossible to work at higher temperatures, for the fringes became very indistinct in the vicinity of the absorption line. This results from the circumstance that one of the interfering beams is weakened by absorption, and interference then takes place between two beams of unequal intensity: moreover it was more difficult to hold the temperature constant during the time of exposure at the higher temperatures. The pictures are scarcely suitable for reproduction as they were made with a small quartz spectrograph, the only instrument at my disposal, nevertheless the five enlargements produced on Pl. III. fig. 10 will serve to give a general idea of the distortion of the interference fringes in the vicinity of the 2536 mercury line. The temperature of the mercury dispersion tube is recorded on each photograph. The position of the mercury 2536 line is indicated on the

first picture by an ink mark. On some of the plates there was an indication of a slight displacement of the fringes in the iron line immediately to the right of the mercury line even at room temperature (23°). It is very slight however, certainly not more than 0.1 of a fringe width. At 35° the displacement becomes very noticeable, amounting to about a quarter of a fringe width. At this temperature the pressure of the mercury vapour is 0.0004 mm. or four times the pressure which it has at room temperature. The length of the quartz dispersion tube being ten centimetres we can definitely state that light of wave-length 0.4 of an Ångström unit longer than that of the absorption line is retarded 0.25 of a wave-length in traversing a column of the vapour 20 cm. in length (since the light traverses the tube twice). It was expected that the fringe shifts would increase proportionally with the vapour pressure, but this was found not to be the case, for at a temperature of 58° , at which the pressure is 0.0215 mm., or five times as great as at 35° , the displacement of the fringes in this same iron line is only 0.6 of a fringe width, whereas if the retardation was proportional to the pressure we should expect a displacement of 1.25 fringe widths. It was thought at first that a mistake might have been made in the identification of the fringe under observation, and that the displacement might be 1.6 instead of 0.6, but an examination of a very large number of photographs taken at intermediate temperatures showed that no error had been made. The displacements of the fringes in the various iron lines for the vapour at different temperatures were measured as carefully as possible on the dividing-engine, and are given in the following table. The wave-lengths are as follows:—

Iron Line No. 1.. .. .	2535.6
Mercury Line	2536.5
Iron Line No. 2	2536.9
Iron Line No. 3	2539.0

SHIFT IN FRINGE WIDTHS.

Temp.	Pressure, mm.	No. 1.	No. 2.	No. 3.
32	0.0031	0.16	0.25	—
41	0.0062	0.25	0.34	—
45	0.0086	0.30	0.40	0.11
50	0.0122	0.40	0.55	0.18
58	0.0215	0.50	0.65	0.25

It is clear from this table that the refractivity of the vapour, or rather that part of it due to the absorption line in question, does not increase in proportion to the vapour density. It appears therefore very doubtful whether this absorption line is due to the normal mercury molecule. We may call it the dispersing molecule, which may either be an atomic complex, or a molecule in a state of ionization, and it seems probable that these exist in small numbers in comparison with the normal molecules. At all events the percentage of molecules in this condition is less as the vapour pressure increases, for, as the table shows, a sevenfold increase in pressure only triples the action on the wave velocity for Line No. 1, and scarcely more than doubles it for Line No. 2.

I feel a little disappointed with the results as a whole, as I had hoped to secure records over a much wider temperature range, dealing with shifts amounting to many fringe widths, but this appeared to be impossible with the arrangement of apparatus adopted. It is a great pity that we do not have some method intermediate in point of sensitiveness between the interference methods and the prism. It is doubtful whether reliable results could be obtained with a prism of mercury vapour, since we should have to use one with a base of 20 cm. to obtain a retardation of half a wave-length across the entire wave-front at a temperature of 58° . I have, however, obtained fairly good photographs of the selective dispersion at the 2536 line by employing a long tube of steel similar to the ones used with sodium, but as we are dealing in this case with non-homogeneous vapour, the method is wholly unsuitable for quantitative measurements. The results given in this paper, while not as satisfactory as I had hoped for, appear to me to be of some interest in that they have pretty clearly established the fact that not all of the molecules are concerned in the dispersion, and consequently in the absorption. Some time during the coming winter I plan to investigate the absorption of the vapour quantitatively at different pressures and densities. The results obtained in the study of the dispersion would lead us to expect that with a given amount of mercury vapour we should have more powerful absorption as we reduced the pressure, which is precisely the opposite of what is usually observed. The very homogeneous light from the resonance lamp, described in my paper on the selective scattering &c. of resonating gas molecules (*Phil. Mag.* 1912, vol. xxiii.) will greatly facilitate this study.

XLVI. *Resonance Experiments with the Longest Heat-Waves.*

By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University* *.

[Plate III.]

IN the autumn of 1910 H. Rubens and R. W. Wood succeeded in isolating and measuring the longest heat-waves known at the time, by a method based on the circumstance that the refractive index of quartz is much higher for these waves than for light-waves and the shorter heat-waves. A description of the method, which may be termed "focal isolation," will be found in my 'Physical Optics,' 2nd edition (1912); also *Phil. Mag.* Feb. 1911. The waves were emitted from a Welsbach mantle and had a wave-length of over one-tenth of a millimetre ($112\ \mu$), and Rubens and von Baeyer subsequently obtained by the same method waves of greater length (0.3 mm.) from the quartz-mercury arc. As the shortest electric waves obtained by von Baeyer have a length of about 2 mm., it will be seen that the gap between the electric and optical spectrum is very nearly filled up.

The very great length of these heat-waves makes it possible to try experiments analogous to the experiments made by various investigators on the action of metallic resonators on electromagnetic waves. I have already commenced an investigation of this subject, and the results obtained up to the present time will be reported in this paper.

The first experiments were made with very minute particles of metallic copper deposited on quartz plates. The metal can be obtained from the chemists in the form of a very fine powder, and if some of this is violently shaken in a tall glass jar, the finest particles remain suspended in the air. If the jar is then inverted over the quartz plate, and allowed to stand for a few minutes, a beautifully regular deposit settles on the plate. Treating the plate to the process four or five times builds up a deposit which is almost opaque to light, the slight amount which struggles through being of a greenish colour. To my surprise I found that even these very heavy deposits, which by actual measurement transmitted only two or three per cent. of visible light, were perfectly transparent to the long heat-waves. The same amount of metal, in fact a much less quantity, in the form of a uniform film would be

* Communicated by the Author.

absolutely opaque to the heat-waves, for we know that the reflecting power of a metal is practically 100 per cent. for all waves longer than about 10μ . The same thing is true of carbon deposits. When studying the transmission of the waves through various substances in collaboration with Rubens, it was found that a deposit of smoke on a quartz plate, so dense that the Welsbach mantle was invisible through it, transmitted over 95 per cent. of the heat radiation. It seemed of interest to ascertain the relation existing between the transparency of a layer of metallic particles, and the size of the particles, in other words, to carry out experiments analogous to those on the action of tinfoil strips of various size (mounted on glass) on electromagnetic waves. Various methods may be used for the preparation of the resonator plates. We may deposit a film of the metal on a quartz plate and then rule it into small squares or rectangles with a diamond point, on a dividing-engine. This method was tried over fifteen years ago by Rubens and Nichols; much shorter heat-waves were then available (12μ), and though the experiments appeared to indicate electromagnetic resonance, they were not as satisfying as was to be desired.

Another method is to prepare metal particles of uniform size and deposit these over the quartz surface.

This was the method first adopted in the present case. I first tried blowing a fusible alloy into a fine spray with an atomizer (the method used by Professor Millikan and his colleagues).

Very perfect spherical droplets can be obtained in this way, but difficulties were found in sorting them out into groups of uniform size of particles, and in depositing them (after sorting) with any regularity of distribution. It then occurred to me to condense a metallic vapour on the quartz plates in the form of a "dew." This method worked admirably. A small quantity of mercury was heated in a beaker, and the quartz plate suspended in a horizontal position about 2 cm. above the surface of the metal. Very regular deposits were obtained in this way, the size of the globules varying with the duration of the exposure of the plate to the metallic fumes.

Photographs of the deposits taken with a microscope are reproduced on Pl. III. figs. 1 to 6 inclusive. A photograph of a "stage micrometer" scale is reproduced immediately below the figures. One division on this scale corresponds to 0.01 mm. As is apparent from the photographs, the diameters of the drops of a given deposit are fairly constant and their distribution is pretty regular.

The diameters are as follows on the plates photographed : fig. 1 ($\cdot 005$ mm.), fig. 2 ($\cdot 01$ mm.), fig. 3 ($\cdot 02$ to $\cdot 03$ mm.), fig. 4 ($\cdot 03$ to $\cdot 04$ mm.), fig. 5 ($\cdot 05$ mm.), fig. 6 ($\cdot 06$ to $\cdot 08$ mm.). Thus the smallest particles used had a diameter equal to about $1/20$ of a wave-length, and the largest $2/3$ of a wave-length. The transmission of each plate of resonators was compared with that of a clean plate of quartz of the same thickness, for radiation of wave-length 1μ , and the 112μ waves obtained by focal isolation. The transmission of the 1μ waves gives us a rough measure of the ratio of the covered to the uncovered portion of the surface, for the metal droplets act merely as opaque obstacles for these very short heat-waves. The observations were made with Dr. Pfund's infra-red spectrometer, which he kindly placed at my disposal. The transmission of the 112μ waves was measured with a radiomicrometer of the same type as the one used in the experiments carried out in collaboration with Professor Rubens. The instrument was made for me by Herr Obst, the mechanician of the Berlin Physical Institute, but as it arrived with the thermo-electric junction damaged it was fitted up with a much lighter junction, which Dr. Pfund made for me, with perhaps $1/10$ of the heat capacity of the original one. It proved far more sensitive than the one used in the earlier work, giving about double the deflexion for the same period, with the 112μ waves obtained under identical conditions. The transmissions of a number of resonator plates are given in the following table :—

	Percentage transmitted of Radiation $\lambda = 1\mu$.	Percentage transmitted of Radiation $\lambda = 112\mu$.	Diameter of Spheres.
Fig. 1.	45	100	$\cdot 005$ mm.
Fig. 2.	26	95	$\cdot 01$
Fig. 3.	32	82	$\cdot 02$ – $\cdot 03$
Fig. 4.	45	58	$\cdot 03$ – $\cdot 04$
Fig. 5.	26	50	$\cdot 05$
Fig. 6.	30	27	$\cdot 07$ – $\cdot 08$

This table shows us that the droplets have no effect on the very long heat-waves until their diameter exceeds about $1/10$ of a wave-length. When the diameter is about $\frac{1}{4}\lambda$, as in fig. 4, the transmission is not much greater for the 112μ waves than for the short ones. For the case shown in fig. 5 we have slightly larger spheres packed much closer together however, so that we have only 26 per cent. transmission for short waves ; even now 60 per cent. of the energy of the 112μ radiation is passed by the plate. On a further increase of size, fig. 6, the transmission is about the same for both wave-lengths.

It appears to me to be worthy of remark that in *no case* is the opacity of the resonator plate greater for the long waves than for the short, in other words, each sphere is able to stop only that portion of the energy of the wave-front which falls upon it, in other words it does not drain the region surrounding it. This rather surprised me, for I had expected to find that with spheres of a certain size we should have moderate transparency for short waves and absolute opacity for the long ones.

I have been unable to find any investigation, either theoretical or experimental, of the action of spherical metal obstacles arranged in close proximity, upon electromagnetic waves, so that there is nothing with which to compare these results at the present time.

Investigations have, however, been made with linear rectangular resonators, and I accordingly commenced experimenting with these. Silver was deposited on quartz and ruled into small squares with a dividing-engine, but I found that the film was quite as opaque to the $112\ \mu$ waves after the cross ruling, as before, though the size of the squares was less than $1/10$ of the wave-length. A photograph of the film with one set of rulings is reproduced on Pl. III. fig. 8. This I have alluded to in a previous paper on Electron Atmospheres of Metals (Phil. Mag. Aug. 1912). It was found that the ruling had not altered the conductivity of the film, though the microscope indicated that the diamond had cut clear through the silver down to the quartz. If the conductivity is not affected we should not expect the opacity of the films to be decreased. The question as to why the conductivity is not affected was discussed in the previous paper. In order to obtain satisfactory results with resonators prepared in this way, it will be necessary to devise a way of making wider cuts, and leaving less metal between them, and experiments in this direction are now in progress.

XLVII. *The Satellites of the Mercury Lines.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University*.

[Plate IV.]

THERE have been many discrepancies among the observations, made by different observers, of the structure of the mercury lines, and even at the present time, with all of the work which has been done with echelons and interference

* Communicated by the Author.

plates, it is difficult to say positively just what is the actual structure of the lines. This is due in part to the circumstance that, with the most powerful echelons, the distance between the successive orders is less than the width of the group of satellite lines under observation, and in part to the ghosts and false lines which many instruments show. An excellent summary, with charts of the observations made by different observers, will be found in a paper by Gale and Lemon in the 'Astrophysical Journal' for Jan. 1910. The authors of this paper made a series of photographs of the mercury lines with a large Michelson grating, and though these photographs do not show as much fine structure as has been found by observers working with echelons, they are more convincing than any photographs which have been published, so far as I know.

Having recently installed at my East Hampton laboratory a plane grating outfit of 42 feet focal length, for the study of the iodine absorption spectrum, and as it appeared that this instrument was far more powerful than the one employed by Gale and Lemon, it seemed worth while to make a study of the structure of the lines as shown under the enormous resolving power of this instrument.

It was found feasible to photograph the blue mercury line (4359) in the fifth order spectrum, for which the resolving power is 375,000 or about that of a large echelon. The green line and the two yellow lines were photographed in the fourth order, for which the resolving power was 300,000. That the grating actually yielded its full theoretical resolving power was amply proved in the study of the absorption spectrum of iodine vapour.

A description of the grating and the method of mounting will be found in a previous paper (Phil. Mag. 1912, vol. xxiv. p. 673), and I need only state in the present paper that it was a very excellent plane grating ruled by Dr. Anderson on the 15,000 machine, ruled surface $3\frac{1}{2} \times 5$ inches (or 75,000 lines in all) mounted in the Littrow form behind a six-inch achromatic lens, kindly placed at my disposal by Professor Campbell of the Lick Observatory. The focal length of the instrument was double that of the one used by Gale and Lemon, and the resolving power of the grating was certainly three times as great as theirs, as will be seen from a comparison of the photographs which accompany this paper with theirs (fig. 4 of Pl. IV. in particular).

The source of light was a Cooper-Hewitt mercury arc, used "end-on." The use of the tube in this position materially shortens the exposure, without giving rise to any reversal

effects so far as I can see, though the relative intensities of some of the satellite lines appears to be a little different from that which obtains when the light is taken from the side of the tube. This is of course due to what we may term the first stage of reversal, certain satellite lines being weakened by absorption more than others, the phenomenon being analogous to one which I mentioned some years ago, namely that a hydrogen tube appears red when viewed from the side, and bluish white when seen end-on (*Phys. Zeitschrift*, 1906, p. 926). The time of exposure varied from 30 minutes to an hour, which compares favourably with the time required with large echelons.

The last paper on the structure of the mercury lines which I have been able to find is that of Lunelund (*Annalen der Physik*, xxxiv. p. 505, 1911), and as comparative tables of the observations made by all previous observers are given in this paper, I shall make no other references. From a comparison of these tables with the photographs obtained with the grating one cannot but help feeling grave doubts about accepting the results yielded by the echelon or interference plate until they have been checked up with a grating, except in special cases. This is especially so in the cases where the width of the group of satellite lines is greater than the distance between the spectra of adjacent orders, which is often the case.

It is customary to give the positions of the satellite lines to the right and left of what is called the main line, in terms of + and - fractions of an Ångström Unit. Some ambiguity results from this owing to the circumstance that different observers do not always choose the same point for the main line ; as for instance in cases where the main line is a doublet, an observer working with an instrument incapable of resolving it would choose its centre of gravity as his zero point, while an observer who resolved the line would choose the stronger component. An example of this will be found in the case of my results on the 4359 line.

My own study of the lines was made at the end of the summer, just before the closing up of my laboratory, with a view of determining whether any new data of value could be obtained. At the time I was unable to refer to any of the previous papers on the subject, and consequently was unable to make a further study of the discrepancies which were found as soon as comparisons were made. Next summer it is my plan to place the spectrograph in an underground tunnel, and secure a larger grating if possible, for the results obtained already indicate that but very little further improvement will

make the instrument equal in resolving power that of the largest interference spectroscope, and at the same time furnish results about which there will be no ambiguity. We will now consider the results obtained in the case of the four lines which I have already investigated.

THE 5769 YELLOW LINE.

A photograph of this line made in the fourth order is reproduced in fig. 1 (Pl. IV.). I have indicated the middle of the main line in each case with an ink dot. The positions of the satellites are as follows :—

$$\begin{array}{r} +\cdot042 \\ 0 \text{ Main line.} \\ -\cdot055 \\ -\cdot112 \end{array}$$

An inspection of the photograph is sufficient to convince us that all of these satellites are real, and yet the one to the left ($\cdot112$) was missed by Gale and Lemon, as well as by all of the other observers except Lunelund, who gives it the same value ($\cdot112$), and Janicki, who placed it at $\cdot113$. Nagaoka records a satellite at $-\cdot109$, which may be identified with it, but his photographs indicate the presence of so many false lines and ghosts that it is difficult to be very sure of anything. I cannot understand why the Michelson grating failed to record it, though, as I have already stated, the use of the tube "end-on" intensifies many of the fainter companion lines. Lunelund's other values agree very well with those given above, though I find no trace whatever of the satellites $+\cdot084$ and $+\cdot121$, which he regards as probably real. He gives their intensities as about one-half that of the one at $-\cdot112$; yet the most careful scrutiny of my photograph fails to reveal the slightest trace of them, though $-\cdot112$ is fully four times as black as the minimum visible on a photographic plate. I feel therefore quite certain that these satellites are spurious.

THE 5790 YELLOW LINE.

This line is shown by fig. 2 (Pl. IV.), and the satellites are as follows :—

$$\begin{array}{r} +\cdot222 \\ +\cdot164 \\ +\cdot131 \\ 0 \text{ Main line.} \\ -\cdot124 \\ -\cdot191 \end{array}$$

and two lines at $-\cdot944$ and $-1\cdot007$.

About these last two there is absolutely no question. Gale and Lemon found them, and I have repeatedly seen them as a single line very close to the main line with a low-power spectroscope (plane grating and lens of 1-metre focus). I never regarded this companion line of the yellow line as a satellite, and was surprised to find it so close to the satellite group with the 42-foot spectrograph. There is on the plate perhaps a faint suggestion of the satellite at $+0.082$, but I should want to take another photograph with a longer exposure before being sure of it. No trace appears of the fainter components given by Lunelund, and I am surprised to find that he does not include the close pair well to the left of the group in his list of lines the existence of which is established, for the photograph published by Gale and Lemon established their reality beyond question.

THE 5461 GREEN LINE.

The spectrograph was not giving its best definition on the evening on which this photograph was taken, on account of a high wind, and the resolution is no better than the one made by Gale and Lemon. I have only to record the discovery of a broad faint band on the short wave-length side of the satellite at -0.233 . The edges of the band are at -0.327 and -0.414 . It is very distinct on the original plate, but has lost much in the process of enlargement, and as it may vanish entirely in the reproduction I have retouched it in the upper half of the picture (fig. 3, Pl. IV.). No trace of this has been found by any previous observer, but there is no doubt about its existence.

THE 4359 VIOLET LINE.

This line was photographed in both the fourth and fifth orders. The fourth order showed the middle line double, a sharp narrow line to the left and a broad one to the right. The fifth order divided the broad component into two, the middle line being resolved into a triplet. I believe that it is still more complex. This photograph is reproduced in fig. 4 (Pl. IV.), print *a* being made darker than *b* to bring out the division of the middle line. The superior resolving power of the grating is well shown by comparing this picture with the one made by Gale and Lemon. I suspect that some of their trouble arose from vibrations and striæ due to air currents, for their photograph made in the fifth order does not appear to show any greater resolving power

than the one made in the third. The positions of the satellites are as follows :—

+·212	Faint : not shown on print, and never observed
+·168	[previously.
+·130	
+·091	
+·029	
0	Main line.
—·034	
—·111	} Barely resolved.
—·124	
—·174	
—·219	} Very faint and never observed previously.
—·282	

These values agree well with the ones found by Gale and Lemon, though we have not taken the main line at the same point, which results in a slight shift of the one set of readings with respect to the other. I consider the position of the main line which I have taken to be the correct one, for the middle line (triplet) is clearly resolved and the central component is by far the brightest. Gale and Lemon evidently took the left-hand component, but there is scarcely any trace of resolution in their photograph.

The satellite +·168, which is the narrow bright one to the right in my photographs, was found by von Baeyer (given as +·188) but was not found by Janicki, Galitzin, or Lunelund, which is sufficient evidence that the interference spectroscopes are not very reliable.

The resolving power of the best ones is only a very little greater than that of the grating with which I have worked, and in my opinion they can only be used to advantage for a supplementary study of the groups of satellite lines after the chief features of the group have been ascertained with the grating.

It is my opinion that the four photographs reproduced with this paper furnish the most reliable information regarding the structure of these mercury lines which we have at the present time.

The placing of the large spectrograph in an underground tunnel will improve its performance, I am sure, as I always found some trouble from striæ ("schlieren") stirred up by air-draughts down the long tube. It is my hope also that a somewhat larger grating may be available by that time.

Note added Feb. 10.—Prof. Hale has just sent me a photograph of the iodine absorption spectrum made with one of

Prof. Michelson's gratings, in their 75-foot spectrograph (Tower telescope), which is superior to those which I made at E. Hampton. Prof. Michelson's grating shows even more than full theoretical resolving power, and is superior to the one with which my work was done.

XLVIII. *On the Imprisonment of Radiation by Total Reflexion.*

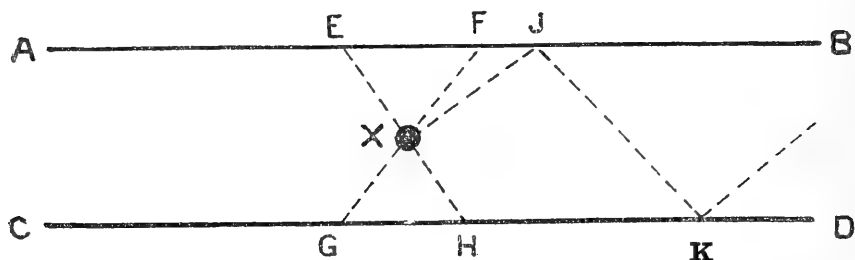
By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University* *.

MY attention was recently drawn to a somewhat surprising circumstance in connexion with fluorescence by Dr. Cooper Hewitt. As is well known, he has now perfected his rhodamine fluorescent reflectors for the mercury arc to such a point that the red fluorescent radiation, plus the direct light of the arc, makes a fairly good imitation of daylight. He found that if the celluloid film stained with rhodamine was backed by white paper the fluorescence was many times brighter than when a backing of silver paper was used. I verified the matter by depositing silver chemically over a small circular area in the centre of a white porcelain plate, and flowing the whole with the rhodamine solution, or with water containing a little fluorescein. Notwithstanding the very high reflecting power of the polished silver film, the intensity of the fluorescence over the circular area was so feeble that it appeared almost black in contrast with the brilliant fluorescence displayed over the surface of the porcelain. The plate was illuminated with the mercury arc in the case of the rhodamine, or with that of the carbon arc, passed through dense cobalt glass in the case of the fluorescein, the experiment being well suited for lecture purposes. If we strip off the coloured celluloid film from the porcelain plate we find its fluorescence becomes even less brilliant than that of the portion backed by silver. The action of the white porcelain surface in raising the intensity of the fluorescence of the film covering it appeared a little puzzling at first. It was noticed, however, that the films which had been stripped from the surface glowed brilliantly *along the edges*, and this circumstance gave me the clue to the action of the matt reflecting surface. The greater luminosity of the edges was evidently due to the circumstance that more radiation was able to escape here than through an equal area of the surface of the film. The action of the matt surface will be

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clear from reference to fig. 1, in which AB represents the upper, and CD the lower surface of a celluloid film stained

Fig. 1.



with rhodamine. Let X represent a fluorescent molecule from which radiation of equal intensity escapes in all directions. Of all the rays leaving X it is clear that only those within the solid cones EXF and GXH can escape into the air. The rays within the cones FXH and EXG are imprisoned by total internal reflexion, the ray XJ for example being reflected back and forth between the parallel surfaces of the film. Silvering the lower surface will cause the rays in the cone GXH to escape through the upper surface, but will not affect the paths of the other rays. If now we bring a white matt surface into optical contact with the lower surface of the film, it will liberate all of the rays which were totally reflected. Take the ray XJ for example: it is diffusely reflected at K, and that portion of the energy within a cone of the same aperture as that of the cone EXF escapes through the upper surface. The rest is totally reflected from the upper surface, and returned to the white surface, when the process is repeated, all of the energy, except that lost by absorption, eventually passing out through the upper surface. The action of the matt surface liberates the energy imprisoned by internal reflexion. If there were no absorption the edges would appear of dazzling brilliancy, as all of the imprisoned energy would be thrown out here. The greater brilliancy of the edges of a fluorescent film was utilized by Becquerel in observing the faint luminosity of certain compounds of uranium, and by Greinacher in the case of the fluorescence of mica films caused by radio-tellurium (*Phys. Zeit.* 1906).

We may test the above theory of the action of a matt surface in increasing the brilliancy of the fluorescence by making photometric measurements. The ratio of the energy within the two cones of rays which can escape without the aid of the matt surface, to the energy imprisoned by reflexion,

is represented by

$$\frac{1 - \cos \theta}{\cos \theta},$$

which is the ratio of the area on a sphere described around the luminous molecule, cut out by the cone of rays EXF, to the area of the hemisphere minus this portion. For celluloid the critical angle is about 40° , *i. e.*, $\theta = 40^\circ$ and

$$\frac{1 - \cos \theta}{\cos \theta} = 0.31;$$

in other words, the imprisoned energy is about three times greater than the energy which escapes. Its liberation by the matt surface should therefore give us about fourfold increase in luminosity. This point was tested with the photometer. As a standard source a rhodamine screen (matt) illuminated by the light of the mercury arc was used, its light being passed through two Nicol prisms by which its intensity could be varied by a known amount. It was compared with a rhodamine film in part covering white porcelain, and in part highly polished silver. The photometer used was a very simple but very satisfactory one made by Dr. Pfund, a semicircle of silvered glass taking the place of a Lummer-Brodhun prism. Equality of luminosity of the two fields of the instrument, with disappearance of the dividing line, was secured in the two cases with the nicols rotated 11° and 22° from the position of extinction. Which means that the rhodamine film on porcelain is 3.8 times brighter than the one on silver, which is in good agreement with the calculated value (4). In making the observations a red glass was placed in front of the photometer to exclude everything except the fluorescent light. (White porcelain alone, illuminated by the mercury arc, appeared practically black when viewed through the red glass.) On completing the work it occurred to me that the case was similar to the one to which I drew attention several years ago, namely that a fused bead of microcosmic salt, raised to the highest temperature possible with a blast-lamp, emits little or no light when removed from the flame, though the platinum wire supporting it glows vividly. This is of course a fine case of the failure of a transparent body to radiate, which is what Kirchhoff's law demands. But as the bead cools down it solidifies and numerous cleavage planes appear. At the moment of crystallization it glows with a dull red light, which persists for several seconds. I found difficulty in explaining this (see *Phys. Optics*, 2nd edition, page 598), but a suggestion

made by Prof. C. E. Mendenhall certainly gives us a satisfactory hypothesis, though there still remain some points which are not quite clear to me. Professor Mendenhall considered that the action of the cleavage planes was merely that they interfered with the imprisonment of radiation by total reflexion. All rays originating within the ball which strike the surface at an angle greater than the critical angle are reflected around the inner surface over and over again, so that they eventually may be considered as having traversed a layer of the medium of infinite thickness. If the medium has any absorption at all, and no media are perfectly transparent, this radiation will be of the same type as that of a black body at the same temperature. Scratches on the surface or internal cleavage planes liberate this energy by interfering with the total reflexion.

Professor Mendenhall has suggested that I include some of his observations in the present paper.

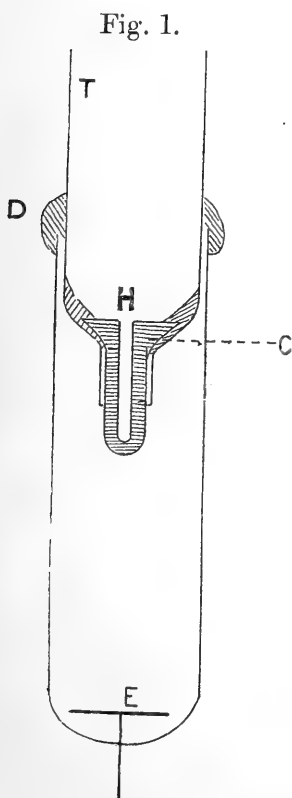
He writes me that he made a scratch on the surface of a ball of fused quartz, which was then heated in a Bunsen burner. The black-body temperature of the scratch, as observed with an optical pyrometer, was 850°C. , while that of the rest of the ball was barely 600°C.

From similar considerations he concludes that a uniformly heated, nearly transparent sphere should appear more luminous towards the limb. (A solid incandescent sphere appears as a uniformly illuminated disk, as a result of the cosine law.) I have verified this with a hollow glass bulb filled with a very dilute solution of rhodamine, illuminated by the mercury arc and viewed through red glass. If a spot on the surface of the bulb is finely ground with flour emery, this spot appears extremely luminous when near the limb, as a result of the liberation of the fluorescent rays which are undergoing total internal reflexion. The bulb appears slightly more luminous at the limb, even when the surface is not roughened. I have observed the same thing in films of celluloid stained with rhodamine, which appear much more luminous when viewed obliquely, at nearly the angle of grazing emergence, than when observed by rays which leave the surface nearly parallel to the normal.

In regard to the microcosmic bead, I am now of the opinion that most of the light comes from the hot wire. It is difficult to devise a means of supporting a fused bead on a non-luminous support; but I have watched their fall from the fifth floor of the laboratory at night, and have found no evidence of any brightening during the drop of five stories.

XLIX. *Temperature of the Cathode and Anode in a Geissler Tube.* By B. HODGSON, M.Sc., Ph.D., Assistant Lecturer in Physics, The University, Bristol*.

§ 1. **W**HILST working on gas-absorption and cathode disintegration in vacuum-tubes, the possibility suggested itself that the temperature of the cathode might play some important part in the phenomena. The following experiments were undertaken to investigate the temperature of the cathode under different conditions of current and gas pressure, other conditions determined by the tube used—as, for example, loss of heat by conduction, &c.—remaining constant. Their chief interest, however, lies in certain theoretical deductions.



§ 2. *Apparatus.*—A high tension battery giving 3200 volts supplied the current. The electrical circuit consisted of this battery, the vacuum-tube, a variable liquid resistance, and a galvanometer reading to 10^{-6} amp. and shunted for higher currents. A Gaede pump was used for evacuating. The vacuum-tube used was of the form shown in fig. 1. C is the cathode shaped to fit closely into the tube T and sealed in position by means of picéin. H was a cavity drilled into the cathode and of such a size as to hold the bulb of a thermometer. The tube T just passed inside a larger one D and the whole was made air-tight at D by means of picéin. The anode consisted of an aluminium disk E.

§ 3. The current was kept constant by means of the variable resistance, and the cathode ultimately took up a temperature at which the rate of supply of heat-energy by the bombarding positive ions was equal to the rate of cooling by radiation, conduction, and, to some extent, convection.

§ 4. *Results.*—The following tables and curves give the results of some experiments in air, oxygen, and carbon

* Communicated by the Author.

dioxide. In the tables, i is the current in amps., and T the excess temperature of the cathode above air temperature.

TABLE I.—Air.
Pressure = 2·8 mm.

i .	T (°C.).
0·00084	5·07
0·00127	9·35
0·00200	14·10
0·00230	16·45
0·00282	19·35
0·00295	20·10

TABLE II.—Air.
Pressure = 1·0 mm.

i .	T (°C.).
0·00067	5·05
0·00119	8·05
0·00155	10·20
0·00194	13·30
0·00220	15·75
0·00280	19·20

TABLE III.—Air.
Pressure = 0·41 mm.

i .	T (°C.).
0·00015	0·80
0·00090	6·15
0·00180	11·35
0·00195	13·30
0·00220	14·85
0·00230	16·00
0·00265	18·00

TABLE IV.—Air.
Pressure = 0·17 mm.

i .	T . (°C.).
0·00043	3·10
0·00058	4·85
0·00082	6·65
0·00115	9·45
0·00183	16·30
0·00187	15·55
0·00210	19·55

TABLE V.—Oxygen.
Pressure = 3·7 mm.

i .	T (°C.).
0·00080	6·40
0·00127	10·10
0·00175	13·40
0·00220	17·05
0·00245	18·80
0·00250	19·50

TABLE VI.—Oxygen.
Pressure = 1·65 mm.

i .	T (°C.).
0·00085	6·70
0·00155	11·10
0·00215	15·75
0·00265	19·15

TABLE VII.—Oxygen.
Pressure = 0·57 mm.

i .	T (°C.).
0·00057	3·9
0·00120	8·8
0·00185	13·1
0·00225	16·2
0·00280	20·2

TABLE VIII.—Oxygen.
Pressure = 0·20 mm.

i .	T (°C.).
0·00060	4·8
0·00125	10·2
0·00180	15·0
0·00220	18·8
0·00230	19·55

TABLE X.—Carbon dioxide.

Pressure = 1.9 mm.

<i>i.</i>	T (°C.).
0.00135	10.1
0.00205	16.0
0.00247	18.8
0.00272	20.8

TABLE IX.—Carbon dioxide.

Pressure = 7.0 mm.

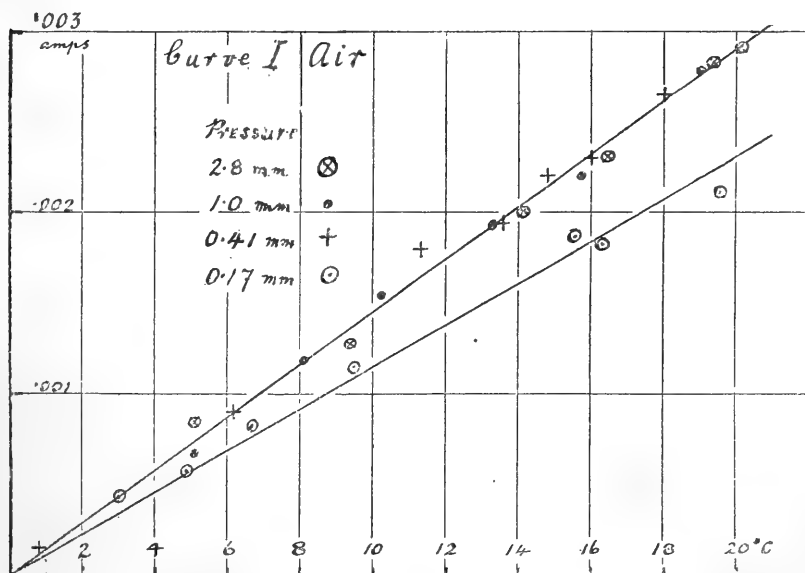
<i>i.</i>	T (°C.).
0.00063	6.30
0.00147	13.40
0.00167	16.75
0.00175	17.65
0.00180	17.55
0.00197	19.35
0.00216	18.55
0.00235	21.15
0.00240	23.15

TABLE XI.—Carbon dioxide.

Pressure = 0.30 mm.

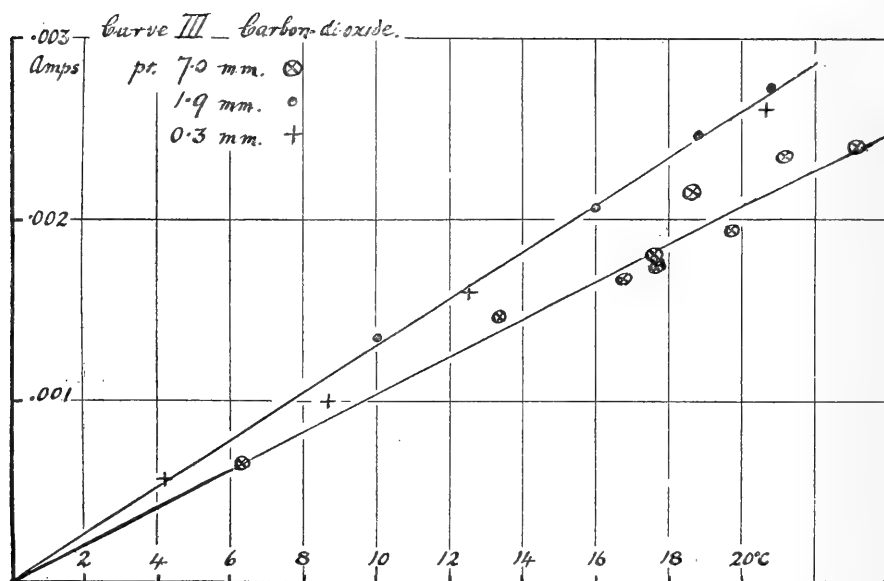
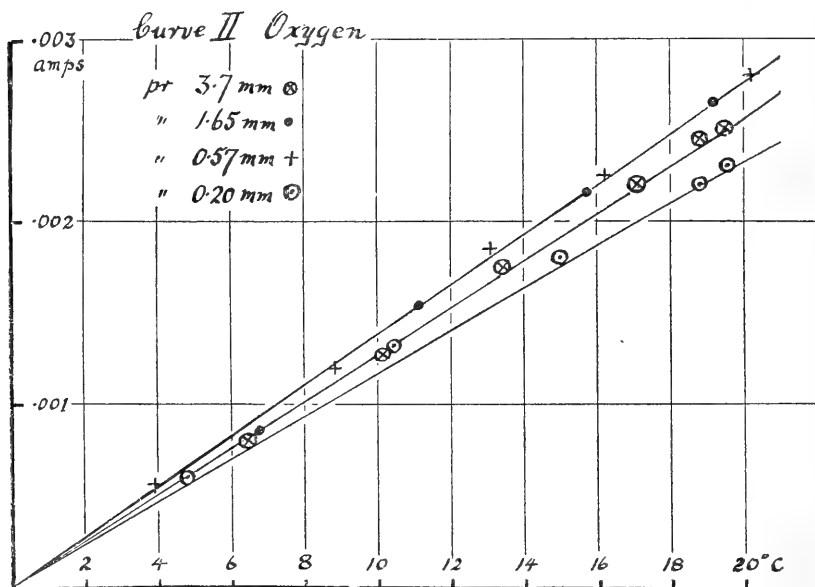
<i>i.</i>	T (°C.).
0.00057	4.2
0.00100	8.7
0.00160	12.5
0.00260	20.7

These results are shown in Curves I., II., and III. The curves show that for the range of temperature obtained, a



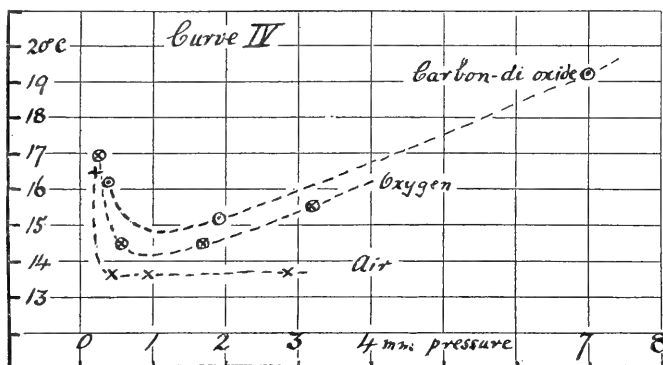
linear relationship exists between the current and the temperature of the cathode for all the gases. This is to be expected if the rate of cooling of the cathode is proportional to its excess temperature above that of the air. The cooling curves obtained showed that this was nearly so.

There appears also to be some pressure at which the heating effect for constant current is a minimum. This is shown in



Curve IV., where the temperature-pressure curve is given for a current of 0.002 amp. Sufficient points were not obtained, but further experiments are being carried out to fix it definitely for different gases. It was thought that the effect might be spurious owing to different rates of cooling of the cathode for different pressures; but no change in the cooling rate was detected by experiment. It is possible that

this minimum coincides with that found by Ebert * at which a discontinuity occurs in the relationship between pressure and width of the dark space, and further experiments on this point are in progress.



§ 5. *Anode Temperature.*—By using the same electrode and reversing the current in the tube, the anode temperature could be investigated.

The following tables show the results obtained.

TABLE XII.—Air.

Pressure = 2.7 mm.

<i>i.</i>	T (°C.).
0.0019	2.55
0.0038	4.80
0.0051	6.70
0.0065	9.00
0.0071	9.35

TABLE XIII.—Air.

Pressure = 1.05 mm.

<i>i.</i>	T (°C.).
0.0036	3.4
0.0050	4.9
0.0074	6.8
0.0081	7.5

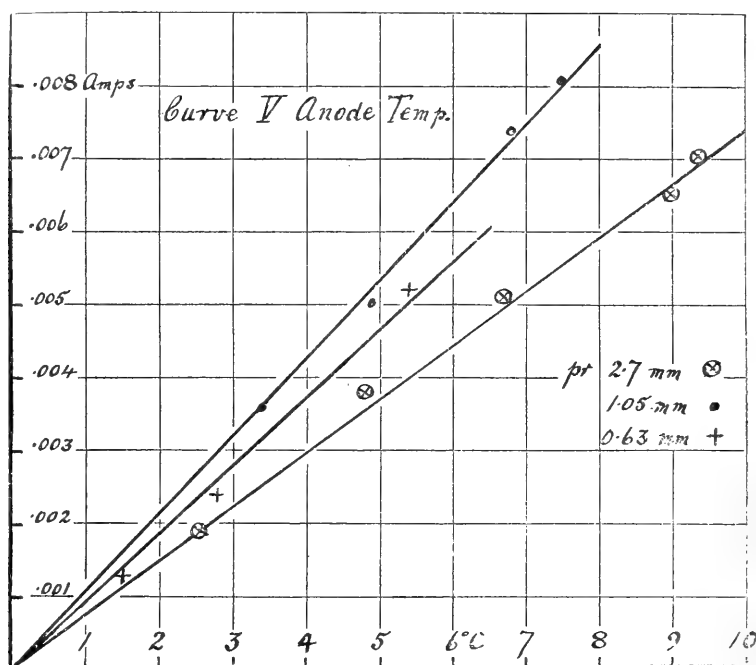
TABLE XIV.—Air.

Pressure = 0.63 mm.

<i>i.</i>	T (°C.).
0.0013	1.5
0.0024	2.8
0.0052	5.4

* Ebert, *Ver. Deut. Phys. Ges.* ii. p. 99 (1900).

These results are shown in curve V. There is, again, a linear relationship between T and i , but the anode temperature is only about $\frac{1}{7}$ that of the cathode for the same current.



The change in pressure produces much greater changes in temperature than in the case of the cathode.

§ 6. The lack of definite knowledge of the mechanism of the discharge in the cathode dark space introduces difficulties in the way of theoretical discussion.

If we assume the normal cathode fall to be the potential through which a positive ion must fall in order to gain sufficient energy to ionize the cathode metal*, the relative number of positive and negative carriers at the surface of the cathode can be found.

The mass of the copper cathode was 135 grams, and the rate of cooling at $13^{\circ}.5$ C. excess temperature (above air temperature) was $0^{\circ}.456$ C. per minute. Thus the energy lost per second was 4.1×10^6 ergs; and this quantity was supplied per second by the bombardment of the positive ions. If we now suppose that the majority of the positive ions originate just outside the cathode dark space, and that each ion on striking the cathode produces an electron, we have

$$ne = \frac{i}{2},$$

where n is the number of positive ions striking the cathode

* Stark, *Winkelmann's Hdbk. der Physik*, Bd. iv. p. 516.

per second, e is the charge per ion (4.65×10^{-10} e.s.). This gives, for $i = 0.00197$ amp. (the current producing an excess temperature of $13^{\circ}.5$ C.)

$$n = 6.36 \times 10^{15},$$

so that the mean energy given to the cathode per ion

$$= 6.5 \times 10^{-10} \text{ erg.}$$

Now the cathode fall of potential is insufficient to supply this energy. The cathode fall for copper in air is 252 volts*, which gives the ion passing through it only

$$3.9 \times 10^{-10} \text{ erg.}$$

This leads to the conclusion that all the positive ions do not ionize, and that there is an excess of positive over negative carriers taking part in the discharge. The electron leaving the cathode gains energy sufficient to ionize many times in passing through the cathode dark space, and the positive ions produced inside the cathode dark space will give up their energy wholly as heat. Recent experiments by Sir J. J. Thomson† indicate that ionization takes place inside the cathode dark space. Further, owing to collision, some of the positive ions originating outside the cathode dark space may lose energy by collision and also cease to be ionizers.

Now if n positive ions reach the cathode per second and ionize, and m per second give up their energy to the cathode as heat, then

$$\begin{aligned} e(2n + m) &= i \\ 2n + m &= 12.72 \times 10^{15}. \end{aligned}$$

A minimum value for m can be found if we further assume that the n ions which ionize do not impart any heat energy to the cathode. If the average energy of the m carriers is E , then

$$mE = 4.1 \times 10^6 \text{ ergs.}$$

Now E is less than the energy gained by falling through the cathode fall (*i. e.* 252 volts), so that

$$m > 1.04 \times 10^{16}$$

and

$$n < 0.12 \times 10^{16}.$$

Thus only $\frac{12}{116}$ or $\frac{1}{10}$ of the current at the surface of the cathode is carried by electrons.

* Rottgardt, *Ann. d. Phys.* xxxiii. p. 1193 (1910).

† Sir J. J. Thomson, *Phil. Mag.* August 1912, p. 225.

These relations are true whether the cathode glow is normal or abnormal; for the linear relationship between current and temperature holds with both these states.

It might be argued that the mean energy of 6.5×10^{-10} ergs per ion was due to ions originating outside the cathode dark space and falling through a greater potential than 252 volts. In order to gain this energy a fall of about 400 volts is necessary, and since the potential gradient outside the cathode dark space is considerably smaller, these ions would have to pass a distance much greater than the width of the dark space to gain this energy. The frequency of collision in the comparatively high pressures used makes the acquisition of energy in this way very improbable.

§ 7. In the case of the anode, lower temperatures prevail for the same current. A current of 0.0051 amp. produced an excess temperature of 63.9 C. in air at 2.7 mm. pressure. At this temperature the loss of energy per second was

$$1.9 \times 10^6 \text{ ergs.}$$

If each negative carrier ionizes, then

$$n = 1.6 \times 10^{16},$$

and the average energy per carrier is

$$1.2 \times 10^{-10} \text{ erg,}$$

corresponding to a fall of potential of about 80 volts, much greater than the anode fall of potential, which is about 24 volts in air.

If only a small fraction of the negative carriers ionize, then the negative ion must fall through about 40 volts in order to account for the heating effect, and this potential drop is still greater than the anode fall. Thus though the cathode fall is able to account for the heat energy given to the cathode, the anode fall alone cannot do so for the anode.

§ 8. *Summary.*—1. There exists a linear relationship between the current through a vacuum-tube and the heat energy communicated to the cathode both for normal and abnormal cathode glow.

2. There exists a pressure at which this effect is a minimum.

3. The ratio between the positive and negative carriers at the cathode is approximately 10 : 1.

4. A linear relationship between current and heat energy exists at the anode—though for the same pressure and

current the heat communicated is much less than in the case of the cathode.

5. The anode fall alone is not able to account for the heat energy communicated to the anode.

The above work was done in the physical laboratory of the University of Bristol, and I wish to record my thanks to Dr. A. M. Tyndall for placing at my disposal the necessary apparatus.

Note.—Since the above paper was written it has come to the author's notice that the result of Summary (1) was obtained by Granqvist in a paper on cathode disintegration (*Kon. Vet.-Akad. För. Stockholm*, 1898, No. 10, p. 726).

L. *A Spectroscopic Study of the Electric Brush Discharge in Water and Salt Solutions.* By HAROLD SMITH, M.Sc., Research Student of Armstrong College*.

[Plate V.]

WHEN the various types of electrical discharge are made to occur under the surface of liquids, and the light examined with a spectroscope, it is found that the spectra emitted are of quite a different character from the spectra of the same discharges occurring in air.

The electric arc burning under liquids has been the subject of an investigation by Konen†. He found that the lines were sharper, fainter, and with fewer self-reversals than was the case with the arc in air. Moreover, he found that the nature of the surrounding liquid had no influence on metallic spectra, except in the case of very concentrated solutions of barium and calcium salts. In these two cases the strongest lines of barium and calcium appeared.

The spark-discharge in liquids has been investigated by Wilsing‡, Lockyer§, Hale||, Konen†, and Finger¶. It was found that the nature of the liquid had no effect upon the spectrum, except in the case of certain very concentrated salt solutions, just as with the arc. Hale, using iron electrodes, also found that various salt solutions caused almost the whole of the iron spectrum to be reversed.

* Communicated by Professor Stroud, D.Sc.

† *Ann. der Phys.* iv. 9. p. 742 (1902).

‡ *Astrophys. Journ.* x. p. 113 (1899).

§ *Proc. Roy. Soc.* lxx. p. 31 (1902).

|| *Astrophys. Journ.* xv. p. 132 (1902).

¶ *Zeitschr. wiss. Phot.* vii. pp. 329 and 369 (1909).

If the secondary of an induction-coil is connected to two electrodes immersed in a liquid, one electrode being a metal plate and the other a wire enclosed in glass with only the extreme end exposed, a luminous *brush* is obtained at this enclosed electrode. Konen (*l. c.*) examined this brush in various liquids and found that the nature of the pole did not affect the spectrum, while the nature of the liquid was all important. He examined this brush in a large number of liquids and weak solutions. Distilled water gave the D lines of sodium and the hydrogen lines, while weak solutions gave also the strongest lines of the metal of the dissolved salt. He looked for, but was unable to find, the lines of oxygen. He does not mention whether he observed both the spectra of hydrogen. Ether, alcohol, and glycerine gave the hydrogen lines and the Swan spectrum. Glycerine also gave the oxygen lines. Ammonia gave the D lines, the spectrum of hydrogen, and the ammonia bands.

Konen's observations were limited because they were visual only and because he was unable to produce a condensed brush. He found that the insertion of a condenser in parallel with the discharge cell destroyed the brush.

This type of discharge seems to have received no attention since Konen's account of it, and as it presents interesting features which are quite different from the arc and the spark-discharge in liquids, the present research was undertaken to investigate it more fully. The brush and the capillary discharge, in distilled water and in a few weak salt solutions have been studied.

Apparatus.

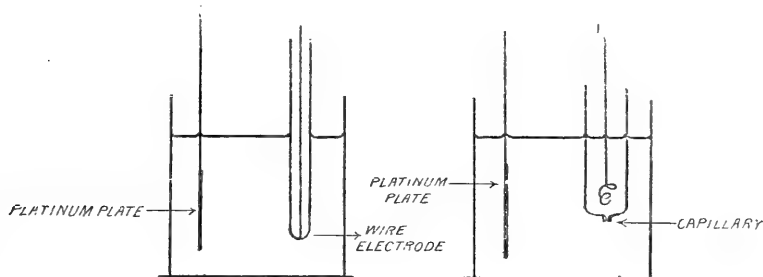
A large induction-coil, the primary being fed with alternating current, was used to produce the discharge. The electrodes used for producing the brush were made from platinum wires of various diameters. These were sealed into glass tubes, the protruding end of each wire being filed off till the platinum was quite flush with the glass. The liquid cell in which the brush was produced contained one of these electrodes, the second electrode being a square inch of platinum foil (fig. 1).

Another type of cell used was one in which the enclosed electrode was replaced by a tube made of fused silica. The part of the tube immersed in the liquid ended in a fine capillary. The tube was filled with the same liquid as that in which it was immersed, and either a platinum plate or a

wire was suspended in it to act as an electrode (fig. 2). In this case no visible discharge occurred at either electrode, but the capillary, if sufficiently fine, was rendered luminous by a high tension current. The volume of all the cells used in these experiments was 200 c.c.

Fig. 1.

Fig. 2.



In the case of distilled water and weak solutions it was possible to obtain a luminous discharge in either form of cell simply by connecting the electrodes to the secondary of the induction-coil. If the points protruded, or were too broad, or if the capillary was too wide, or the solution too strong, no luminous discharge occurred.

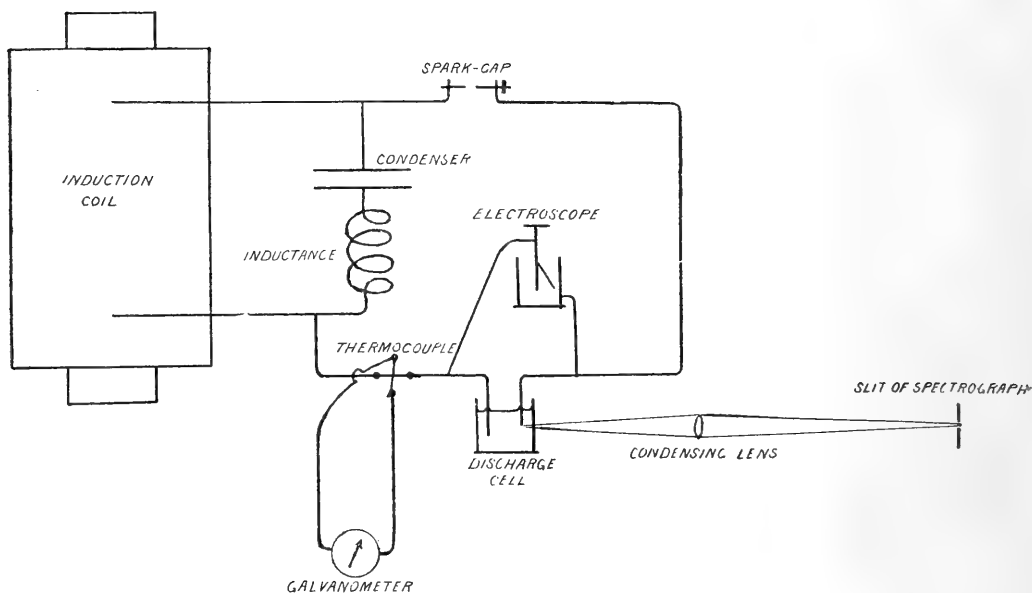
The introduction of a spark-gap in series with the cell had no noticeable effect. The insertion of a condenser in parallel with the cell increased the luminosity in weak solutions and acids. If a spark-gap was now put in series with the cell the discharge increased in luminosity and violence. In this type of discharge the width of the point or capillary was of little importance. Even a protruding point yielded a brush with the condenser and spark-gap discharge; the brush in this case confined itself chiefly to the extreme end of the wire, although it occasionally appeared at the junction of the platinum and the glass. In distilled water and very weak solutions the condensed brush was always feeble. It was brightest and most violent in fairly strong solutions.

A mirror, rotated by hand, was used to observe changes occurring in the brush or capillary discharge. When no condenser or spark-gap was used it showed the discharge drawn out into long bands of light, separated by short dark spaces. Each band corresponded to one-half alternation of the current, the dark spaces occurring when the current in the primary had reached its maximum or minimum value. The introduction of a condenser broke each of these bands up into a series of dots—generally about twenty. The

insertion of a spark-gap diminished the number of dots but increased their brightness. As the spark-gap was lengthened the dots in a series diminished still further in number till there was but one very brilliant one. The number of these dots in a series gave the number of times the condenser discharged through the brush per half alternation of the current.

An image of the brush, or of the discharge in the capillary, was focussed upon the slit of a Hilger fixed-arm spectrograph. The limits of the spectrum obtained lay between about $\lambda=6700 \text{ \AA}$ and $\lambda=4200 \text{ \AA}$. Photographs were taken for different liquids, points and capillaries being used of various diameters. The electrical conditions were varied as much as possible. The general arrangement of the apparatus is shown in fig. 3.

Fig. 3.



An attempt was made to correlate the results with the electrical conditions of the discharge. For this purpose the current was measured with a type of hot-wire ammeter often used for high-frequency current measurements in wireless telegraphy. A single strand of very fine platinum wire was stretched across the junction of a copper-constantan thermocouple made of very fine wires. The platinum wire was in series with the cell, the thermocouple in series with a suitable galvanometer. The heating effect of the platinum wire at the junction was sufficient to produce a current in the thermocouple circuit which would give measurable deflexions on the galvanometer scale. The coil of the galvanometer

was connected to the outer case ; this was found necessary in order to avoid electrostatic effects.

The potential difference between the electrodes was measured by means of an electroscope in parallel with the cell ; the electroscope being standardized by comparison with a Kelvin electrostatic voltmeter. No change in either current or potential difference was noticed when the platinum plate was moved close up to the brush, which shows that the potential difference measured was very little different from the actual potential drop through the brush.

No great accuracy in these measurements was possible, however, owing to fluctuations in the electrical conditions. These were steadiest with the uncondensed discharge, and with the condensed discharge without a spark-gap. Readings taken every five minutes varied 2 or 3 per cent. from the mean value, but they were often constant for five or ten minutes. Fluctuations in the condensed discharges were often very large, the current dropping to a small value owing to arcing occurring at the spark-gap, which needed constant attention.

It will be seen in the values given beside the photographs (Pl. V.), that while the current increases with the intensity of the discharge the potential difference generally falls. The fall in potential is of course only apparent as the sparks through the brush become less frequent, as the discharge becomes heavier. The fact noted, however, shows that the resistance of the liquid (which resides chiefly in the brush) is broken down most completely with the heaviest discharges.

Character of the Discharge.

The character of the discharge varies with the conditions under which it is produced. The following Tables (pp. 466 & 468) summarise the main features. The reference to the spectrum of each type of discharge is also given. Figs. 5, 6, 7 in text (p. 467) give representations of the various types of discharge referred to in Table I. They are magnified about twice.

As regards the brush in distilled water, the current and potential difference fall as the water becomes hot, owing to the action of the discharge. Boiling water is almost kept boiling by the discharge, and the brush in this case is very feeble. The radical difference in the colour between the brush in cold distilled water, and the brush in the same water after it has been boiled and allowed to cool, is rather remarkable.

Phil. Mag. S. 6. Vol. 25. No. 148. April 1913. 2 K

TABLE I.—Brush Discharge.

	SPECTRUM. [Pl. V.]	LIQUID.	CONDENSER AND SPARK-GAP.	EVOLUTION OF GAS, ETC.	APPEARANCE AND COLOUR.	APPEARANCE IN ROTATING MIRROR.
A.....	Fig. 6 a.	Distilled water : cold and not previously boiled.	No Con- denser or Spark- gap.	Large cloud of very fine bubbles shot out from point, rendering water milky. (<i>v. fig. 5.</i>) Hissing noise.	Close bundle of fine hair-like fila- ments (about 5 mm. long) which emit brilliant pale blue light.	Continuous bands of light crossed by fine bright vertical lines.
B.....	Fig. 6 c.	Distilled water : hot.	Do.	Emission of bubbles much dimin- ished. (<i>v. fig. 5.</i>) Hissing noise.	Brush becomes shorter, fainter, and redder as temperature rises ; changing at length to a weak blue.	Do.
C.....	Fig. 6 b.	Distilled water : cold, having been previously boiled.	Do.	Emission of bubbles same as in B. (<i>v. fig. 5.</i>) Hissing noise.	Brush similar to B, but emitting a brilliant red light.	Do.
D.....	Fig. 1 a. 3 a. 4 a. 5 a.	Dilute H_2SO_4 (about .05 o/o) and dilute salt solutions.	Do.	Emission of fine bubbles ceases. Large stationary bubble (about 3 or 4 mm. in diameter) forms at the point. Portions detach every 2 or 3 secs. as it grows. (<i>v. fig. 6.</i>) Hissing noise.	A pale blue luminous discharge is spread over top of bubble. A bright yellow discharge stretches from the point for about 1 mm. into the bubble.	Continuous bands of yellow light.
E.....	Fig. 1 b. 2 b. 3 b. 4 b. 5 b.	Do.	Condenser and no Spark- gap.	Stationary bubble destroyed while a stream of small bubbles are ejected from the point. (<i>v.</i> <i>fig. 5.</i>) Harsh rattling noise.	Brush very small, consisting of bundle of fine filaments emitting fairly bright pink light.	Bands broken up into large number of sepa- rate dots. Bands are alternately red and blue in a lithium salt solution.
F.....	Fig. 1 c, d. 2 c, d. 3 c, d. 4 c, d. 5 c, d.	Do.	Condenser and Spark- gap.	Large bubbles flung out of brush with great violence. Noise re- sembles series of rapid explosions. (<i>v. fig. 7.</i>)	Brush increases in length and bril- liancy with length of spark-gap. It consists of a bundle of lumi- nous forks emitting brilliant pink light.	Series of dots as above ; number of dots in a series diminishes with increasing length of spark-gap.

The bright blue colour of the brush in the first case is evidently due to the amount of continuous spectrum in the blue region

Fig. 4.



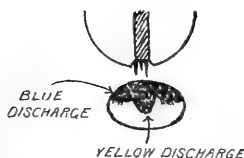
Wire electrode enclosed in glass tube showing decayed point.

Fig. 5.



BRUSH-DISCHARGE: Represents types A, B, C, & E, which differ only in extent and colour.

Fig. 6.



BRUSH-DISCHARGE: type D.
(Separation of bubble from point a little exaggerated.)

Fig. 7.



BRUSH-DISCHARGE: type F.
(Enlarged drawing of a photograph.)

from H_β to H_γ (see Pl. V. fig. 6, *a*). In the case of type D, which is produced without a condenser, the stationary bubble mentioned sometimes collapses, and gives place to a stream of much smaller bubbles, the discharge somewhat resembling type E. If this stationary bubble is examined with a low-power microscope, it will be seen that it is separated from the point by a short space. Occasionally a fine luminous streamer strikes out from the point across this space, while at odd intervals the space is completely ruptured. When this occurs, the bubble collapses, and a discharge somewhat similar to type E (Table I.) occurs. Inversion of the electrode does not cause the bubble to float away. Consequently the point must hold it in its neighbourhood by electrical action (see fig. 6 in text).

All the types of capillary discharge tend to become violent with long capillaries. The rotating mirror shows the discharge under this condition drawn out into bands of light, each band headed by one or more bright streamers.

The formation of the stationary bubble which forms at each end of a capillary immersed in a dilute acid or salt solution, is only possible where the capillary is short, not exceeding 2 mm. at most.

TABLE II.—Capillary Discharge.

	SPECTRUM. [Pl. V.]	DIAMETER OF CAPILLARY.	LIQUID.	EVOLUTION OF GAS, ETC.	APPEARANCE AND COLOUR.	APPEARANCE IN ROTATING MIRROR.
A.....	Fig. 9 <i>a, b, c, d.</i>	About .05 mm.	Distilled water.	Small bubbles given off at each end of capillary, chiefly at lower. Hissing noise.	Capillary glows a brilliant red, the luminous discharge extending a very short distance beyond each end of capillary.	Continuous bands of light.
B.....	Fig. 8 <i>a, b, c, d, e, f.</i>	Do.	Dilute H_2SO_4 and dilute salt solutions.	Stationary bubble forms at end of capillary, portions detaching at intervals. (<i>v.</i> Table I., D above). Hissing noise.	Capillary glows a brilliant red, while a blue discharge is spread over the bubble, just as in the case of type D, Table I., except that the yellow discharge is missing.	Do.
C.....	About .2 mm.	Distilled water.	Emission of fine bubbles from ends of capillary as in type B, Table I. Hissing noise.	Glow in capillary much feebler than in above cases. Brush occurs at each end of capillary, the brush resembling that in type B, Table I.	Do.
D.....	Do.	Dilute H_2SO_4 and dilute salt solutions.	Same as in type B, above.	Same as in type B above, except that glow in capillary is much feebler.	Do.
E.....	1 mm.	Distilled water.	Emission of small bubbles from each end of capillary. Harsh noise.	Capillary glows with a weak blue light, the luminous discharge ex- tending a short distance beyond each end of capillary. There is no brush.	Patchy bands of light.

Observation of Spectra.

The spectra I have observed in the brush and capillary discharge are those of :—

Hydrogen.—Series spectrum, and many-lined or secondary spectrum.

Oxygen.—Series spectrum, and many-lined or elementary-line spectrum.

Electrode.—Spark lines of platinum. These were observed by Konen only in the condensed spark between two platinum poles.

Solute.—Complete spectrum, in visible part, of the metal.

Impurities.—D lines, red and green doublets of sodium; blue line ($\lambda=4227$) and occasionally the red and green bands of calcium.

Hydrogen.

The lines H_α , H_β , H_γ of the series spectrum could nearly always be discerned. Both this spectrum and the secondary spectrum appear best in distilled water or very weak solutions. In stronger solutions they are much feebler. This is best shown by comparing Pl. V. fig. 1, *a* & *b* with fig. 3, *a* & *b*. The insertion of a condenser has generally very little effect on the series spectrum, but when the spark-gap is opened the lines increase in brightness and begin to broaden. With the heaviest discharges the lines are very broad and bright, and a continuous spectrum stretches from the far violet to beyond H_β . If we compare one of these photographs, say fig. 4, *d*, with the spectrogram of the brush in distilled water, fig. 6, *b*, we see how relatively feeble H_γ is in the former compared with the increased brilliancy of H_α . Fig. 4, *d* and fig. 9 show this still better.

The secondary spectrum of hydrogen decreases in intensity as the discharge increases. This is shown in the series of spectrograms, Pl. V. fig. 1, *a*, *b*, *c*, *d*, but best of all in the series fig. 5. As these lines always appear very faintly at the highest discharges, even in a series where they have not been apparent in the uncondensed discharge (see Pl. V. fig. 3), it would appear that they increase with the current at a very much slower rate than the series lines. The decrease shown in the photographs alluded to above is probably only apparent, and due to the falling off in the number of sparks per second.

Comparing these results with the capillary discharge, we find that a fine capillary (about 0.5 mm. diameter or less)

shows the series lines brightly and secondary lines faintly (see fig. 9, *a*). A slightly broader capillary shows the secondary lines with much greater relative intensity (see fig. 9, *b*). Thus increasing the current density in the capillary has the same effect as increasing the intensity of the discharge through the brush, except that in the former case little broadening of the series lines occurs, and the relative intensity of the series lines is not altered.

These results are quite compatible with those obtained with a discharge-tube. Both spectra appear with the ordinary induction-coil discharge, while the secondary is reduced or disappears when the tube forms part of a condenser and spark-gap circuit*.

Oxygen.

The series spectrum of oxygen is much feebler than that of hydrogen. Its behaviour, however, is very similar, though the lines show no appreciable broadening nor any variation of intensity among themselves. They appear in the brush in distilled water only very faintly. In the uncondensed brush in solutions they do not appear at all, but they show distinctly in the spectrum of the condensed brush when the discharge is heavy. They are shown fairly well in Pl. V. fig. 2, *e*. The line $\lambda = 6157$ is easiest to detect. It can be seen a little to the right of the lithium orange line $\lambda = 6104$: fig. 3, *d*, Pl. V., shows these two lines of nearly the same intensity. The fine capillary discharge shows the series spectrum best (see Pl. V. fig. 8, *a* or fig. 9, *a*). The wider the capillary, the fainter are the series lines (compare fig. 9, *a* & *b*: *b* is with the slightly wider capillary). Indeed with a capillary about .2 mm. wide the series spectrum is difficult to detect. Within the limits of these experiments, then, it would appear that the higher the current density, the brighter will the series spectrum be.

The many-lined or elementary-line spectrum of oxygen behaves in a somewhat inexplicable way. Its behaviour is quite different from that of the secondary spectrum of hydrogen. It appears in the brush in distilled water faintly, but stronger than the series lines (see Pl. V. fig. 6, *a* & *b*). The doublet at $\lambda = 4416$ is the most readily distinguishable part of the spectrum. It appears also in the brush in solutions, occurring only at the feebler, and vanishing almost completely at the higher discharges (compare Pl. V. fig. 4, *a*, *b*, *c*, *d*). It is also brighter in a solution of lithium sulphate than in a solution of lithium carbonate (compare fig. 3 with fig. 4, Pl. V.).

* Dufour, *Ann. Chim. et Phys.* ix. 403-5 (1906).

In the capillary discharge, even with the finest capillaries, the elementary-line spectrum occurs very feebly, if, indeed, at all. This is true both as regards distilled water and solutions, if we disregard the stationary bubble at either end of the capillary in the latter case. In dilute sulphuric acid the discharge spread over the top of the bubble is a deep blue, which fluctuates in extent and intensity. If an image of the discharge is focussed by means of an achromatic lens on the slit of a spectrograph, the resulting photograph shows that the spectrum of the bubble consists mainly of the elementary-line spectrum. Very little trace of this spectrum is found in the capillary portion. This point is illustrated in fig. 8, where perhaps spectrogram *c* shows it most clearly.

If all the photographs are considered it will be found that where the elementary lines are strong the series lines are weak and *vice versa*. Everything would appear to point to the fact that the elementary-line spectrum was due to low current density. We should obtain this spectrum, then, if we reduced the current through the fine capillaries or used wider capillaries. I have tried both methods and obtained negative results. Fig. 9, *b, c, d* represents a series of photographs with a fine capillary, the current being reduced by choking down the primary current of the induction-coil. Fig. 8 is a similar series for dilute sulphuric acid. It will be noticed that in the latter case the elementary lines in the spectrum of the bubble intensify a little at first, though they do not do so in the spectrum of the capillary.

As it is the elementary line-spectrum which occurs in the spark in air, and in a vacuum-tube when excited by the discharge of a condenser through a spark-gap, it is generally associated with high current density. Runge and Paschen have, however, observed it in the wide part of a vacuum-tube which was excited by the ordinary induction-coil discharge, the capillary portion giving the series spectrum*. It seems impossible, therefore, to account for this spectrum from the point of view of current density alone.

Solute.

I have made observations on salts of lithium, sodium, potassium, and calcium. The greater part of the observations have been confined, however, to the sulphate and carbonate of lithium. The lines of the metal only appear. In the uncondensed brush the lines appear equally well in

* *Ann. der Phys.* lxi. p. 641 (1897).

solutions varying in strength from .005 to .1 per cent. ; with much stronger solutions the brush does not occur. With the condensed brush, the spark-gap being closed, the spectrum of the metal of the salt generally increases in brightness ; but on opening the spark-gap, the spectrum for the weaker solutions grows fainter, disappearing eventually as the spark-gap is further extended. In the stronger solutions the intensity of the spectrum either remains stationary or increases very slowly.

I have chosen a few of the spectrograms for lithium salts to illustrate these points (Pl. V. figs. 1-5). It will be seen that the lithium red line $\lambda=6708$ increases in brightness at first more rapidly than the H_{α} line of hydrogen. Subsequently the H_{α} line greatly exceeds in brightness the lithium line.

Another point to notice in connexion with the lithium spectrum is that it is produced much more brightly with the sulphate than with the carbonate. (Compare fig. 4 *b* with fig. 3 *b* Pl. V.) For the same percentage strength, the lithium-sulphate solution has a lower resistance than the lithium-carbonate solution. The current is consequently much larger, though not of course comparable with the strength of the higher condensed discharges which tend to destroy the spectrum. This difference in current may account for the difference in brightness of the spectrum of lithium for the two solutions.

There is, however, a very great difference in the relative intensities of the lines which can scarcely be accounted for by this. In Pl. V. fig. 4, *a* & *b* it will be seen that the lithium blue line $\lambda=4602$ and the lithium orange line $\lambda=6104$ are very nearly of the same intensity as the red line. This is very far from being the case in any of the spectra with lithium carbonate. In fig. 4 it will be seen that while the red line persists, though faintly, right through to the heavier condensed discharges, the blue and orange lines are scarcely discernible when the discharge is heavy. The distribution of intensity is now very similar to what it is in all the photographs with lithium carbonate.

If the uncondensed brush is examined visually, the lithium lines will be observed to fluctuate a good deal, sometimes flashing up very brightly, sometimes appearing very feeble. All the time the electrical conditions may remain quite steady, while the hydrogen lines do not show the slightest variation in brightness. After the discharge has taken place for a few minutes it will be found that the spectrum has brightened and become, on the whole, steadier, while the potential difference has risen. If the point be now examined

with a lens it will be found that it has slightly decayed (see fig. 4 in text). There is thus interposed between the point and the outer liquid a very short capillary. The resistance of this capillary evidently enabled the potential to rise and thus give a brighter discharge.

If a fine wire is used (about .1 mm. diameter), then after continued use it will be found that the lithium lines have decreased very considerably in brightness, the rest of the spectrum being unchanged. The point, in one case, when examined was found to have decayed so much that a capillary of 2 mm. in length intervened between it and the liquid. It was this that first suggested to me the examination of the capillary discharge with the apparatus shown in fig. 2. Fused silica was used as the material because glass capillaries cracked too readily with the heat. It was found with capillaries ranging from .05 mm. diameter to 1 mm. diameter in various strengths of solutions, that the lithium lines appeared only very faintly. If the wire electrode which was immersed in the fused silica tube were now brought just to touch the top of the capillary, it became covered with a faint luminous glow which gave the spectrum of hydrogen and lithium (if a solution of a lithium salt were used). The lithium spectrum grew brighter as the point was pushed further down into the capillary, while the discharge at the bottom of the capillary changed over to the brush discharge (the *bubble* discharge as described above). Just before the point reached the bottom of the capillary the brush became fainter, and the luminosity vanished completely as the wire emerged through the capillary.

To produce the spectra in fig. 7, A & B (Pl. V.) the image of a capillary was focussed on the widened slit of a spectrograph. The capillary tapered, being narrowest at the bottom. The discharge occurred only in this narrow portion of the capillary when the electrode was kept away from it. Fig. 7, B is the spectrum under these conditions. The capillary is inverted in the photograph so that the spectrum of the narrow portion appears at the top (*a*) instead of the bottom (*b*). It will be seen that the lithium lines are very feeble. Fig. 7, A is the spectrum of the same capillary, the wire electrode now being just at the top of the capillary (bottom in the photograph). The spectrum of the glow surrounding it is shown clearly in fig. 7, A, *b*. Thus while the hydrogen gives a bright spectrum both in the narrow part of the capillary and round the point, the lithium lines (and the D lines of sodium) appear brightly in the light surrounding the point, but scarcely at all in the narrow part

of the capillary. For fig. 7, c the slit was narrowed and the wire electrode was pushed right down till it reached nearly to the bottom of the capillary. It is interesting to compare this spectrum with fig. 1, b; the red line of lithium ($\lambda=6708$) in each case is of about equal intensity.

There can be little doubt then of the importance of the point in the production of the lithium spectrum. As lithium sulphate is a better electrolyte than lithium carbonate and produces the lithium spectrum more readily, it seems suggestive that the lithium accumulates close to the point due to electrolytic action, being there vaporized and rendered luminous. Unfortunately I was not able to test this point further by examining a unipolar brush, but if the brush were examined with a rotating mirror, at the feebleness of discharges, one of the alternate bands was a deep red and the other blue. This might easily have been due to the presence of the lithium spectrum in the red band and its absence from the blue. At the higher discharges the bands were the same bluish colour—a result we would expect, considering the relative feebleness of the lithium spectrum at the higher discharges.

Platinum.

The spark-lines of platinum occur as the discharge through the brush becomes heavy, and they increase with the intensity of the discharge (see Pl. V. figs. 1–4). In the uncondensed brush in distilled water, as the water gets hotter the current and voltage drop, while the brush becomes feebler. The various spectra of oxygen and hydrogen which appeared at first grow fainter, and at length, when the water is on the point of boiling, the platinum lines show up very faintly (see Pl. V. fig. 6, c).

Summary.

The series spectrum of hydrogen in both the capillary and brush discharge increases with increase of current density, while the secondary spectrum decreases in relative intensity to the series lines. The series lines broaden considerably with the condensed discharges, and the relative intensity of the lines falls off towards the violet.

The series spectrum of oxygen appears only with the higher current density discharges, being brighter with higher current density. The elementary-line spectrum appears in the brush with the feebleness of discharges only, its brightness also depending on the nature of the solution. It

appears in the spectrum of the capillary, in the capillary discharge, only very faintly if at all, but in the discharge in dilute sulphuric acid it is the most important part of the spectrum of the bubble which forms at each end of the capillary.

The lines of the metal of the dissolved salt appear in the brush. In the case of lithium their relative intensity varies with the salt used and also with the current. In weak solutions the metal lines are destroyed by the heavier condensed discharges. The metal lines appear very feebly in a capillary, and they are produced strongly only in the immediate neighbourhood of a metal electrode.

The spark-lines of platinum appear with the condensed discharges when a spark-gap is used.

In conclusion I wish to thank Professor H. Stroud, of Armstrong College, for the kind interest shown in this investigation. My thanks also are due to Mr. H. Morris-Airey, who suggested to me this problem for research and who was at all times willing to offer criticism and advice.

LI. *A Contribution to the Theory of Electrocapillarity.*

By DAVID LEONARD CHAPMAN*.

FOR any substance which satisfies the laws of a perfect gas we obtain by equating to zero the variation of the sum of the potential and free energy the equation

$$P_1 - P_2 + Rt \log_e p_1 - Rt \log_e p_2 = 0,$$

P_1 and P_2 being the potential energies at the points 1 and 2 of a gram molecule of the substance, and p_1 and p_2 the respective hydrostatic pressures.

If the potential energy is electrical the above equation becomes

$$(V_1 - V_2)q + Rt \log_e p_1 - Rt \log_e p_2 = 0,$$

in which V is the line integral of electromotive intensity, and q the charge on a gram molecule of the substance.

The potential† of a monovalent metal in contact with a solution of one of its salts is therefore, according to Nernst's

* Communicated by the Author.

† Although it sometimes leads to confusion, we shall for brevity adopt the usual convention of calling the line integral of electromotive intensity potential. Throughout the electrostatic system of units will be used.

double-layer theory, given by the equation

$$V_s - V_m + \frac{Rt}{\epsilon} \log_e \frac{p_s}{p_m} = 0^*,$$

in which ϵ is the charge on a gram ion of the metal, and s and m refer to points at some distance within the solution and on the surface of the metal respectively.

The above equation only holds if it is assumed that the charge on the metal is much closer to the surface than the charge in the solution—an assumption which can be shown to be in complete accord with Schuster's estimate of the concentration of the free negative electrons in conductors.

Assuming provisionally that the charge on the metal resides entirely on its surface, and that there is accordingly no difference of potential between the surface of the metal and its interior, we propose to investigate the distribution of potential and electric density within the solution, and thence to deduce the capacity of the condenser which the double layer forms.

Consider a plane surface of the metal, and let x be the perpendicular distance of a point in the solution from the surface of the metal. Let the potential at any point x be represented by V_x , and the pressure of the metal ion at the same point by p_x . Then

$$V_x - V_\infty = \frac{Rt}{\epsilon} \log_e \frac{p_\infty}{p_x} \dots \dots \dots (A)$$

Indicating by the affix ' that the symbol for a dimensional magnitude refers to the negative ion we obtain similarly for the anion .

$$V_x - V_\infty = \frac{Rt}{\epsilon} \log_e \frac{p_\infty'}{p_x'} \dots \dots \dots (A')$$

From (A) and (A')

$$p_x' = \frac{p_\infty'^2}{p_x} \dots \dots \dots (i.)$$

since $p_\infty = p_\infty'$.

If by ρ_x we indicate the electric density of the positive charge on the metal ion

$$\rho_x = \frac{\epsilon p_x}{Rt},$$

whilst

$$\rho_x' = - \frac{\epsilon p_x'}{Rt}.$$

* We shall leave out of consideration the effect of potential energy arising from non-electrical forces at the surface.

Whence

$$\begin{aligned}\rho_x + \rho'_x &= \frac{\epsilon}{Rt} (p_x - p'_x) \\ &= \frac{\epsilon}{Rt} \left(p_x - \frac{p_\infty^2}{p_x} \right) \quad (\text{from (i.)})\end{aligned}$$

We shall now show that, with the assistance of Poisson's equation,

$$\nabla^2 V = -\frac{4\pi\rho}{K},$$

the electric state of any point in the field can be found, and the charge on the double layer condenser expressed as a function of the difference of potential between the solution and the metal.

In the special case under investigation Poisson's equation becomes

$$-\frac{d^2 V_x}{dx^2} = \frac{4\pi}{K} \frac{\epsilon}{Rt} \left(p_x - \frac{p_\infty^2}{p_x} \right). \quad \dots \quad (B)$$

On substituting the value of $\frac{d^2 V}{dx^2}$, which can be obtained from (A), this reduces to

$$\frac{R^2 t^2}{\epsilon^2} \frac{K}{4\pi} \frac{d^2}{dx^2} \log_e p_x = p_x - \frac{p_\infty^2}{p_x}.$$

The above differential equation admits of solution in a simple form. Multiplying both sides of the equation by $d \log_e p_x$, and integrating between $x=x$ and $x=\infty$, we obtain

$$\frac{R^2 t^2}{\epsilon^2} \frac{K}{8\pi} \left[\left(\frac{d}{dx} \log_e p_\infty \right)^2 - \left(\frac{d}{dx} \log_e p_x \right)^2 \right] = -p_x + 2p_\infty - \frac{p_\infty^2}{p_x};$$

but since $\frac{d}{dx} \log_e p_\infty$ is zero, this reduces to

$$\frac{Rt}{\epsilon} \sqrt{\frac{K}{8\pi}} \frac{d}{dx} \log_e p_x = \pm \left(\sqrt{p_x} - \frac{p_\infty}{\sqrt{p_x}} \right).$$

It is obvious that the negative sign must be taken on the right-hand side of the equation; so that we obtain finally as the first integral of the differential equation

$$\frac{Rt}{\epsilon} \sqrt{\frac{K}{8\pi}} \frac{d}{dx} \log_e p_x = \frac{p_\infty}{\sqrt{p_x}} - \sqrt{p_x}, \quad \dots \quad (C)$$

or

$$\frac{Rt}{\epsilon} \sqrt{\frac{K}{8\pi}} \frac{dp_x}{dx} = \sqrt{p_x} (p_\infty - p_x). \quad \dots \quad (C')$$

The solution of (C') is

$$\frac{Rt}{\epsilon} \sqrt{\frac{K}{8\pi p_{\infty}}} \cdot \log_e \frac{\sqrt{p_x} + \sqrt{p_{\infty}}}{\sqrt{p_x} - \sqrt{p_{\infty}}} \cdot \frac{\sqrt{p_0} - \sqrt{p_{\infty}}}{\sqrt{p_0} + \sqrt{p_{\infty}}} = x.$$

The last equation is not at present of much practical importance.

What we require to know in order that we may be able to test the theory of electrocapillarity by a direct comparison of the experimental values of surface tension with those calculated from the theory, is the magnitude of the charge on the double-layer condenser for a given difference of potential between the solution and the metal.

By integrating Poisson's equation between 0 and ∞ we obtain

$$\frac{dV_0}{dx} = \frac{4\pi}{K} Q,$$

in which Q is the charge on unit surface of the solution. But

$$\frac{dV_0}{dx} = - \frac{d}{dx} \frac{Rt}{\epsilon} \log_e p_0.$$

Substituting in this equation the value of $\frac{d}{dx} \log_e p_0$ obtainable from (C), we deduce that

$$Q = \sqrt{\frac{K p_{\infty}}{2\pi}} \left(\sqrt{\frac{p_0}{p_{\infty}}} - \sqrt{\frac{p_{\infty}}{p_0}} \right).$$

A more convenient form of the above equation is

$$Q = \sqrt{\frac{K p_{\infty}}{2\pi}} \left(e^{\frac{\epsilon V}{2Rt}} - e^{-\frac{\epsilon V}{2Rt}} \right), \quad . \quad . \quad . \quad (D)$$

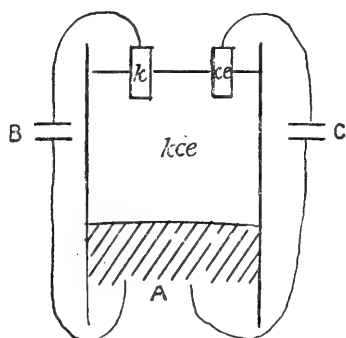
where V is the difference of potential between the solution and the mercury.

*Calculation of the Surface Energy of Mercury in
contact with an Electrolyte.*

The surface energy of the mercury in a capillary electrometer can be deduced in the following way.

Suppose that a layer of mercury A is in contact with a solution of potassium chloride which also contains mercurous chloride at a very low concentration. Assume also that the means exist for increasing and diminishing the surface of the mercury in contact with the potassium chloride. In the

solution of potassium chloride are immersed alloys of the elements potassium and chlorine with substances that are insoluble in water. The ionic solution pressures of the alloys are equal to the osmotic pressure of the potassium



and chlorine ions in the solution. The alloys are in electrical contact with the mercury, and electromotive forces can be inserted in the circuits thus formed at B and C. The potential difference between the solution and the mercury can be increased by removing from the solution small amounts of ionic mercury and chlorine by means of the circuit C.

With this engine we perform the following reversible cycle of operations, keeping the concentration of the potassium chloride constant.

I. We start with a negligible amount of mercury surface in contact with the solution, the osmotic pressure of the mercury ions being equal to the solution pressure of the mercury. Mercurous chloride is withdrawn from the solution until the difference of potential between the solution and the mercury has risen to V . The work performed in this operation is in any case negligibly small, and is, moreover, almost completely recovered in a subsequent operation. After this operation there will be a negative charge on the metal and a positive charge in the solution.

II. The mercury surface is increased by unity. Now the positive charge in the solution close to the surface of the metal exists by reason of there being in that region a large excess of potassium ions, a large deficiency of chlorine ions, and a small excess of mercury ions. Therefore, if the concentration of the solution is kept constant as the surface increases, potassium and mercury ions must be introduced into the solution, and chlorine ions removed with the assistance of the circuits B and C. As the potassium ions with their positive charges enter the solution an equal amount of negative electricity passes from K to A. Let the quantity

of electricity which passes from K to A during the formation of unit surface be $-q$. It changes in potential by an amount $-V$, and therefore the work performed is qV . Let the negative charge on the chlorine ions removed from the solution during the formation of unit surface be $-q'$. This charge also passes to the mercury surface, and an amount of work $q'V$ is performed. The electrical energy required to introduce the small excess of mercury ions can be neglected. The total electrical work performed is $(q+q')V$ or QV , Q being the charge on unit surface of the mercury. An amount of work equal to T_v , the surface tension corresponding to a difference of potential V , is also performed.

III. Mercurous chloride is introduced into the solution until the difference of potential between the mercury and the solution is zero. This work is opposite in sign and almost equal to that performed in operation I. During the destruction of the double layer the excess of potassium ions re-enter the potassium alloy, whilst the deficiency of chlorine ions is supplied by the chlorine which entered the chlorine alloy during the formation of the surface. It is easy to see that the electrical work performed by the engine in order to effect this change will be

$$\int_0^V V \cdot dQ.$$

IV. The surface is reduced by unity, and the work performed by the engine is T_0 , the maximum surface tension.

If we sum the work performed on the engine in the cycle of operations and equate it to zero we obtain

$$T_0 - T_v = QV - \int_0^V V dQ = \int_0^V Q dV.$$

Now it has generally been assumed that the capacity of the condenser formed by the double layer is constant. This assumption would obviously make $T_0 - T_v$ proportional to V^2 ; but the first part of this investigation shows that the assumption is not justified.

Substituting in the above equation the value of Q from equation (D), we find that

$$\begin{aligned} T_0 - T_v &= \int_0^V \sqrt{\frac{K p_\infty}{2\pi}} \left(e^{\frac{\epsilon V}{2Rt}} - e^{-\frac{\epsilon V}{2Rt}} \right) dV \\ &= \frac{2R}{\epsilon} \sqrt{\frac{K p_\infty}{2\pi}} \left(e^{\frac{\epsilon V}{4Rt}} - e^{-\frac{\epsilon V}{4Rt}} \right)^2. \end{aligned}$$

This equation can of course only be true so long as the ions behave as perfect gases. The increase in osmotic pressure of an ion for a change in potential of 0.1 volt is about 80-fold. So that if the solution were decinormal potassium chloride it would scarcely be legitimate to use the formula for a greater value of V than 0.1 volt. Unfortunately, the change in surface tension for an alteration in the applied electromotive force of 0.1 volt when the surface tension is at its maximum is so small that it cannot be accurately measured. I estimate from S. W. J. Smith's* electrocapillary curves and Quincke's value for the surface tension of mercury in contact with hydrochloric acid (assuming that the surface tension of mercury in contact with hydrochloric acid is the same as that of mercury in contact with a solution of potassium chloride), that the fall in surface tension when V is 0.1 volt lies between 3.5 and 4 c.g.s. units when the mercury is in contact with $\frac{N}{10}$ KCl. The fall in surface tension

calculated from the above formula for the same change in the applied electromotive force is 4.8 c.g.s. units. It is therefore very probable that the observed change in surface tension can, as Helmholtz postulated, be largely accounted for by the electric charges in the double layer.

It is obvious that what is most needed to elucidate the mechanism of the capillary electrometer is a very thorough examination of the electrocapillary curve in the region of maximum capillarity, preferably with solutions which give no electromotive force in contact with mercury, such as those used by Palmaer† to investigate the electromotive force of the calomel electrode.

Jesus College, Oxford.

LII. *On the Electrification associated with Dust-Clouds.* By
W. A. DOUGLAS RUDGE, *Professor of Physics, University
College, Bloemfontein* ‡.

[Plates VI. & VII.]

THE author has shown § that a considerable amount of electrification is imparted to the atmosphere by clouds of dust raised by the wind, and it seemed of interest to investigate the electrification developed by raising clouds.

* *Zeit. f. Phys. Ch.* xxxii. p. 467 (1900).

† *Zeit. Elektrochemie*, ix. p. 754 (1903).

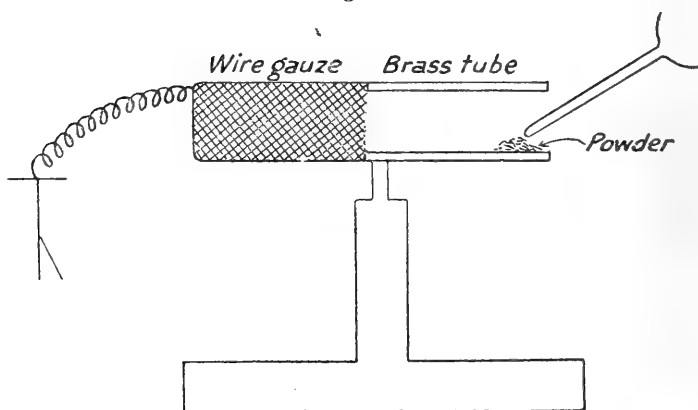
‡ Communicated by the Author.

§ *Phil. Mag.* June 1912; *Proc. Roy. Soc. South Africa*, 1912; *South African Journ. Sci.* 1912.

of dust composed of various materials, by artificial means. As has been shown *, the electrification developed during dust storms in South Africa is invariably negative, neutralizing and reversing the positive charge usually present in the air. In England, in places where the matter was tested, the clouds of dust raised by motor-cars had the effect of *increasing the positive charge*. In South Africa the dust is usually of a siliceous character, whether it comes from the sea-shore, inland wastes, cultivated soils, or the mine-heaps in the neighbourhood of Johannesburg. In England "road dust" is usually calcareous. It is quite easy to show the production of a charge of electricity by raising a cloud of dust. If a small quantity of flour is placed upon the plate of an electroscope and then suddenly blown away, the electroscope will indicate a charge whose magnitude will depend to some extent on the fineness of the flour. The experiment can be performed in a room, but the effect is very much greater if it is done out in the open air. By raising a cloud of flour-dust in any way and catching the particles in a hollow insulated vessel, it is always possible to show the presence of a charge of electricity.

The apparatus used for systematic investigation consisted of a small cylinder of fine wire-gauze 10 cm. in length and 2 cm. in diameter, which was attached to a hollow brass cylinder of the same diameter. A nozzle projected a short

Fig. 1.



distance into the brass cylinder, and if some powder was arranged in front of the nozzle a sharp puff of air would blow it into a cloud, and the particles would be carried through the meshes of the wire gauze and give up a portion

* Phil. Mag. June 1912; Proc. Roy. Soc. South Africa, 1912; South African Journ. Sci. 1912.

of their charges to it (fig. 1). The cylinder was insulated by an ebonite rod and connected to a sensitive gold-leaf electroscope of the pattern designed by C. T. R. Wilson. An ordinary instrument suffices in most cases, as the charges developed are quite strong. The air current was usually obtained from a Fletcher bellows, but a sharp puff from the mouth was quite efficacious. When fine sand or dry earth was used a strong positive charge was indicated, as would have been expected from what was shown in a previous paper * ; but on using other material, the charge was *positive* or *negative*, according to the nature of the material.

Almost the only references to the electrification of dusts are those relating to the production of Lichtenberg's figures, by shaking a mixture of red lead and sulphur in a muslin bag, and allowing the powders to fall upon an irregularly electrified plate composed of some non-conducting material. A separation of the red lead and sulphur particles is effected because of the opposite charges acquired by these materials, the sulphur particles being stated to be negatively electrified, whilst those of the red lead are positive. Now, powdered sulphur when blown into a cloud in the apparatus acquires a POSITIVE charge, and red lead a NEGATIVE one. This fact seemed sufficient to warrant an investigation into the kind of electrification accompanying the raising of clouds of dust from different materials.

A great many experiments were made with those materials usually found in the chemical laboratory, and very shortly it was seen that the electrification developed appeared to follow some general laws ; and although there are many apparent exceptions—probably due to the use of materials whose purity is doubtful—the laws given below are fairly well established by the experiments. The materials used were taken from the stock-bottles in the laboratory and no attempt was made to purify them. The experiments were conducted out of doors, and the results are tabulated below.

Law I. *Non-metallic elements give positively charged clouds when the finely divided material is blown into a cloud by a current of air.*

Of course, only solid elements can be dealt with in this manner.

* Phil. Mag. June 1912.

TABLE I.

Element.	Charge.	Remarks.
Carbon	+	Magnitude of charge varied with the kind of carbon.
Sulphur	+	Very strong charge.
Phosphorus	+	Amorphous and carefully dried.
Silicon	+	Strong * charge.
Boron	+	" "
Selenium	+	" "
Tellurium	+	" "
Iodine	+	" "
Arsenic	+	Fairly strong.

* By strong, one means that a few centigrammes of the substance would produce sufficient electricity to send the gold-leaf out to a right angle.

Particular note should be taken that the so-called *metallic* arsenic is included in the above list. Carbon occurs in several modifications, and of these wood and sugar charcoal and diamond dust were strongly positive, graphite not very definite and sometimes strongly negative, whilst "animal" charcoal, a mixture of various substances, gave practically no electrification. Sulphur in all its modifications was always strongly positive. Amorphous phosphorus was, of course, the only kind which could be used.

Law II. *Metallic elements give negatively charged clouds when the finely divided material is blown into a cloud by a current of air.*

As a positive charge seemed to be associated with a non-metallic dust-cloud, it seemed likely that a metallic dust should give a negatively charged cloud, and this was borne out by the experiments ; but, as is seen from Table II., some important exceptions occur.

The list of metals is far from being complete, but it is very remarkable that those which are so definitely "metallic" in their character should acquire a negative charge ; whilst tungsten and vanadium, which form strongly acid oxides, *i. e.* approximating to the nature of a non-metal, should, under the same circumstances, give positive charges. Uranium and titanium should probably be included in the same category, but the charges obtained were indefinite, and only a small quantity of the material was available. One would expect zirconium to behave similarly to calcium or aluminium, but the material was probably impure. Only those metals could be used which were obtainable in a finely

divided state. In the case of iron the results were the same, whether filings or reduced iron was used.

TABLE II.

Metal.	Charge.	Remarks.
Aluminium	—	Strong. .
Antimony	—	"
Bismuth.....	—	"
Cadmium	—	Weak.
Calcium.....	—	Very strong.
Cobalt	—	Strong.
Copper	—	Weak.
Iron	—	Strong.
Lead	—	"
Magnesium	—	"
Nickel	—	Variable.
Silver.....	—	Weak.
Tin.....	—	"
Titanium	?	Variable.
Tungsten	+	Strong.
Uranium	?	Variable.
Vanadium.....	+	Very strong.
Zinc	—	"
Zirconium.....	+	Weak.
Platinized Asbestos* ...	—	Strong.

* Compare Asbestos, Table IX.

The charges obtained on the clouds of dusts of metals and non-metals are thus of a character opposite to those associated with the ions of the elements when in solution, and from this the inference was drawn that clouds of dusts from solid acids should also be positively charged, and here again the inference was strikingly substantiated, only one exception being noted. The acids used are mainly organic ones, as only solid acids could be used.

TABLE III.

Acid.	Charge.	Acid.	Charge.
Anthranilic	—	Malonic	+
Benzoic	+	Molybdic	+
Boric	+	Mobic	+
Citric	+	Oxalic.....	+
Chromic	+	Phthalic.....	+
Ferrocyanic	+	Salicylic	+
Gallic	+	Sulphanilic	+
Hippuric	+	Tartaric.....	+
Metastannic	+		

The anthranilic acid was not tested as to its identity, as the quantity was very small.

A systematic investigation of the oxides of metals and non-metals was made, the results being shown in Table IV. Oxides may roughly be divided into "acidic" and "basic" groups, the former being oxides of non-metals and the latter those of metals, but of course the rule is not rigidly followed, as many metals give acid oxides. We should thus expect to find that some oxides should give positive clouds, and others negative ones.

TABLE IV.

Oxide.	Charge.	Oxide.	Charge.
Aluminium Al_2O_3	—	Magnesium MgO	—
Antimony Sb_2O_4	—	Manganese MnO	+
" Sb_2O_5	+	" MnO_2	+
Arsenic As_2O_3	+	Molybdenum..... MoO_3	+
" As_2O_5	+	Mercury..... Hg_2O	—
Barium BaO	—	" HgO	—
" BaO_2	—	Nickel NiO	—
Bismuth..... Bi_2O_3	—	Phosphoric P_2O_5	+
Cerium Ce_2O_3	—	Tin SnO_2	+
Copper Cu_2O	—	Titanium TiO	+
" CuO	—	Tungsten WO_3	+
Chromium..... Cr_2O_3	+	" W_2O_5	+
Iodine I_2O_5	+	Uranium UO_3	+
Iron FeO	—	" UO_2	+
" Fe_2O_3	—	Vanadium V_2O_5	+
Lead PbO	—	Zinc ZnO	—
" PbO_2	—	" ZnO_2	—
" Pb_3O	—	Zirconium ZrO	—

Manganous oxide MnO and chromic oxide might be expected to give negative charges as they are decidedly basic. Molybdenum, tungsten, and uranium form strongly acid oxides. One oxide of antimony is basic and the other acidic. The oxides of arsenic, phosphorus, and iodine are, of course, very strongly acidic. From this table and the preceding one another law may be deduced.

Law III. *Solid acids and acid-forming oxides give positively charged clouds, and basic oxides negatively charged ones.*

Assuming the truth of law III, it was of interest to speculate as to what should be the nature of the charge obtained on the cloud formed by raising a dust from a finely powdered salt. Would the character of the base or the acid

predominate? With this idea in view, groups of salts were studied in which the acid was "strong" or "weak" relatively to the base, and Table V. shows the results obtained with the carbonates. Carbonic acid may be regarded as a "weak" acid, so that the electrification due to the base might be expected to be dominant.

TABLE V.

Carbonate.	Charge.	Carbonate.	Charge.
Ammonium	— ?	Iron	+
Barium	—	Lead	—
Beryllium	—	Magnesium	—
Bismuth	—	Manganese	—
Cadmium	+	Lithium	—
Calcium	—	Potassium	—
Cobalt	—	Sodium	—
Chromium	+	Strontium	—
Copper	—	Zinc	—

There are three exceptions occurring in this table, which may have been due to contamination, as it seems anomalous that chromium and iron carbonates should differ from the carbonates of cobalt, manganese, and nickel.

Nitric and hydrochloric are "strong" acids, and here it might be expected that the electrification produced would be positive, if the reasoning applied to the carbonates was correct, and this is substantiated by Table VI. Even aniline chloride obeys the rule.

TABLE VI.

Salt.	Charge.	Salt.	Charge.
Ammonium chloride ...	+	Potassium chloride	+
Barium " ...	+	Sodium " 	+
Calcium " ...	+	Strontium " 	+
Copper " ...	+	Barium nitrate	+
Lead " ...	+	Bismuth " 	+
Mercurous " ...	+	Lead " 	+
Mercuric " ...	+	Potassium " 	+
Aniline " ...	+		

Sulphides gave very strongly charged clouds, which were generally positive.

TABLE VII.

Sulphide.	Charge.	Sulphide.	Charge.
Antimony, Red	+	Mercuric Black	+
Antimony, Black	+	Mercuric Red	+
Barium	+	Potassium	0
Calcium	+	Tin	+
Copper	+	Zinc	—
Iron	+		

Reasoning by analogy with the carbonates, we might have expected sulphides to give negative charges, because hydro-sulphuric is a weak acid in solution, but sulphides are very stable compounds, so that perhaps in combination the acid is strong.

Sulphates show considerable variation, but an isomorphous group produced the same charge. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, gives a positive charge, but after the water of crystallization was driven off by heating, the anhydrous sulphate gave a negatively charged cloud.

The alkaloids are a well-known group of basic bodies, and all give strong charges when blown into clouds. With these were studied some allied bodies, and the results obtained are shown in Table VIII.

TABLE VIII.

Substance.	Charge.	Substance.	Charge.
Aconitine	—	Morphine chloride	+
Atropine	—	Quinine	—
Brucine	—	Quinine sulphate	—
Caffeine	+	Strychnine	—
Cantharidine	—	Salicin	+
Cinchonine	—	Tannin	+
Cocaine	—	Theine	+
Codeine	—	Vanillin	+
Morphine	—	Guaiaicum	+

It is very remarkable that all those alkaloids which are of more or less similar constitution should give negative charges, whilst morphine chloride behaves as other chlorides and gives a positive charge. Theine and caffeine are undoubtedly the same substance, and although classed with the alkaloids

are really derivatives of uric acid and should be called ureides; salicin, tannin, vanillin, and guaiacum are probably glucosides, and all give similar charges to each other but different from those of the alkaloids.

In Table IX. there is given a number of miscellaneous substances which do not admit of convenient classification, but those materials to which an acidic character is usually attributed do in general give rise to positive electrification.

TABLE IX.

Substance.	Charge.	Substance.	Charge.
Calcium fluoride	—	Fine soil	+
Zinc chromate	+	Asbestos	+
Precipitated silica	+	Lycopodium	—
Dextrose	—	Methyl orange	—
Dextrine	—	Calcium acetate	—
Starch	+	Potassium iodide	+
Flour	—	„ bromide	+
Lead tartarate	+	„ permanganate ..	—
Tartar emetic	+	„ chromate	—
Sodium aluminate	—	„ bichromate	+
„ salicylate	—	„ fluosilicate	+
„ bisulphite	—	„ hydrate	—
Ammon. bichromate	+	„ ferrocyanide ..	+
Copper cyanide	+	„ phosphate	+
Lead chromate	—	„ sulphite	—
Resorcin	+	„ bitartarate	—
Pyrogallol	—	Urea	+
Carborundum	+	Urea nitrate	+
Tricalcic phosphate	—	Toluidine	—
Monocalcic phosphate	+	Naphthylamine	—
Sand	+	Diphenylamine	—

In this table it may be noted that neutral potassium chromate acquires a negative charge, but the acid bichromate acquires a positive. The same thing is seen with the neutral tricalcic phosphate and the acid monocalcic phosphate. Carborundum is a compound of two non-metallic elements, and should be expected to give a positive charge. Emery-powder is oxide of aluminium, and should behave as a basic oxide and thus give a negative charge. The alcohol pyrogallol, commonly known as pyrogallic “acid,” is not an exception to the rule that acids should give positive charges. It is rather remarkable that starch should give a positive charge, and flour a negative one; urea is only very slightly charged, but urea nitrate yields a strong charge.

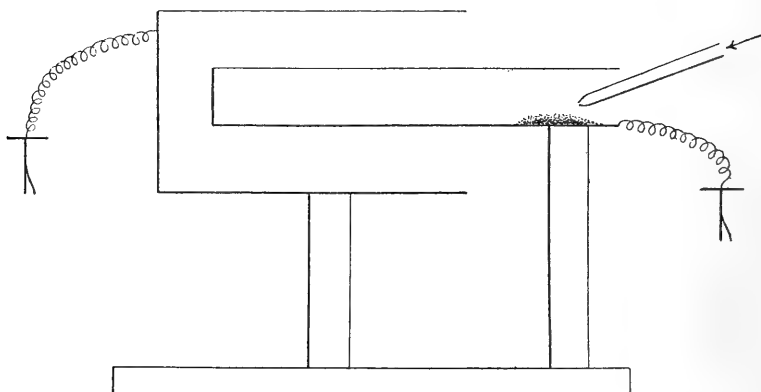
In all cases it is to be presumed that the air would acquire a charge opposite to that upon the dust, and this was first

shown to be true in the case of the iron dust-cloud. As indicated in Table II., iron acquires a negative charge, and the air should consequently be positive. In order to show this, the wire-gauze cylinder was placed between the poles of a strong electromagnet, and an insulated brass tube made to surround the end portion. A cloud of iron dust was raised in the usual manner, but most of the iron particles were retained by the magnet, and the current of air impinging upon the outer tube gave it a distinct positive charge which could be detected by removing it from the neighbourhood of the inner cylinder.

In order to be certain that the charges were actually attached to the dusts, and to the air, the method of conducting the experiments was altered. It might be considered probable that the charges shown by the metal cylinder were due to the friction of the particles upon the insulated wire gauze, but this is not the case, for if so, the charge upon the cylinders would be opposite to that upon the dust.

A second insulated wire gauze cylinder was arranged around the first (fig. 2), and on raising a cloud in the inner cylinder the dust was carried through the meshes of the gauze,

Fig. 2.



and reached the outer cylinder. *The charge indicated by both cylinders was the same.* This was not due to an induction effect, for on removing the inner cylinder the charge persisted upon the outer one. A third cylinder surrounding the second one also acquired a charge similar to that on the innermost one, so that it seems to be quite conclusive that the charge observed is actually attached to the dust particles.

The air is also carried through the cylinders with the dust, so that the charge acquired by the outer cylinder will be the sum of the charges given up by the dust and air, and these charges would of course be opposite in sign. It is possible,

however, to stop most of the dust and to deal mainly with the charge carried by the air.

A small cylinder was constructed of several layers of the finest wire gauze obtainable, and this was covered over with several layers of "chiffon," so that only the finest particles of dust could pass, but the air could do so without much hindrance. Using this cylinder, it was found possible to stop most of the dust, so that the charge acquired by the outer cylinder was mainly that due to the air. Some of the dust did get through, but probably most of the charge it possessed was removed by keeping the inner cylinder "earthed." Table X. gives the results obtained in some typical cases. The inner cylinder was insulated and earthed alternately. When insulated, the charge indicated by the outer cylinder was that due to the dust particles which succeeded in getting through, and also to the inductive effect of the inner cylinder, which had caught most of the charge upon the dust. On earthing the inner cylinder, the charge upon the dust would be removed, but sufficient would be carried by the air to give a definite charge to the outer cylinder.

TABLE X.

Substance.	Inner cylinder.	Charge upon outer cylinder.
Flour	Insulated.	—
	Earthed.	+
Sulphur	Insulated.	+
	Earthed.	—
Fine sand	Insulated.	+
	Earthed.	—
Litharge	Insulated.	—
	Earthed.	+
Boracic acid	Insulated.	+
	Earthed.	—

These examples show very conclusively that charges of opposite sign are carried by dust and by air.

Another form of apparatus was also devised, by which the dust particles could be separated from the air by allowing them to settle upon an insulated plate and then determining the

nature of the charge acquired by the plate, and also the charge upon the air could be indicated (Pl. VI. fig. 3).

A box measuring $40 \times 30 \times 30$ cm. having a well fitting door was taken. Through the top a thick plug of ebonite was passed, and through this plug a wire was joined to a plate of wire gauze. To the door of the box an insulated plate was attached, so that on opening the door a connexion could be established between the plate and an electroscope, and any charge it possessed indicated. A hole at the bottom allowed of a blast of air being introduced, and another at the top allowed the air and dust to escape (Pl. VI. fig. 3).

Some flour was placed on the bottom of the box and both electrodes earthed. A blast of air was sent in from the bellows, and after a short time the earth connexion was broken, and the top of the box tapped so as to shake off as much flour as possible from the upper electrode. On putting the electroscope in communication with this electrode, a POSITIVE charge was seen to be present. On opening the box and testing the lower plate upon which some of the flour particles had settled, a NEGATIVE charge was shown to be present. The charges were not as strong as those obtained in the open air, but they were quite sufficiently strong to admit of identification. On repeating the experiment with sulphur, the upper electrode became POSITIVE, and the lower one NEGATIVE. The charge upon the upper electrode was always more marked than that on the lower one, and the small effect in the latter case appeared to be due to (1) the particles of dust giving up their charge to the walls of the box, and (2) the comparative fewness of the particles reaching the plate.

"Lichtenberg" figures may very readily be obtained from the dust clouds formed in the box used for the last experiment; and a very marked difference is seen when the charges upon the plate are different:

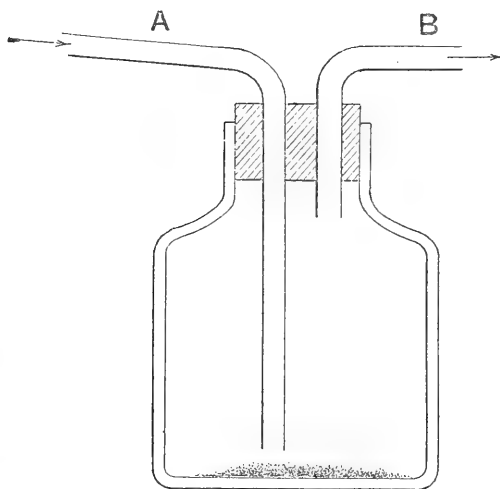
A cleaned ebonite plate was touched for an instant with the knob of a charged leyden-jar. A cloud of dust was raised in the box, and as quickly as possible the charged plate was put inside. The particles of dust were attracted to the charged surface, and a well-defined "Lichtenberg" figure obtained. If flour was used, the figure was strongly developed when a positive charge had been "splashed" upon the plate; and if sulphur, then the same thing was seen if the charge was negative. Figures, however, could be obtained with both charges, but were of a different character. No doubt the electrified air moving with the dust would effect some slight modification. The photographs show some

of the results obtained by this mode of experimenting (Pl. VII. figs. 5, 6, 7, 8, 9, 10).

No. 5 is formed by starch dust, 6 from sulphur, 7 from boracic acid, 8 from aluminium, 9 that due to merely sifting sulphur upon the charged plate. Here the particles which were uncharged, simply lie as they fall, and are not directed along definite lines as is the case with the particles from the dust clouds. 10 is due to sulphur sprayed, and consequently charged, upon a positively charged surface.

The easiest way to obtain these figures is to raise the dust in a kind of wash-bottle. A wide-mouth bottle has a cork with two bent tubes fixed in it (fig. 4). One of the tubes

Fig. 4.



passes nearly to the bottom, and the other passes just below the cork. Some powder is placed in the bottle, and a stream of air sent in through A. The dust and air coming out at B are strongly charged, and on directing the stream against a charged plate very beautiful figures are obtained. The same apparatus can also be used for demonstrating the charges developed by raising dust in general, for by allowing the stream to impinge upon an insulated conductor connected to an electroscope, very strong charges can be obtained, even in a small room, but it is very difficult to determine whether the effect seen is due to the charge upon the air or upon the dust. If the current of air supplied is a gentle one, then the normal electrical effect will be seen, *i.e.* red lead will give a negative charge, but if the current is a strong one, the main effect may be that due to the charge upon the air, and red lead then apparently gives a positive charge, but the charge really comes from the air which accompanies the

dust. Pl. VI. fig. 4A shows the arrangement of apparatus. A disk of very fine wire gauze is supported upon an ebonite rod, and the streams of dust directed against it from the bottle. The wire gauze is connected to an electroscope.

Summary.

(1) Nearly all kinds of finely divided material when blown into a cloud of dust by a current of air, give rise to electrical charges upon the dust and upon the air.

(2) The nature of the charge resident upon the dust particles depends upon the chemical characteristics of the material.

(3) In general, the charge obtained upon the dust is opposite to that associated with the "ion" of the same substance when in solution, *i.e.* strongly basic bodies give **NEGATIVELY** charged dusts, and strongly acidic bodies give **POSITIVELY** charged dusts.

(4) In the case of salts the charge apparently depends on the relative strengths of the acidic and basic ions.

(5) Similarly constituted bodies give similar charges.

LIII. *A New Micromanometer.* By J. D. FRY, *Lecturer and Demonstrator in Physics in the University of Bristol* *.

THE following is an account of a new micromanometer which has been designed by the author and which is now in use in the Physics Department of the University of Bristol.

The principle of the instrument is simple. The difference of pressure to be measured is applied to the two sides of a stretched circular membrane. It is arranged that the centre of the membrane by its displacement twists a mirror which is suspended in a special manner, the pressure difference being finally indicated by the deflexion of a spot of light on a scale.

It is clear that with certain slight modifications of construction a manometer working on this principle may be adapted to the measurement of small differences of pressure at any absolute pressure. The form herein described has been designed for use at atmospheric pressure. The conditions governing the sensitiveness of a gauge of this type,

* Communicated by the Author.

its construction, and its calibration are discussed below ; but it may be mentioned at this point that in its most delicate form the new manometer possesses a sensitiveness at least ten times that of any micromanometer previously described.

The displacement of a stretched membrane is dependent on (1) its tension ; (2) its stiffness. In order that the displacements may be proportional to the pressures applied, it is important that of these two factors the tension should predominate. To achieve this it is necessary to use a very thin membrane and to arrange that the tension to which it is subjected is considerable.

If the stiffness may be neglected and the displacement be not too great, the tension will remain constant : the displacement is then equal to $\frac{pr^2}{2T}$, where p is the pressure difference between the two sides, r the radius of the membrane, and T the tension in the membrane.

The selection of the membrane to be used will depend on the order of magnitude of the pressure differences which the manometer is required to measure. The following substances have been tried :—

Thin sheet-rubber.—This was the first substance to be used. It provides a membrane of extreme sensitiveness, but it is not possible to put it under sufficient tension to eliminate entirely a drift of zero, and it is for this reason unsatisfactory.

Goldbeater's skin.—This has a thickness of approximately 0.0025 cm., but cannot be obtained in sufficiently large sheets to be of much service.

Cyclostyle paper.—Being both thin and impervious to air, cyclostyle paper is a satisfactory membrane when the highest sensitiveness is not required.

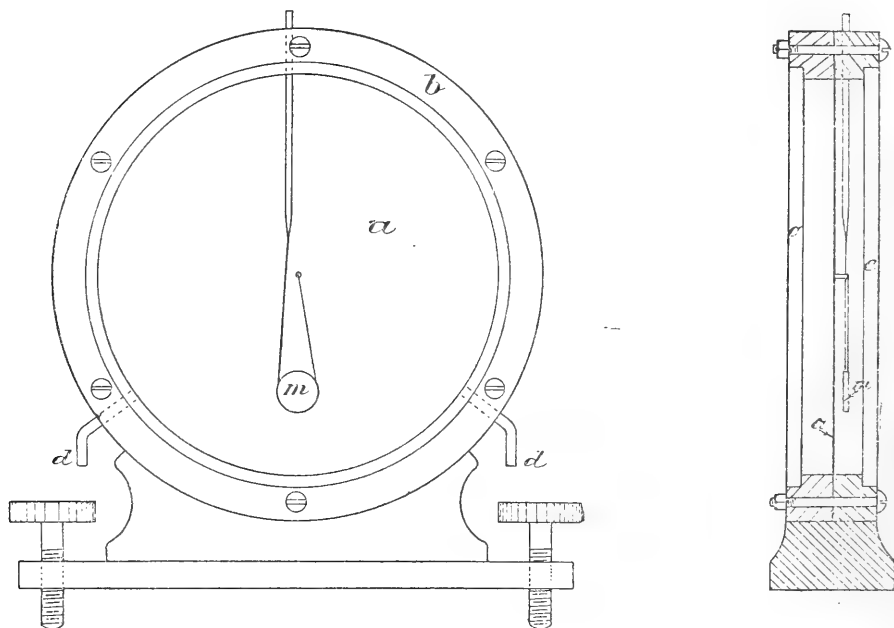
Thin copper.—Copper sheets cannot be obtained much thinner than 0.004 cm., but membranes of this thickness, or even greater, may be employed with advantage for the measurement of comparatively large pressures.

“Badische.”—For the indication of the smallest pressures this is so far the most suitable membrane which has come to the author's notice. It is a thin animal membrane, and has been supplied by Messrs. Ferris & Co. of Bristol. It may be obtained in sheets about 25 cm. square and is considerably thinner than goldbeater's skin, some sheets having an average thickness of about 0.001 cm. By coating this membrane with a thin petrol-resin varnish it is rendered impervious to air.

Construction of Manometer.

The final form of the manometer is shown in fig. 1. The membrane *a* is stretched and clamped between two circular

Fig. 1.



cast-iron rings *b*. The method of uniformly stretching and clamping the membrane varies with the different materials used.

Method (i.). For use with thin metal sheets or cyclostyle paper :—

In one of the circular cast-iron rings a circular V groove is turned, and on the other a corresponding V projection. The membrane on being placed between the two rings, which are subsequently bolted together, is thus stretched as well as clamped.

Method (ii.). For use with the animal membrane :—

One of the rings has its temperature raised to about 80°C . and its surface covered with a thin layer of “piceïn*,” which is plastic at that temperature. The membrane is then placed in position and uniformly stretched. In this condition its surface is carefully damped all over with a wet sponge. This causes the membrane to expand and become slack; the slackness is removed by gently pulling at the circumference, the “piceïn” being sufficiently tacky to keep it adhering to the ring during this process. The second ring is then placed upon the first, and the two are firmly bolted

* Walter, *Ann. d. Physik*, Bd. xviii. p. 860 (1905).

together. In the process of drying the tension considerably increases, and when the membrane is thoroughly dry it presents a uniform taut surface. The petrol-resin varnish is then applied.

The special attachment for the measurement of the pressure is set up in the following way:—In front of one face of the membrane a light mirror *m* is hung by a quartz bifilar suspension, the points of support of which are not at the same level. Thus one fibre is attached to a short style projecting from the centre of the membrane, and the other fibre to a point above it which is rigidly fixed to the iron ring. When a small difference of pressure is set up between the two faces of the membrane, the style follows the motion of the centre, and the mirror is rotated through a small angle. The angle of rotation for a given pressure difference depends on the horizontal distance *S* between the two points of support of the mirror; the manometer is therefore mounted on a metal base fitted with levelling screws, and by means of these *S* and consequently the sensitiveness of the gauge may be varied over a wide range. The upper limit of sensitiveness is reached when *S* is practically zero and instability sets in.

Disks of plate glass *C* are cemented to recesses which have been turned one in each casting. In this way an air-tight chamber is obtained in front of each face of the membrane. Glass tubes *d*, cemented to holes through each ring, enable excess pressure to be applied to either chamber.

In testing for leak through the membrane a soap-bubble affords a very convenient means of detection. The manometer, being rendered sufficiently unsensitive, is connected on one side to the interior of a hemispherical soap-bubble blown on a flat plate, the other side being left open to the atmosphere. This produces a deflexion on the instrument which, in the absence of leak, remains steady, but which increases if the bubble grows smaller owing to passage of air through the membrane.

In dealing with small pressure differences, it is found necessary to make all the connexions with tubes of reasonably large diameter, since with tubes of small bore effects due to viscosity become troublesome, and the manometer takes a considerable time to attain its final reading.

Calibration of the Instrument.

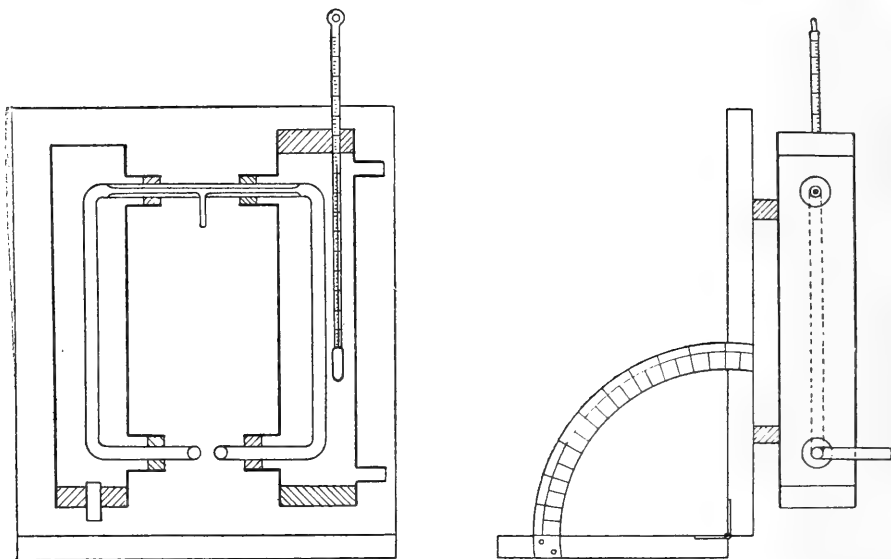
The instrument is obviously one for which the constant cannot be found *à priori*. It has therefore to be calibrated,

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and for this purpose it is necessary to apply to it a series of very small known differences of pressure. The author has found the following method convenient for this purpose :—

The two limbs of an inverted **U**-tube (fig. 2) containing air are kept at a fixed difference of temperature. This causes

Fig. 2.



a small difference of pressure between their lower ends if the latter are connected to opposite sides of the manometer. This **U**-tube with its jackets is mounted on a board hinged so that the plane of the **U** may be inclined at any angle to the vertical, thus making it possible to obtain a series of pressures ranging from zero when the limbs of the **U** are horizontal to a maximum when they are vertical.

The complete expression for the difference of pressure applied is then :—

$$p = K \left(\frac{B}{T_1} - \frac{B}{T_2} \right) \cos \theta;$$

where

$$K = \frac{L \Delta_0 T_0 g}{760},$$

L = Length of each limb of the **U**-tube,

Δ_0 = Density of air at N.P.T.,

B = Height of barometer,

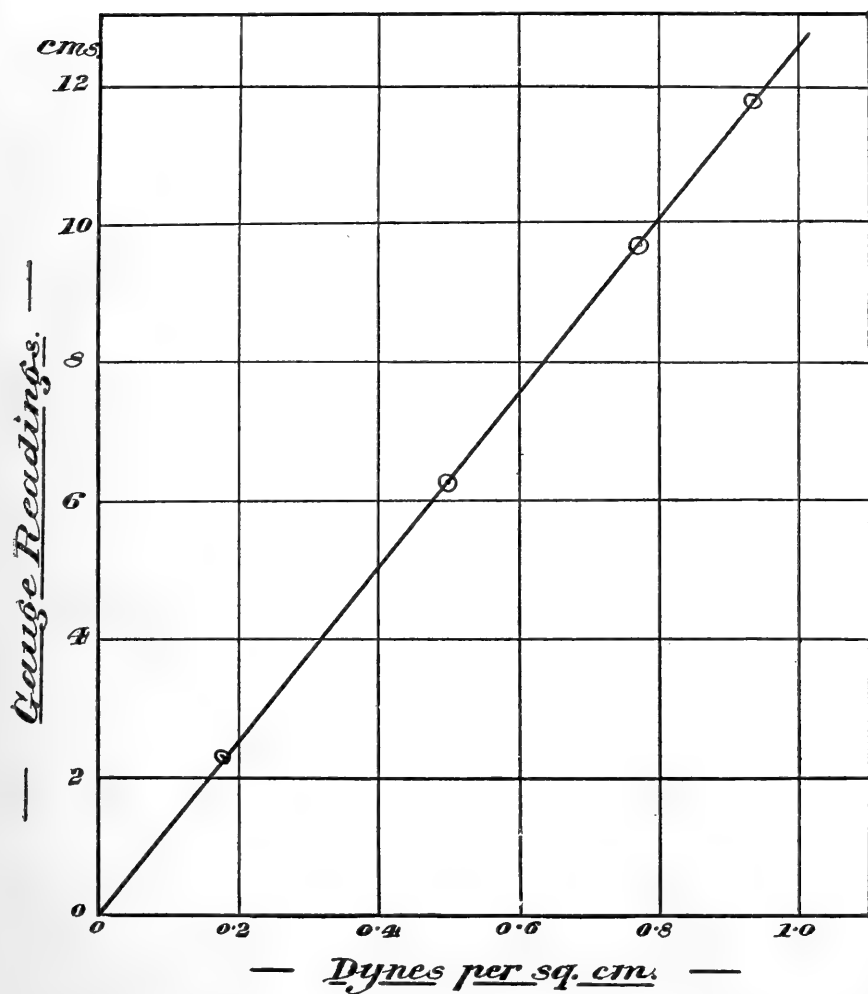
T_1 and T_2 = The absolute temperatures of the two limbs,

θ = The angle at which the **U**-tube is inclined to the vertical.

In one of the calibrators used in obtaining the calibration curves below, the limbs of the **U**-tube were 15 cm. long and the temperatures of the two limbs were 0° C. and 15° C. respectively. This gives a pressure difference of about one dyne per cm.² with the **U**-tube in a vertical position.

Curves I. and II. show calibrations of the same manometer

CURVE I.

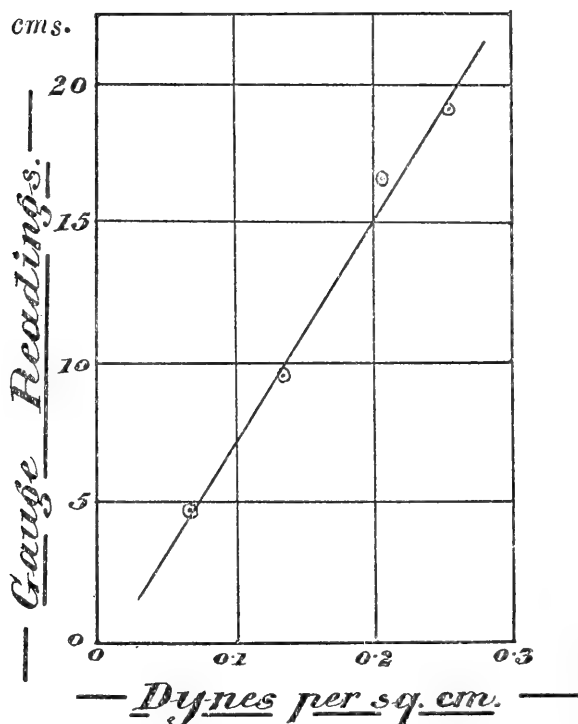


under different conditions of sensitiveness. The pressures are in dynes per cm.², and the gauge readings deflexions of a spot of light on a centimetre scale placed one metre from the instrument. Curve I. was obtained with the manometer in an unsensitive condition, the application of a pressure difference of 1 dyne per cm.² producing a deflexion of about

12.5 cm. on the scale. Curve II. was obtained with the manometer near the limit of its working sensitiveness, and shows deflexions of the order of 75 cm. per dyne per cm.², so that pressure differences as small as a thousandth of a dyne per cm.² may be readily detected.

The form of calibrator described above is one which obviously enables the manometer to be used as a zero instrument, the manometer acting as an indicator and the pressure differences being obtained from the calibrator.

CURVE II.



The following table gives references to various recognized types of sensitive manometer, and serves as a rough comparison in relative sensitiveness. For the purpose of this comparison the numbers in the last column have been deduced from the available data, and are all expressed in the same units. They can only be regarded as approximate values, as it has not been possible in every case to determine from the published records the value of the smallest pressure which the various instruments are capable of detecting.

Type.	Principle employed.	Reference.	Smallest detectable pressure.
Rayleigh	Tilting mercury U-tube.	Phil. Trans. A 196, p. 205 (1901).	0·68 dyne per cm. ²
Morley & Brush .	„ „ „	Amer. Journ. Sci. xiii. June 1902.
Threlfall	Micrometer screw adjustments to surfaces of water U-tube.	Inst. Mech. Eng. Proc. Feb. 1904, p. 273.	0·5 dyne per cm. ²
Hering	Tilting mercury U-tube with electric contacts.	<i>Ann. d. Phys.</i> xxi. 1906.	0·3 „ „
Scheel & Heuse...	Metal diaphragm with interference fringes.	<i>Deutsch. Phys. Gesell.</i> Jan. 1909.	0·1 „ „
Chattock & Fry...	Tilting water U-tube with benzene bubble indicator.	Stanton, Proc. Inst. C. E. clvi.	} 0·01 „ „
		Morrow, P. R. S. A 76, 1905.	
		Chattock & Tyndall, Phil. Mag. xix. p. 450 (1910).	
		Fry & Tyndall, Phil. Mag. xxi. p. 348 (1911).	
Fry.....	Diaphragm.		0·001 „ „

Experiments on a manometer of this type for use at low absolute pressures are now in progress.

University of Bristol.
Jan. 1913.

LIV. *On certain Small Corrections in a Newton's-rings System.* By ALLAN FERGUSON, B.Sc. (Lond.), Assistant Lecturer in Physics in the University College of North Wales, Bangor*.

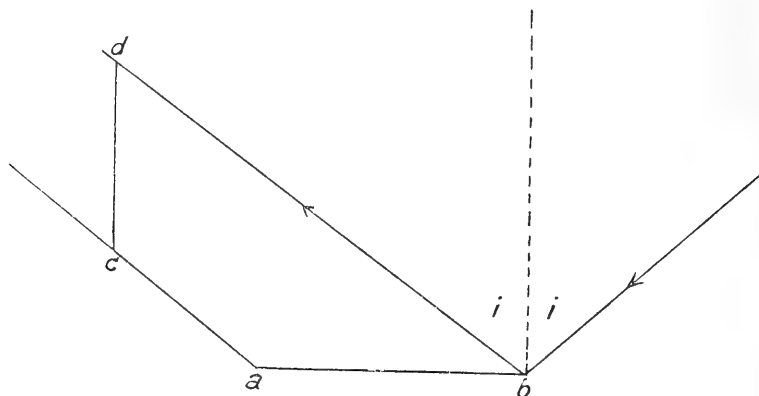
IN the progress of some experimental work which demanded the production and examination of a system of Newton's rings formed under oblique incidence, it seemed that measurements of the diameters of the rings—which, of course, viewed under oblique incidence appear elliptical—would furnish an accurate and easy method for the determination of the angle of incidence.

For if the rings be viewed through a microscope provided with independent vertical and horizontal scales, and the

* Communicated by Professor E. Taylor Jones.

minor axes of the ellipse be measured *on the vertical scale*, then, as the figure shows,

Fig. 1.



$$\tan i = \frac{ab}{cd},$$

if we assume that the rings are truly circular, and concentric with the point of contact of the surfaces between which they are formed, so that ab may be assumed to be given by the measurement of the major axis of the ellipse.

Such a method is probably more satisfactory than those which depend on the measurement of the inclination either of microscope or collimating system, but its use obviously depends on the correctness of the assumption italicised above.

This assumption again depends on the manner in which the equations of the ring-curves are formed. It is a remarkable fact that, even in the definitive treatises on the subject, it is tacitly—or, as for example in the case of Airy's "Undulatory Theory," overtly—assumed that the parallel-plate formulæ can be used without modification, and this, despite the fact that there is a somewhat extensive literature dealing with the subject *. The papers cited below deal fairly exhaustively with a variety of points of importance—*e. g.* the exact shape of the interference surfaces, and the plane in which the fringes are formed—but the expressions arrived at are somewhat cumbrous in form, and not well adapted for practical use.

The variety and importance of the measurements of physical quantities which depend on the production of interference systems, are such as render it desirable to put

* See *e. g.*, Wangerin, Pogg. *Ann.* cxxxi. p. 497 (1867); Feussner, Wied. *Ann.* xiv. p. 564 (1881); Sohncke and Wangerin, Wied. *Ann.* xii. pp. 1 & 207 (1881), and Wied. *Ann.* xx. pp. 177 & 391 (1883); Mascart, *Traité d'Optique*, i. pp. 439 *seqq.*

into convenient form the more important of the above-mentioned corrections.

In the analysis here given a different course is followed. Whilst only attempting to provide a first approximation, it is hoped that it will show clearly the conditions under which the parallel-plate formulæ can be used, and the magnitude of the correction to be applied in the cases of practical importance where the use of the parallel-plate formulæ is not legitimate.

Suppose, then, that we have a plano-convex lens resting on a plane reflecting surface. The central assumption usually made is that ϕ , the angle of incidence of the light on the lower reflecting surface, is, to the first order, the same as the angle of incidence i of the light on the upper plane surface of the lens. In which case the well-known relation

$$2\mu e \cos i = n\lambda \quad . \quad . \quad . \quad . \quad . \quad (i.)$$

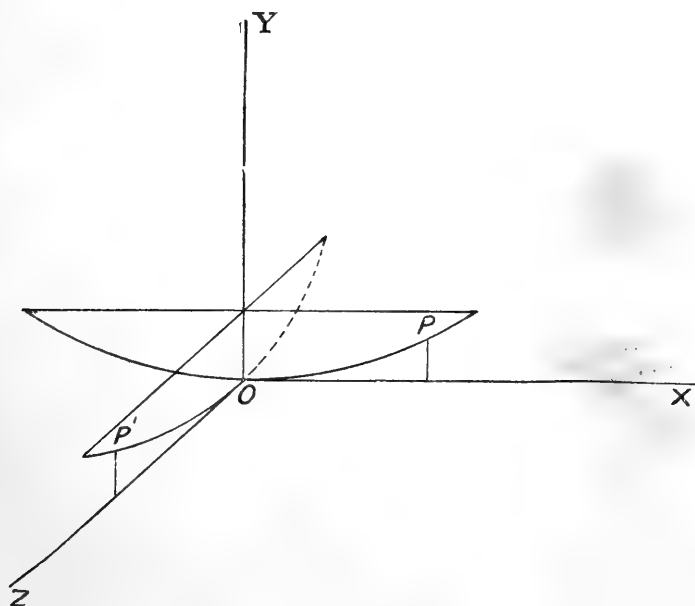
gives at once for the radius x of the n th dark ring

$$x^2 = Rn\lambda \sec i.$$

For our purpose, it will be sufficiently exact to determine ϕ as a function of i , and to substitute the value of $\cos \phi$ so obtained in the equation

$$2\mu e \cos \phi = n\lambda.$$

Fig. 2.



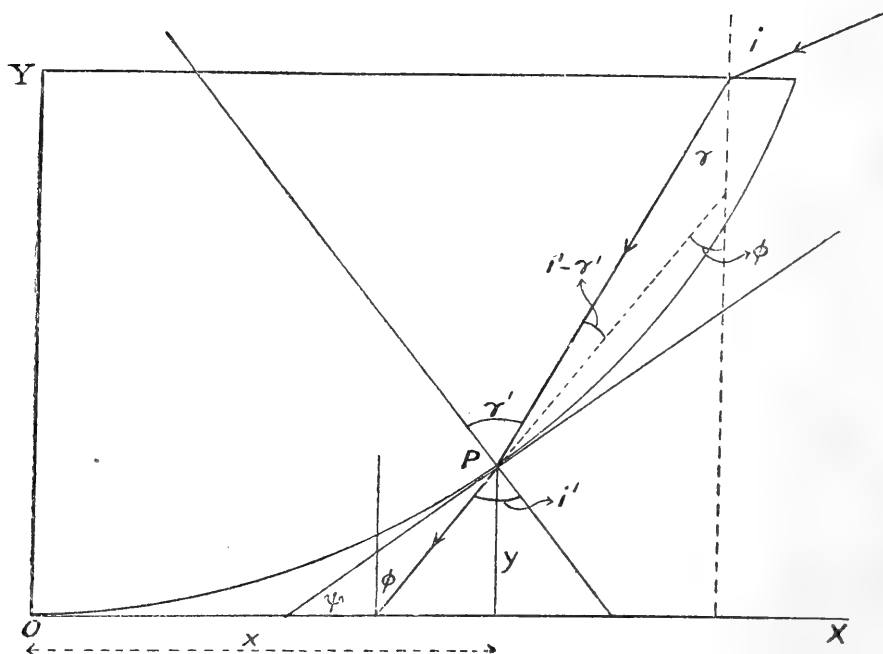
Two cases are of special interest.

Taking rectangular axes as shown (fig. 2), let light be incident at an angle i on the upper surface of the lens in a plane

parallel to the plane of xy . We shall consider the magnitude of the correction to be applied for light which, after refraction at the upper surface of the lens, is incident at the symmetrical points P and P'.

Let R be the radius of the lens-surface and x the radius of the n th dark ring, and let us assume in what follows that $\frac{x^2}{R^2}$ and $\tan^2 \psi$ ($\tan \psi \equiv \frac{dy}{dx}$) are negligible compared with unity. Taking first the case in which the refraction occurs at P, we have from fig. 3

Fig. 3.



$$\phi = i' - r' + r, \quad \dots \dots \dots (ii.)$$

and $\psi = i' - \phi.$

Also, if the origin be at O,

$$x^2 + y^2 - 2Ry = 0,$$

and therefore $\tan \psi = \frac{dy}{dx} = \frac{x}{R-y},$

giving $\sin \psi = \frac{x}{R} = p, \text{ say.}$

Again,

$$i' - \phi = \psi = \tan \psi = \sin \psi = p, \quad . \quad . \quad . \quad (\text{iii.})$$

to the order considered, which, combined with (ii.), gives

$$r' = r + p.$$

Hence

$$\sin i' = N \sin r' = N \sin (p + r) = N(p \cos r + \sin r).$$

Similarly from (iii.),

$$\sin i' = \sin (p + \phi) = p \cos \phi + \sin \phi,$$

$$\text{and therefore } p \cos \phi + \sin \phi = N(p \cos r + \sin r),$$

which, solving for $\cos \phi$ and reducing, gives

$$\cos \phi = \cos i + \frac{x}{R} \sin i \left\{ 1 - \frac{\sqrt{N^2 - \sin^2 i}}{\cos i} \right\}.$$

Hence $\cos \phi$ is *not* equal to $\cos i$, but is subject to a small first-order correction. It is important to notice that the correction vanishes to the first order for normal incidence.

Turning now to the case (fig. 2) where the ray is incident at P', a point in the YZ plane, the direction-cosines of the ray after refraction at the plane surface of the lens are

$$l_2 = \sin r, \quad m_2 = \cos r, \quad n_2 = 0.$$

If the tangent at P' makes an angle ψ with OZ, the direction-cosines of the normal at P' are

$$p' = 0, \quad q' = \cos \psi, \quad r' = \cos (90^\circ + \psi) = -\sin \psi.$$

Then if ϕ_1 and ϕ_2 be the angles between the ray and the normal before and after refraction at P', l_3 , m_3 , n_3 the direction-cosines of the ray after refraction at P',

$$\cos \phi_1 = m_2 q' = \cos r \cos \psi,$$

$$\cos \phi_2 = m_3 \cos \psi - n_3 \sin \psi.$$

From the general formulæ for refraction, where μ and μ' are the "absolute" refractive indices for glass and air* (so that $\frac{\mu}{\mu'} = N$),

$$\left. \begin{aligned} \mu l_2 - \mu' l_3 &= (\mu \cos \phi_1 - \mu' \cos \phi_2) p', \\ \mu m_2 - \mu' m_3 &= (\mu \cos \phi_1 - \mu' \cos \phi_2) q', \\ \mu n_2 - \mu' n_3 &= (\mu \cos \phi_1 - \mu' \cos \phi_2) r'. \end{aligned} \right\} . \quad . \quad . \quad (\text{iv.})$$

* Heath, 'Geom. Optics,' p. 21.

From the first of these we have

$$\mu l_2 - \mu' l_3 = 0,$$

and therefore $l_3 = N \sin r,$

Hence

$$m_3^2 + n_3^2 = 1 - l_3^2 = 1 - N^2 \sin^2 r. \quad . \quad . \quad . \quad (v.)$$

From the second or third of (iv.) we obtain

$$m_3 \sin \psi + n_3 \cos \psi = N \cos r \sin \psi.$$

Substituting this value of n_3 in (v.), we obtain, if $\tan^2 \psi$ be negligible compared with unity,

$$m_3^2 = 1 - N^2 \sin^2 r = \cos^2 i.$$

If, then, ϕ be the angle between the ray in the film and a line parallel to OY whose direction-cosines are therefore 0, 1, 0, we have from the usual formula

$$\cos \phi = m_3 = \cos i.$$

It seems, then, that the correction, which is of the first order in the plane of XY, and only vanishes there at normal incidence, is of the second order in the YZ plane, vanishing there for all angles of incidence. These results are in substantial agreement with those of Wangerin*.

If it be desired, therefore, to eliminate first-order corrections, the analysis points to the following experimental precautions. (α) Either the light must be used at normal incidence, or (β) if obliquely incident light be used, measurements must be restricted to those rings for which $\frac{x}{R}$ is small compared with unity. But, in this case, it is only to the measurement of diameters in the plane of incidence to which this restriction applies. Even with oblique incidence the diameters of the rings measured perpendicularly to the plane of incidence are only subject to a second-order correction.

* *Loc. cit.*

LV. *On the Theoretical Shape of Large Bubbles and Drops, with other Allied Problems.* By ALLAN FERGUSON, B.Sc. (Lond.), Assistant Lecturer in Physics in the University College of North Wales, Bangor*.

[Plate VIII.]

OF the various methods that have been proposed, from time to time, for the measurement of capillary constants, those which depend on the measurement of the dimensions of bubbles and drops hold an important place. The results obtained by the practice of these methods are not, however, free from uncertainty, and it forms one of the objects of the present paper to point out how some sources of error may be avoided. Formulæ are also developed by the use of which it is hoped that reliable measurements of surface-tensions may be made by studying the form and dimensions of drops and bubbles of all sizes.

In a recent paper† the writer has pointed out a method by which the first integral of the differential equation of the capillary surface in external contact with a cylinder of large radius may be obtained. The methods there employed may also be used to determine the approximate shape of large bubbles and drops.

The classical investigation on this subject is that of Poisson‡; the analysis given below is more simple and direct, but leads to results which are in substantial agreement with Poisson's, although, as the analysis will show, the small correcting term in the expression for the diameter of a large bubble or drop differs slightly from that given by Poisson.

A very close method of approximation to the outline of the capillary surface under gravity is that developed by Bashforth and Adams§, but the labour involved in the development renders it almost prohibitive as a practical method. It is hoped that the results of the present analysis will point to methods that are both reliable and reasonably rapid.

Let us take, then, as our first problem, the determination of the depth (q) of a large bubble of radius r , as shown in

* Communicated by Prof. E. Taylor Jones.

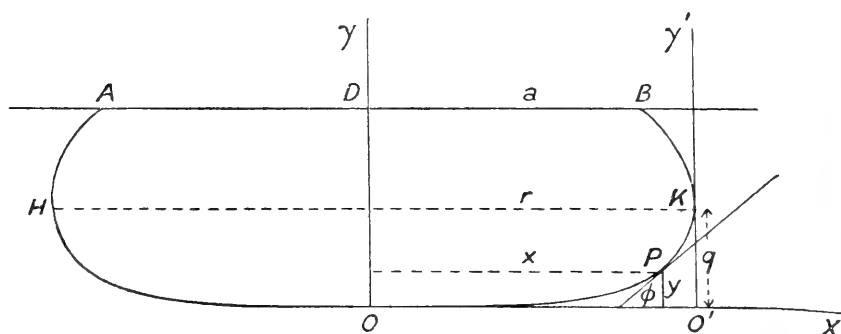
† Phil. Mag. Dec. 1912, pp. 837 *seqq.*

‡ 'Nouvelle Théorie de l'action capillaire,' pp. 212 *seqq.*

§ Bashforth and Adams, 'Capillary Action.' (Camb. Univ. Press.)

fig. 1, measured from the plane of greatest horizontal section to the vertex of the bubble. For greater exactness, we

Fig. 1.



assume that the bubble has a large but finite radius of curvature μ , at the vertex O. The march of the argument is exactly as in the paper cited*, and the main steps therefore only are given.

At the point P, the differential equation to the surface is

$$\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{\mu} = \frac{y}{a^2}.$$

Substituting for R_1 and R_2 , and transferring the origin to O' , we obtain

$$\begin{aligned} a^2 \frac{dp}{dx} - \frac{a^2 x}{r} \cdot \frac{dp}{dx} + \frac{a^2 p}{r} (1+p^2) - \frac{2a^2}{\mu} (1+p^2)^{\frac{3}{2}} + \frac{2a^2 x}{\mu r} (1+p^2)^{\frac{3}{2}} \\ = y(1+p^2)^{\frac{3}{2}} - \frac{xy}{r} (1+p^2)^{\frac{3}{2}}. \quad \dots \quad (i.) \end{aligned}$$

Putting x equal to ∞ in (i.), and substituting the approximate value of $a^2 \frac{dp}{dx}$ so obtained in the second term on the left-hand side of (i.), we have, after a few reductions similar to those already given†,

$$\frac{a^2 p}{(1+p^2)^{\frac{3}{2}}} \cdot \frac{dp}{dy} + \frac{a^2 p}{r \sqrt{1+p^2}} - \frac{2a^2}{\mu} = y, \quad \dots \quad (ii.)$$

giving, when r is infinite,

$$\frac{a^2 p dp}{(1+p^2)^{\frac{3}{2}}} = \left(y + \frac{2a^2}{\mu} \right) y.$$

* Phil. Mag. Dec. 1912 (hereinafter referred to as *l. c.*).

† *L. c.* p. 841.

As before* we have, very closely,

$$\frac{p}{\sqrt{1+p^2}} = \frac{y \sqrt{4a^2 - y^2}}{2a^2},$$

which, substituted in the small term in (ii.), gives on integration

$$a^2 \left(1 - \frac{1}{\sqrt{1+p^2}} \right) = \frac{y^2}{2} + \frac{(4a^2 - y^2)^{\frac{3}{2}}}{6r} + \frac{2a^2}{\mu} y - \frac{4a^3}{3r}, \quad \text{(ii. a)}$$

when $y=q$, $p=\infty$, giving

$$\begin{aligned} 2a^2 &= q^2 - \frac{8a^3}{3r} + \frac{(4a^2 - q^2)^{\frac{3}{2}}}{3r} + \frac{4a^2 q}{\mu} \\ &= q^2 + \frac{4a^2 q}{\mu} - \frac{2a^3}{3r} (4 - \sqrt{2}), \end{aligned}$$

putting $q^2=2a^2$ in the small term involving r .

If we adopt Poisson's notation, in which

$$a_1^2 \left(\equiv \frac{2T}{g\rho} \right) = 2a^2,$$

we get

$$a_1^2 = q^2 + \frac{2a^2 q}{\mu} - \frac{a_1^3}{3r} (2\sqrt{2} - 1). \quad \text{(ii. b)}$$

In most practical cases the bubble or drop may be taken plane at the vertex, in which case we have

$$\begin{aligned} a_1^2 &= q^2 - \frac{a_1^3}{3r} (2\sqrt{2} - 1) \\ &= q^2 - 606 \frac{a_1^3}{r}. \quad \text{(iii.)} \end{aligned}$$

Following the second method of approximation of the paper cited†, and assuming the bubble plane at the vertex, we obtain, taking account of sign,

$$\frac{d\phi}{dy} + \frac{1}{r} = \frac{y}{a^2 \sin \phi},$$

which gives as before, proceeding by the method of variation of parameters,

$$y dy = \left(\frac{a^2}{r} \sin \frac{c}{r} - \frac{a^2 y}{r^2} \cos \frac{c}{r} \right) dc. \quad \text{(iv.)}$$

* *L. c.* p. 841.

† *L. c.* p. 842.

Poisson's formula have interpreted r' as being the radius of the bubble in the plane of greatest horizontal section. Their results, therefore, happen to be in accordance with equation (iii.) of the present paper, but would differ slightly from results computed on the basis of Poisson's formula.

We now proceed to formulate in a similar manner the expressions which give the *total* depth (k) of a large bubble or drop in terms of its capillary constants.

Let fig. 1 inverted represent a large drop of mercury lying on a horizontal surface. The differential equation to the surface at P, a point on the meridional curve between the plane of greatest horizontal section and the surface on which the drop is sessile, will be

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{k-y}{a^2}.$$

Proceeding as in the formation of equation (i.), putting $r=\infty$ in the resulting equation, and substituting in the small terms as before, we obtain

$$-\frac{a^2 p}{(1+p^2)^{\frac{3}{2}}} \cdot \frac{dp}{dz} + \frac{a^2 p}{r \sqrt{1+p^2}} = z, \quad \dots \quad (\text{vi.})$$

where z is put for $k-y$.

Put $r=\infty$ in (vi.) and integrate, when

$$z^2 = 2a^2 \left(1 + \frac{1}{\sqrt{1+p^2}} \right),$$

remembering that $z^2 = q^2 = 2a^2$ when $p=\infty$. Hence we obtain

$$\frac{p}{\sqrt{1+p^2}} = \frac{z\sqrt{4a^2-z^2}}{2a^2},$$

which, substituting in the small terms of (vi.) and integrating, gives

$$\frac{a^2}{\sqrt{1+p^2}} = \frac{z^2}{2} - \frac{q^2}{2} + \frac{1}{6r} (4a^2 - z^2)^{\frac{3}{2}} - \frac{1}{6r} (4a^2 - q^2)^{\frac{3}{2}},$$

determining the integration constant from the fact that $z=q$ when $p=\infty$.

When $y=0$, *i. e.* when $z=k$, $p = \tan \phi_1$, giving

$$2a^2 \cos \phi_1 = k^2 - q^2 + \frac{1}{3r} (4a^2 - k^2)^{\frac{3}{2}} - \frac{1}{3r} (4a^2 - q^2)^{\frac{3}{2}}, \quad (\text{vii.})$$

Also, as we have seen,

$$q^2 = 2a^2 + \frac{2a^3}{3r} \{4 - \sqrt{2}\} = 2a^2 \text{ (approx.)}.$$

Substituting the exacter value of q in the important terms of (vii.) and the more approximate value in the small term, we obtain, after a few reductions,

$$2a^2(1 - \cos \omega) = k^2 - \frac{8a^3}{3r} + \frac{1}{3r} (4a^2 - k^2)^{\frac{3}{2}}, \quad \text{(viii.)}$$

where ω , the angle of contact, is the supplement of ϕ_1 .

Putting the approximate value

$$k^2 = 2a^2 (1 - \cos \omega)$$

in the small term on the right-hand side of (viii.) we obtain finally,

$$k^2 = 4a^2 \sin^2 \frac{\omega}{2} - \frac{8a^3}{3r} \left(1 - \cos^3 \frac{\omega}{2}\right), \quad \text{(ix.)}$$

which in form agrees exactly with Poisson's result, but, as in the case of equation (ii. a), will give slightly different numerical values, owing to the different interpretation of the length r .

We turn now to the explanation of a method which, while rather more laborious, is, on some counts, preferable to those which depend on the application of formulæ (iii.), (v.), and (ix.). It has further the advantage that the formulæ developed can be applied either to large or small drops and bubbles. A photograph of the drop or bubble is taken, and its contour explored in a manner previously described by the writer*. Taking the case of a pendent drop, and considering the equilibrium of the portion below the plane ABCD (fig. 2), we have, resolving vertically,

$$2x_1 T \sin \phi = g\rho(h - y_1)x_1^2 + g\rho \int_0^{y_1} x^2 dy.$$

Resolving horizontally for the portion B OCD,

$$2x_1 T \cos \phi + 2g\rho h \int_0^{y_1} x dy - 2g\rho \int_0^{y_1} xy dy = Ts.$$

Whence, eliminating $g\rho h$ between the above equations, we obtain

$$T = \frac{g\rho}{x_1} \left\{ \frac{2Cx_1^2 + AB - Ax_1^2 y_1}{2A \sin \phi + 2x_1^2 \cos \phi - x_1 s} \right\}, \quad \text{(x.)}$$

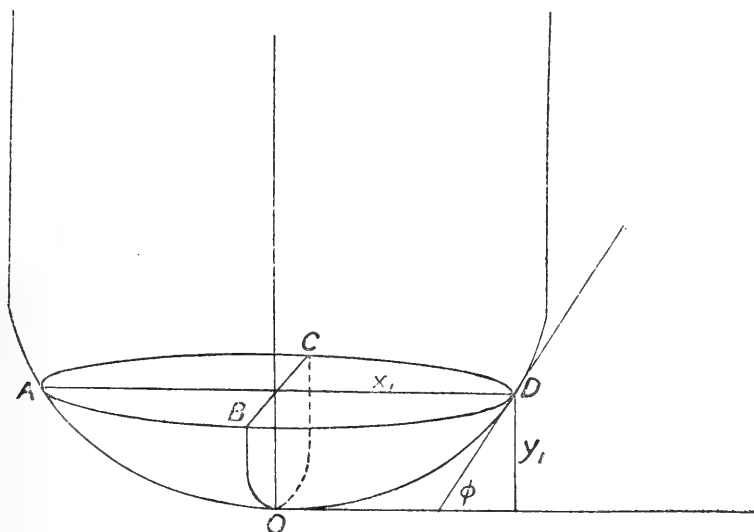
* Ferguson, Phil. Mag. March 1912.

where, for brevity,

$$C \equiv \int_0^{y_1} xy dy, \quad B \equiv \int_0^{y_1} x^2 dy, \quad A \equiv \int_0^{y_1} 2x dy,$$

and s is the length of the arc AOB.

Fig. 2.



Suppose, then, that the coordinates of a large number of points on the photograph of the meridional section of the drop are measured off, and referred to the vertex as origin. Three curves may then be plotted out—one having the values of x and y , a second with the values of x^2 and y , and a third with the values of xy and y , as abscissæ and ordinates respectively. The areas of these curves, taken between proper limits, will then be proportional to the integrals A , B , and C respectively. These areas can be measured with considerable accuracy either by square-counting or by the planimeter, afterwards being reduced to their proper values from a knowledge of the magnification. The length s of the arc AOB may be measured either by a rotating wheel, or by fitting a flexible rod to the curve.

If the point (x_1, y_1) be chosen so that the tangent is vertical, equation (x.) simplifies to

$$T = \frac{g\rho}{x_1} \left\{ \frac{2Cx_1^2 + AB - Ax_1^2 y_1}{2A - x_1 s} \right\}, \quad \dots \quad (\text{xi.})$$

a form convenient for the measurement of small drops.

But if the drop or bubble be so large that its surface may

already found. Thus from equation (ii. a) we have

$$1 - \frac{1}{\sqrt{1+p^2}} = \frac{y_2}{2a^2} + \frac{(4a^2 - y^2)^{\frac{3}{2}}}{6a^2r} - \frac{4a}{3r},$$

assuming, to avoid cumbersome algebra, that the radius of curvature at the vertex is infinite. Solving this equation for $\sqrt{1+p^2}$, and squaring, we obtain, after some reductions,

$$p^2 = \frac{y^2(4a^2 - y^2)}{(2a^2 - y^2)^2} \left[1 - \frac{8a^4 \{ 8a^3 - (4a^2 - y^2)^{\frac{3}{2}} \}}{3ry^2(2a^2 - y^2)(4a^2 - y^2)} \right],$$

neglecting terms involving r^{-2} and higher negative powers of r . This gives at once, to the same order of approximation,

$$\frac{dx}{dy} = \frac{1}{p} = \frac{2a^2 - y^2}{y\sqrt{4a^2 - y^2}} \left[1 + \frac{32a^7 - 4a^4(4a^2 - y^2)^{\frac{3}{2}}}{3ry^2(2a^2 - y^2)(4a^2 - y^2)} \right],$$

whence we have

$$dx = \left\{ \frac{2a^2 - y^2}{y\sqrt{4a^2 - y^2}} + \frac{32a^7}{3ry^3(4a^2 - y^2)^{\frac{3}{2}}} - \frac{4a^4}{3ry^3} \right\} dy,$$

which, putting

$$y = 2a \sin \theta,$$

gives

$$x + C = a \int \frac{d\theta}{\sin \theta} - 2a \int \sin \theta d\theta + \frac{a^2}{3r} \int \frac{d\theta}{\sin^3 \theta \cos^2 \theta} + \frac{2a^4}{3ry^2}.$$

This gives at once

$$\begin{aligned} x + C = & a \log \frac{y}{2a + \sqrt{4a^2 - y^2}} + \sqrt{4a^2 - y^2} + \frac{2a^4}{3ry^2} \\ & + \frac{a^2}{3r} \left[\frac{2a^2 \sqrt{4a^2 - y^2} + a(3y^2 - 4a^2)}{y^2 \sqrt{4a^2 - y^2}} + \frac{3}{2} \log \frac{y}{2a + \sqrt{4a^2 - y^2}} \right], \end{aligned}$$

which, as it should do, reduces, when r is infinite, to the usual expression for the equation to the capillary curve formed by the contact of a liquid with a plane wall.

The integration constant is determined from the condition $x=0$ when $y=q$; and substituting in the small terms for q its approximate value $a\sqrt{2}$, we have finally

$$\begin{aligned} \kappa = & a \log \frac{y}{q} \cdot \frac{2a + \sqrt{4a^2 - q^2}}{2a + \sqrt{4a^2 - y^2}} + \sqrt{4a^2 - y^2} - \sqrt{4a^2 - q^2} \\ & + \frac{a^2}{3r} \left[\frac{2a^2 \sqrt{4a^2 - y^2} + a(3y^2 - 4a^2)}{y^2 \sqrt{4a^2 - y^2}} - \frac{\sqrt{2} + 1}{\sqrt{2}} + \frac{3}{2} \log \frac{y}{\sqrt{2}} \cdot \frac{2 + \sqrt{2}}{2a + \sqrt{4a^2 - y^2}} \right]. \end{aligned}$$

We now proceed to give some experimental illustrations of the above formulæ, choosing water as the fluid for examination. It should be premised that, in spite of all the experimental work that has been done on the surface-tension of water, it cannot be claimed that the value of this constant is known even with an accuracy of one per cent. Restricting ourselves to the determinations made during the last twenty years, we find values given for the surface-tension at 12° C. ranging between the limits 71.7 and 77 dynes per cm., with a grouping of the majority of the results round 73 to 75 dynes per cm.

It is not necessary to indulge in any lengthy criticism of the methods used. It may be pointed out in passing, that methods which involve any assumptions as to the magnitude of contact-angles are obviously open to error, and that measurements of capillary ripples are on several counts open to criticism*. On the whole, measurements of bubbles and drops seem to be least open to criticism.

The majority of experimenters along this line have made actual measurements of the bubble or drop itself. To the writer it seemed preferable to photograph the bubble or drop, afterwards making measurements on the photograph. Such a method seems preferable for several reasons. The surface is exposed only for a minimum time, the magnification is increased, giving a corresponding increase in the accuracy of the reading, and a permanent record of the drop or bubble is made, which can be checked at any time.

In the apparatus used by the writer, the drop was blown under a funnel placed vertically in a rectangular glass trough with parallel sides. The size of the bubble could be very exactly regulated by means of a tube and pressure-bulb attached to the funnel. The bubble was illuminated by means of a beam of light from a filament lamp and condensing lens, which beam impinged horizontally on the surface of the bubble, this latter condition being insured by means of several narrow rectangular apertures placed horizontally through which the beam passed.

The plate (Pl. VIII. fig. 3) shows some typical photographs. A shows a bubble 35 mm. in diameter, which is rather too small for the application of equations (ii.b) or (iii.). B and C show a larger bubble, over 50 mm. in diameter, at different stages of extrusion. D and E show pendent *drops* of much smaller size (4 mm. in maximum diameter) formed under different pressures. To quote a few measurements, we have the following results from bubble B (the measurements

* See, in particular, Bohr, Phil. Trans. A. 209 (1909).

were made by means of a travelling microscope provided with vernier scales running parallel to the x and y axes, and are, unless specified to the contrary, given in centimetres):—

Fluid: tap-water.

Temp. 8° C.

$\rho = 1$ gm. per c.c.,

$g = 981 \frac{\text{cm.}}{\text{sec.}^2}$.

Mean vertical distance (q) between plane
of greatest horizontal section and vertex
of bubble, measured on photo = $\cdot 899$ cm.

Mean maximum diameter of bubble = $11\cdot 277$ „

Mean diameter of funnel on photo = $12\cdot 083$ „

Mean true diameter of funnel = $5\cdot 443$ „

\therefore True value of $q = \frac{\cdot 899 \times 5\cdot 443}{12\cdot 083} = \cdot 4051$ „

True value of $r = \frac{11\cdot 277 \times 5\cdot 443}{2 \times 12\cdot 083} = 2\cdot 540$ „

Hence, employing the equation

$$a_1^2 = q^2 - \cdot 606 \frac{a_1^3}{r},$$

and solving for a_1^2 by the method of successive approximations, we find that

$$a_1^2 = \cdot 1502;$$

and therefore

$$T_8 = \frac{\cdot 1502 \times 981}{2} = 73\cdot 65 \frac{\text{dynes}}{\text{cm.}}.$$

This result is in close agreement with the result obtained from measurements of the radii of curvature and pressure of small pendent drops made some time ago by the writer *, which measurements gave

$$T_{11} = 73\cdot 4 \frac{\text{dynes}}{\text{cm.}},$$

and is also in substantial agreement with the value obtained recently by Bohr from measurements of the stationary waves formed on a vibrating jet of liquid †.

We give now an example of the planimetric measurements suggested above, choosing, for the purpose of experimental illustration, the most difficult case—an application of

* Phil. Mag, March 1912.

† Bohr, *l. c.*

equation (x.). With drops large or small, provided they exhibit a maximum point at which a vertical tangent may be drawn, little difficulty is experienced in hitting off the precise coordinates of the point at which the tangent is vertical. Measurements involving the use of equations (xi.) and (xii.) are quite straightforward, and an example of the use of (x.) will serve to exhibit the *minimum* trustworthiness of the method.

All measurements were made by an "*x-y*" microscope, as described above, the vertex of the drop being taken as origin.

Details.

Fluid : tap-water.

Temp. 11° C.

TABLE I.

x	y	xy	x^2
3.606	1.7155	6.187	13.00
3.515	1.6135	5.672	12.36
3.115	1.2235	3.814	9.703
2.715	.9055	2.458	7.371
2.315	.6515	1.508	5.359
1.915	.4285	.8209	3.667
1.515	.2705	.4099	2.295
1.115	.1435	.1600	1.243
.715	.0605	.0433	.5112
.315	.0135	.0043	.0992

With similar figures for
negative values of x .

Magnification of drop on photo = 16.07.

At the point for which $\phi = 45^\circ$,

$$x_1 = 3.502, \quad y_1 = 1.600.$$

Hence, true values of x_1 and y_1 are given by

$$x_1 = \frac{3.502}{16.07} = .2180, \quad y_1 = \frac{1.600}{16.07} = .09959.$$

A curve between x and y was plotted on squared paper, and its area between the proper limits as fixed by the points (x_1, y_1) and $(-x_1, y_1)$ was measured by the planimeter and was found to be 381 sq. cm.

Also 1 sq. cm. on paper = .02 sq. cm. on photo.

Hence,

$$\text{true value of A (vide equation (x.))} = \frac{381 \times .02}{(16.07)^2} = .02952.$$

Similarly, by plotting a curve between x^2 and y , estimating its area (99.72 sq. cm.), and taking account of magnification,

$$B = \frac{99.72 \times 1}{(16.07)^3} = .002405.$$

Similarly, the curve between xy and y (area 72.64 sq. cm.) gave

$$C = \frac{72.64 \times .05}{(16.07)^3} = .0008758.$$

Finally,

s , as actually measured on squared paper = 2×7.847 inches.

And since 1 cm. on graph = .2 cm. on photo, the true value of s on the drop itself

$$= \frac{2 \times 7.847 \times 2.54 \times .2}{16.07} = .4960 \text{ cm.}$$

These values, substituted in equation (x.), give

$$T = \frac{981 \times 1.461}{.218 \times 84} = 76.5 \text{ dyne-cm.}^{-1}.$$

This result, though higher than those obtained by the other methods described by the writer, yet falls within the limits of the varying results made by different experimenters, as previously quoted. And, if it be remembered that this particular drop (E in fig. 3) is very small—its maximum diameter being about 4 millimetres—and, further, if the necessary uncertainty in the determination of ϕ be taken into account, it is fairly reasonable to assume, especially if the small drops will allow of the use of equation (xi.), that such planimetric measurements will give results that can be relied on in cases where it would be difficult to obtain measurements by any other methods, *e. g.* in the case of molten metals, or small drops of magnetic liquids in magnetic fields.

To sum up:—(1) In the present paper methods have been described by means of which approximations to the outlines of large bubbles and drops may readily be made. These approximations differ slightly in their correcting terms from those obtained by other methods.

(2) A mechanical, or planimetric, method of integration has been described which is applicable to drops and bubbles of all sizes.

(3) The more frequent use of photography in such measurements is advocated ; and

(4) Some experimental illustrations of the photographic method and of the use of the formulæ of (1) and (2) have been given.

Experimental work on some of the systems mentioned above is in progress. The results will, it is hoped, be of sufficient interest to form the subject of future communications.

University College of North Wales,
Bangor.
February, 1913.

LVI. *On Measurements of Inductance.*

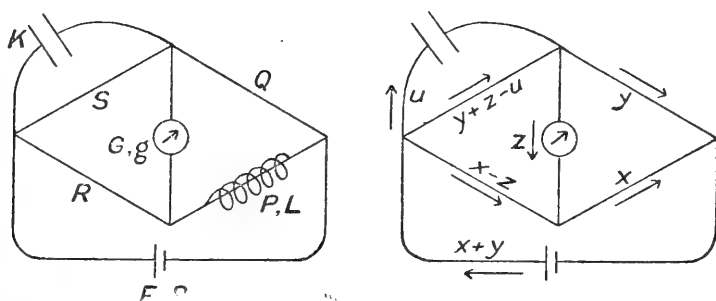
By A. O. ALLEN*.

§ 1. **I**N a report to the British Association in 1883 it was pointed out by Lord Rayleigh that there is a marked difference in the behaviour of a galvanometer used for null methods of inductance measurements according to whether the balance is continuous or merely aggregate; the latter case of course tends to give unsteadiness. The report discusses a particular case, and shows that two conditions must be fulfilled if the balance is to be continuous, but no proof is given that these are sufficient (as they are), and yet it might at first be supposed that there would be others; for the expression for the quantity passing along any arm of the network consists in general of *four* terms, each of which must in the galvanometer arm be identically equal to zero for a continuous balance. Moreover, no general method is indicated for discovering the necessary and sufficient conditions in other cases, if there are such conditions, and I cannot find that the matter is dealt with elsewhere: at all events it is not discussed in Gray's 'Absolute Measurements in Electricity,' which contains very full details of such work. Lastly, it seems that in the cases where there is not a continuous balance it would be useful to know roughly the duration of the flow through the galvanometer in the two directions successively, so as to judge whether the instrument is sufficiently ballistic. These matters form the subject of

* Communicated by the Author.

the following discussion, and most of the ordinary laboratory methods are dealt with.

§ 2. Maxwell's original plan for comparing an inductance with a capacity forms a convenient starting-point, since it illustrates all the principles simply, although the double adjustment needed makes it unworkable in practice. The diagrams show the symbols employed: G, g are respectively



the resistance and inductance of the galvanometer, and the letters x, y, z, u denote quantities which have flowed in the respective arms since some initial moment. If this is the moment of completing the battery circuit, we have

$$\begin{aligned} E - L\ddot{x} &= (P + B + R)\dot{x} + B\dot{y} - R\dot{z}, \\ g\ddot{z} &= R\dot{x} - S\dot{y} - (G + R + S)\dot{z} + S\dot{u}, \\ E &= B\dot{x} + (Q + S + B)\dot{y} + S\dot{z} - S\dot{u}, \\ u &= KS\dot{y} + KS\dot{z} - KS\dot{u}. \end{aligned}$$

Integrating the first two, and putting the symbol D for the operation $\frac{d}{dt}$, we find that x, y, z, u and t are proportional respectively to the five determinants arising from these equations. But it scarcely affects the numerical results (since B is negligible) if the initial moment is that of *short-circuiting* the battery, and this makes the computation somewhat simpler. If we put f for the steady current in the arm P , the equations are

$$\begin{aligned} (LD + P + R)x - Rz - Lf &= 0, \\ Rx - Sy - (gD + G + R + S)z + Su &= 0, \\ (Q + S)y + Sz - Su &= 0, \\ KSDy + KSDz - (KSD + 1)u - KRf &= 0. \end{aligned}$$

Thus, x , $-y$, z , $-u$, and f are proportional to

$$\begin{vmatrix} 0 & -R & 0 & -L \\ -S & -(gD+G+R+S) & S & 0 \\ Q+S & S & -S & 0 \\ KSD & KSD & -(KSD+1) & -KR \end{vmatrix},$$

$$\begin{vmatrix} -R & 0 & -L & LD+P+R \\ -(gD+G+R+S) & S & 0 & R \\ S & -S & 0 & 0 \\ KSD & -(KSD+1) & -KR & 0 \end{vmatrix},$$

$$\begin{vmatrix} 0 & -L & LD+P+R & 0 \\ S & 0 & R & -S \\ -S & 0 & 0 & Q+S \\ -(KSD+1) & -KR & 0 & KSD \end{vmatrix},$$

$$\begin{vmatrix} -L & LD+P+R & 0 & -R \\ 0 & R & -S & -(gD+G+R+S) \\ 0 & 0 & Q+S & S \\ -KR & 0 & KSD & KSD \end{vmatrix},$$

$$\begin{vmatrix} LD+P+R & 0 & -R & 0 \\ R & -S & -(gD+G+R+S) & S \\ 0 & Q+S & S & -S \\ 0 & KSD & KSD & -(KSD+1) \end{vmatrix}.$$

Of these only the 3rd and 5th need now be considered; from them we learn that the 5th operating on z equals the 3rd operating on f , viz. $\{KQRS(P+R) - LR(Q+S)\}f$. As for the 5th, which may be written

$$\begin{vmatrix} LD+P+R & 0 & -R & 0 \\ R & 0 & -(gD+G+R) & S \\ 0 & Q & 0 & -S \\ 0 & -1 & -1 & -(KSD+1) \end{vmatrix},$$

it is clearly a cubic in D , of which the roots may be called α , β , γ , so that the complementary function for z is

$$c_1 e^{\alpha t} + c_2 e^{\beta t} + c_3 e^{\gamma t}.$$

A particular integral is found by dividing

$\{KQRS(P+R) - LR(Q+S)\}f$ by

$$\begin{vmatrix} P+R & 0 & -R & 0 \\ R & 0 & G+R & S \\ 0 & Q & 0 & -S \\ 0 & -1 & -1 & -1 \end{vmatrix},$$

i. e. by $-(P+R)QS - (Q+S)(GP+GR+PR)$. If there is to be a continuous balance, we must have $c_1 = c_2 = c_3 = 0$, and $L(Q+S) = KQS(P+R)$. The initial values of z , \dot{z} , and

\ddot{z} are all zero, provided $P : Q = R : S$, so that $L = KPS$,

$$c_1 + c_2 + c_3 = c_1\alpha + c_2\beta + c_3\gamma = c_1\alpha^2 + c_2\beta^2 + c_3\gamma^2 = 0,$$

or $c_1 = c_2 = c_3 = 0$. In this measurement, then, if a balance is attained at all, it is necessarily continuous. It will save time in dealing with other methods if we notice that this is because \ddot{z} is initially zero; that z and \dot{z} are so is of the essence of the mode of measurement, of course. The reason why we get a cubic in D is that the network comprises, in different arms, three repositories of energy (static or kinetic); the capacity and inductance of the connecting wires being ignored. When the conditions $PS = QR$ and $L = KPS$ are fulfilled the cubic breaks up into

$$(KQSD + Q + S)\{(gD + G + R)(KPSD + P + R) + PS - R^2\} = 0.$$

The roots α, β, γ , with signs reversed, are of course the reciprocals of three time-constants, of which one is $\frac{KQS}{Q+S}$, the time-constant of K discharging itself through Q and S in parallel, or of L discharging itself through R and the short-circuit. The other two lie between $\frac{g}{G+R}$ and $\frac{KQS}{Q+S}$, with which, however, they coincide if $Q = R = \sqrt{PS}$.

At first sight it seems odd that G and g should play any part in determining the rates of decay in the other arms, although no current flows through G , but this is explained later. We may now write

$$x = a_1 e^{\alpha t} + a_2 e^{\beta t} + a_3 e^{\gamma t} + \frac{Lf}{P+R};$$

in y and u we must replace a_1, a_2, a_3 by b_1, b_2, b_3 or d_1, d_2, d_3 respectively, and the constant term by

$$-\frac{R}{Q} \cdot \frac{Lf}{P+R} \quad \text{or} \quad -\frac{Lf}{Q}.$$

To evaluate the constants we have the initial values of x, y, u and their two derivatives, viz.

$$0, 0, 0; \quad f, -\frac{R}{Q}f, -\frac{P+R}{Q}f; \quad -\frac{P+R}{L}f, \frac{R}{Q} \cdot \frac{P+R}{L}f, \frac{(P+R)^2}{QL}f.$$

The proportionality shows that

$$a_1 : b_1 : d_1 = a_2 : b_2 : d_2 = a_3 : b_3 : d_3 = Q : -R : -(P+R).$$

Further, a_1 , $-a_2$, a_3 , and $-f$ are proportional to

$$\begin{vmatrix} 1 & 1 & L/(P+R) \\ \beta^3 & \gamma & -1 \\ \beta^2 & \gamma^2 & (P+R)f/L \end{vmatrix}, \quad \begin{vmatrix} 1 & L/(P+R) & 1 \\ \gamma & -1 & a \\ \gamma^2 & (P+R)/L & a^2 \end{vmatrix},$$

$$\begin{vmatrix} L/(P+R) & 1 & 1 \\ -1 & a & \beta \\ (P+R)/L & a^2 & \beta^2 \end{vmatrix}, \quad \begin{vmatrix} 1 & 1 & 1 \\ a & \beta & \gamma \\ a^2 & \beta^2 & \gamma^2 \end{vmatrix},$$

and it is obvious that (taking α to denote the root $-\frac{P+R}{L}$) the 2nd and 3rd vanish, while the 1st is $\frac{L}{P+R}$ times the 4th. Hence, finally,

$$\dot{x} = fe^{at}, \quad \dot{y} = -\frac{R}{Q}\dot{x}, \quad \dot{u} = -\frac{P+R}{Q}\dot{x}.$$

All the factors are present to fix two rates of decay differing in general from that corresponding to α , but they fail to be operative because the amplitudes are zero. To sum up: the short-circuit isolates the upper half from the lower as if the galvanometer-resistance were infinite; the two halves discharge independently but at equal rates, owing to the equality of the time-constants of the condenser circuit and inductance circuit; when $Q=R$, there is no flow by the short-circuit.

If the battery circuit is not short-circuited but broken, the only difference is that the root α is

$$-\frac{P+Q}{L}, \quad \dot{x} = fe^{at}, \quad \dot{y} = -\dot{x}, \quad \dot{u} = -\frac{P+Q}{Q}\dot{x}.$$

The galvanometer-arm isolates the right-hand side from the left, as if its resistance were zero; the time-constants of the two discharges are $\frac{KRS}{R+S}$ and $\frac{L}{P+Q}$, which of course are equal.

§ 3. In Rimington's method (Phil. Mag. vol. xxiv., July 1887) the double adjustment is avoided, and the continuous balance sacrificed, by putting K in parallel with only a portion s of the resistance S . The equation for \ddot{z} is then

$$g\ddot{z} = R\dot{x} - S\dot{y} - (G+R+S)\dot{z} - s\dot{u}$$

upon short-circuiting, and putting

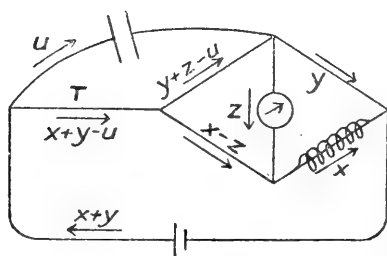
$$f, \quad -\frac{Rs}{S(Q+S-s)}f, \quad -\frac{R(Q+S)}{S(Q+S-s)}f$$

for the initial values of \dot{x} , \dot{y} , \dot{u} , it is evident that \ddot{z} is not

zero at the start, so that c_1, c_2, c_3 cannot all vanish. The equations for x, y, z, u are as above, except that the constant in u is $-\frac{S}{s} \cdot \frac{L f}{Q}$. The cubic in D does not factorize; none of the constants vanish, and they vary in sign, so that it is possible for the current in any arm to be reversed; the proportionality between the constants no longer obtains, so that the reversal in the various arms is not simultaneous. A numerical example is given below.

§ 4. Niven's procedure (Phil. Mag. vol. xxiv., Sept. 1887) only differs in putting K in parallel with a non-inductive portion p of the arm P instead of in the conjugate arm S . The remarks made in the previous paragraph apply here also. [Niven recommends that a non-inductive resistance s be put in parallel with the coil L (of resistance r), in case p would otherwise have to be inconveniently large, and adds that this has the effect of apparently reducing the inductance L , the factor being $\frac{s^2}{(r+s)^2}$. This statement is quite correct for the circumstances to which it is meant to be applied, but must not be applied generally except with the proviso that the total current transmitted through r and s is to be the same as was previously transmitted through r only. In that case the truth of the statement is self-evident, since the energy in the magnetic field is $\frac{L}{2}$ times the square of the current.]

§ 5. W. Stroud's method is superior to the two preceding, since it attains the same end without sacrificing the continuous balance. He interposes a fifth resistance T between

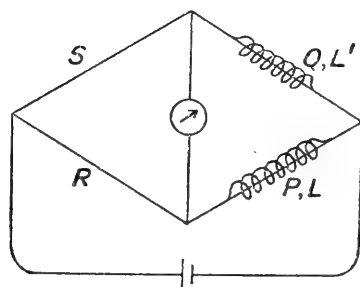


the battery and condenser on one side and the arms R, S on the other, and the adjustment of T annuls the kick on making or breaking the battery connexion. The discussion in § 2 is applicable perfectly, provided we replace the R and S there mentioned by the expressions $R + T + \frac{TP}{Q}$ and $S + T + \frac{TQ}{P}$

respectively. This is easily seen, because T is equivalent to $T \cdot \frac{P+Q}{Q}$ and $T \cdot \frac{P+Q}{P}$ in parallel; these are proportional to R and S , and non-inductive, so that it makes no difference whether they are joined at both ends or only at the battery end; and in the latter case $T \cdot \frac{P+Q}{Q}$ is thrown into R , and $T \cdot \frac{P+Q}{P}$ into S . All the results of § 2 then apply. (I am indebted to Prof. Stroud for this characteristically neat explanation.)

§ 6. Anderson's method is the correlative of the preceding, but interposes T in the conjugate position, *i. e.* between the condenser and galvanometer on one side, and the arms Q and S on the other. The balance is continuous; the method of last paragraph may be used, *i. e.* we may split T into $T \cdot \frac{Q+S}{Q}$ and $T \cdot \frac{Q+S}{S}$, and then throw these into Q and S respectively, and apply all the results of § 2.

§ 7. Maxwell's method for comparing two inductances gives a continuous balance, as would be expected, from the symmetry of the arrangement. Just as in § 2, we may



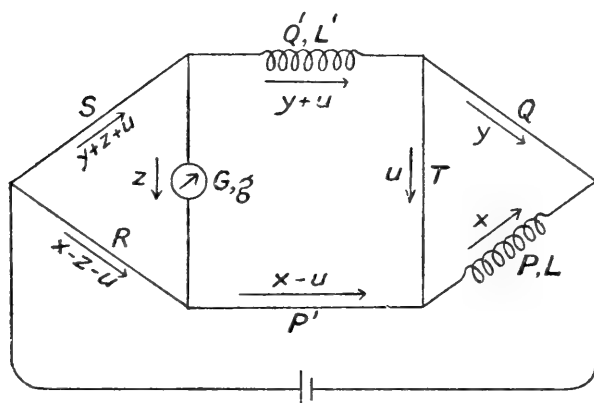
show that short-circuiting isolates the action of the respective halves; L discharges through P and R , L' through Q and S , the two time-constants $\frac{L}{P+R}$ and $\frac{L'}{Q+S}$ being equal.

§ 8. Niven, avoiding the double adjustment, sacrifices the continuous balance again. The equations at short-circuiting the battery include the following :—

$$Rx - Sy - (gD + G + R + S)z - (R + S)u = 0 ;$$

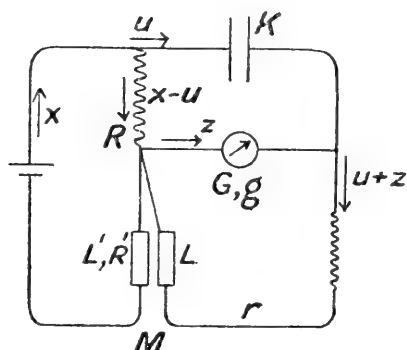
and as initially

$$\dot{x}=f, \quad \dot{y}=\frac{P}{Q}f, \quad \dot{z}=0, \quad \text{and} \quad u=\frac{P+P'+R}{T+P'+R}f,$$



it follows that \ddot{z} does not vanish, and therefore as in § 3 there are at least two successive flows through the galvanometer.

§ 9. In Carey Foster's comparison of mutual inductance with capacity a continuous balance would hardly be expected,



owing to the complex nature of the arrangement. The equations at short-circuiting are :—

$$(L'D + R + R')x - MDz - (MD + R)u - L'f = 0,$$

$$RDx + (gD^2 + GD)z - \left(RD + \frac{1}{K}\right)u - Rf = 0,$$

$$MDx - \{(L + g)D + G + r\}z - (LD + r)u - Mf = 0.$$

Initially $\dot{x}=f$, $\dot{z}=\dot{u}=0$,

$$\therefore \ddot{x} = -\frac{L(R+R')}{LL'-M^2}f, \quad \ddot{z}=0, \quad \ddot{u} = -\frac{M(R+R')}{LL'-M^2}f,$$

and the third derivative of z is $\frac{R(L-M)(R+R')}{LL'-M^2}f$; in general this is not zero. The determinant

$$\begin{vmatrix} L'D+R+R' & -MD & -(MD+R) \\ RD & gD^2+GD & -(RD+1/K) \\ MD & -(L+g)D-(G+r) & -(LD+r) \end{vmatrix}$$

is a quartic in D , and in general does not factorize even when $M=KRr$; calling its roots $\alpha, \beta, \gamma, \delta$, we may write

$$x = a_1 e^{\alpha t} + a_2 e^{\beta t} + a_3 e^{\gamma t} + a_4 e^{\delta t} + \frac{L'-KR^2}{R+R'}f;$$

in u and z we shall have b 's and c 's for the a 's, and the constants will be $-KRf$ and zero. To find the c 's, we have

$$c_1 + c_2 + c_3 + c_4 = 0, \quad c_1\alpha + c_2\beta + c_3\gamma + c_4\delta = 0,$$

$$c_1\alpha^2 + c_2\beta^2 + c_3\gamma^2 + c_4\delta^2 = 0,$$

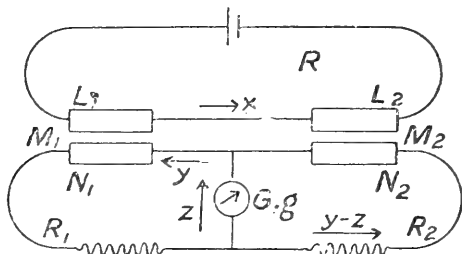
and

$$c_1\alpha^3 + c_2\beta^3 + c_3\gamma^3 + c_4\delta^3 = \frac{R(L-M)(R+R')}{LL'-M^2}f,$$

so that the c 's all vanish and the balance is a continuous one when $L=M$. In this special case the quartic yields two factors, viz. $MgD^2 + (MG + MR + gR)D + R(G+r)$ and $M(L'-M)D^2 + (L'r + MR')D + r(R+R')$. If α and β are the roots of the first equation, and γ and δ those of the second equation corresponding to these factors, I have no doubt that just as in § 2 the coefficients a_1, a_2, b_1, b_2 should be zero, because G and g can play no real part in determining the flow, since no current crosses by G ; but I have not succeeded in verifying this. It is interesting to notice that if, with $L=M$, we adjust the balance $M=KRr$ in such a way that $R=r=\sqrt{M/K}$, the two quadratics break up into linear factors, viz. $MD+R$ and $gD+G+r$ in the first case, $MD+r$ and $(L'-M)D+R+R'$ in the second. The time-constants involved, viz. $\frac{M}{R}$, $\frac{L'-M}{R+R'}$, and $\frac{g}{G+r}$, are respectively those of L (or K) discharging through r (or R), L' through $R+R'$, and G through $G+r$; the actual value of

x is $\frac{L' - M}{R + R'} f (1 - e^{\delta t})$, where $\delta = -\frac{R + R'}{L' - M}$; that of u is complicated and devoid of interest.

§ 10. The comparison of two M 's by Maxwell's method is.



the example quoted in Lord Rayleigh's report. The short-circuit equations are:—

$$\{(L_1 + L_2)D + R\}x - (M_1 + M_2)Dy + M_2Dz - (L_1 + L_2)f = 0,$$

$$M_1Dx - (N_1D + R_1)y - (gD + G)z - M_1f = 0,$$

$$M_2Dx - (N_2D + R_2)y + \{(N_2 + g)D + (G + R_2)\}z - M_2f = 0.$$

Initially $\dot{x} = f$, $\dot{y} = \dot{z} = 0$; the initial values of \ddot{x} , \ddot{y} , \ddot{z} are found by multiplying $\frac{Rf}{\Delta}$ respectively by

$$N_1N_2 + g(N_1 + N_2), M_1N_2 + g(M_1 + M_2), \text{ and } M_1N_2 - M_2N_1,$$

where Δ stands for

$$\begin{vmatrix} L_1 + L_2 & M_1 + M_2 & M_2 \\ M_1 & N_1 & -g \\ M_2 & N_2 & N_2 + g \end{vmatrix},$$

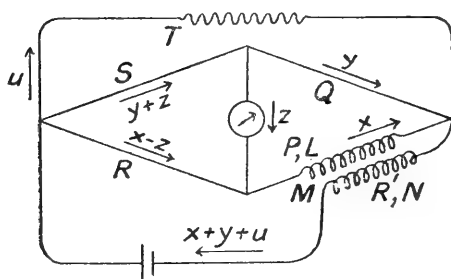
As the equation in D is only a cubic, it will suffice for the vanishing of c_1 , c_2 , c_3 in z that the initial values of z , \dot{z} , and

\ddot{z} should vanish, i. e. $\frac{N_1}{N_2} = \frac{M_1}{M_2}$; further, the condition for

the aggregate balance is $\frac{M_1}{M_2} = \frac{R_1}{R_2}$; these two conditions suffice,

then, for a continuous balance. The cubic then breaks up into $\{(M_1 + M_2)g + M_1N_2\}D + (M_1 + M_2)G + M_1R_2$, and a quadratic factor free from G and g , but involving the other constants.

§ 11. Maxwell's method of comparing the M of two coils with the L of one of them is not always practicable, but



when it is, the balance is continuous. The four equations are:—

$$\begin{aligned}
 & (L-2M+N)(\dot{x}-f) + (N-M)\left(\dot{y}-\frac{P}{Q}f\right) \\
 & + (N-M)\left(\dot{u}-\frac{P+R}{T}f\right) + (P+R+R')x + R'y - Rz + R'u = 0, \\
 & (L-M)(\dot{x}-f) - M\left(\dot{y}-\frac{P}{Q}f\right) - M\left(\dot{u}-\frac{P+R}{T}f\right) \\
 & \quad + g\dot{z} + Px - Qy + Gz = 0, \\
 & (Q+S)y + Sz - Tu = 0, \quad g\dot{z} - Rx + Sy + (G+R+S)z = 0.
 \end{aligned}$$

The initial values are

$$\dot{x}=f, \quad \dot{y}=\frac{P}{Q}f, \quad \dot{u}=\frac{P+R}{T}f, \quad \dot{z}=\ddot{z}=0,$$

so that c_1, c_2, c_3 vanish provided the conditions for aggregate balance are fulfilled, viz.

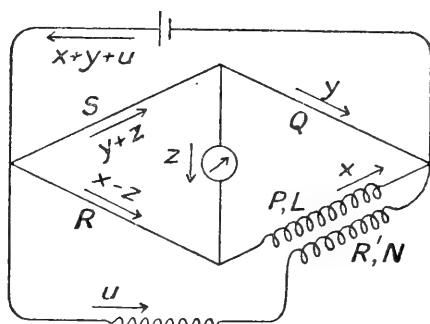
$$PS=QR \quad \text{and} \quad \frac{L}{M} = \frac{P+Q}{Q} + \frac{P+R}{T}.$$

Under these circumstances the cubic yields the factor

$$\frac{L}{M}(ND+R')-MD+P+R;$$

g and G occur only in the other (quadratic) factor; and as in previous examples, the expressions for x, y , and u contain only a single exponential.

§ 12. Brillouin's device for meeting the difficulty in § 11 that M has to be less than L is to put the second coil in the



same branch as T , but this makes a continuous balance impossible. The equations at short-circuiting are:—

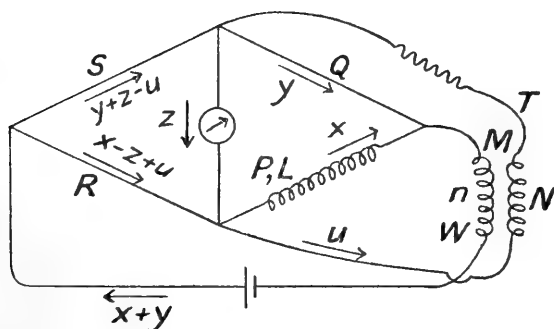
$$L(\ddot{x}-f) + (P+R)x - Rz - M\left(\dot{u} - \frac{P+R}{R'}f\right) = 0,$$

$$(Q+S)y + Sz = 0, \quad Rx - Sy - g\ddot{z} - (G+R+S)z = 0,$$

$$M\ddot{x} - N\ddot{u} - R'u = 0.$$

Initially $\dot{x}=f$, $\dot{y}=0$, $\dot{z}=0$, $\dot{u} = \frac{P+R}{R'}f$, and $\ddot{z} = \frac{Rf}{g}$, so that the c 's cannot vanish.

§ 13. By a method due to Niven the M of two coils is sometimes compared with the inductance of a third, L ,



placed in a balanced quadrilateral. Taking N for the inductance of that one of the pair which is joined in parallel with the galvanometer, and n for the inductance of the one in the battery arm, and the other symbols being as shown,

we have upon short-circuiting :—

$$\begin{aligned}
 (L+n)(\dot{x}-f) + (P+R+W)x + n\left(\dot{y}-\frac{P}{Q}f\right) \\
 + Wy - Rz - M\dot{u} + Ru = 0, \\
 L(\dot{x}-f) + (P+R)x - (Q+S)y - (R+S)z + (R+S)u = 0, \\
 Rx - Sy - g\dot{z} - (G+R+S)z + (R+S)u = 0, \\
 M(\dot{x}-f) - Rx + M\left(\dot{y}-\frac{P}{Q}f\right) + Sy + (R+S)z \\
 - N\dot{u} - (R+S+T)u = 0.
 \end{aligned}$$

The determinant for the various periods is here a quartic in D , so that the c 's will not vanish unless the initial values of \ddot{z} , \dot{z} , z , and \ddot{u} are all zero. Of course x , y , z , and u are initially zero ;

$$\dot{x}=f, \quad \dot{y}=\frac{P}{Q}f, \quad \dot{z}=0, \quad \dot{u}=0 ;$$

$$\ddot{x}=0, \quad \ddot{z}=0, \quad \ddot{y}=\frac{N}{M^2-Nn}\left(P+R+W\cdot\frac{P+Q}{Q}\right)f, \quad \ddot{u}=\frac{M}{N}\ddot{y} ;$$

finally, $g\ddot{z}=(R+S)\ddot{u}-S\ddot{y}$, which in general is not zero, so that as a rule the balance is not continuous. But if, in addition to fulfilling the conditions for aggregate balance, viz. $PS=QR$ and $\frac{L}{M}=\frac{(P+Q)^2}{QT}$, we can also satisfy the

condition $\frac{N}{M}=\frac{P+Q}{Q}$ by backing up the coil N with some extra self-inductance remote from the coil n , \ddot{z} then vanishes, and the balance becomes a continuous one ; and, as must invariably happen in such cases, the determinant factorizes. Its factors are

$$\begin{aligned}
 \frac{L}{N}(ND+T)(nD+W) - \frac{LMD}{N}(MD-P-Q-R) + P(Q+S) \\
 \text{and} \quad (gD+G)\left(ND+R+S+T+\frac{RT}{P}\right) + (ND+T)(R+S) ;
 \end{aligned}$$

the latter quadratic represents two exponentials of which the coefficients are zero in x , y , and u , so that these quantities really consist of only two exponentials, corresponding to the other quadratic.

§ 14. To sum up this discussion, we may notice that in five of the twelve methods considered (§§ 2, 5, 6, 7, 11) a continuous balance is of necessity attained, if a balance is attained at all ; in four (§§ 3, 4, 8, 12) such a balance

cannot possibly occur; and in only three (§§ 9, 10, 13) is the continuous balance dependent upon conditions. Moreover, in these three cases it can only be realized by introducing a double adjustment, a thing which is usually regarded as fatal to the practical utility of any method. The advice to "fulfil the condition for a continuous balance when such a condition exists" may well be supplemented by further advice to choose a method (when possible) in which no special condition need be fulfilled (§§ 5, 6, 11).

§ 15. It only remains to discuss numerically a case in which the balance is merely aggregate. The measurement in § 3 will be selected, and the figures given closely resemble those obtained in an actual laboratory test. Assume $P=220$ ohms, $Q=440$, $R=500$, $S=1000$, $G=1500$, $s=200$; $K=2\frac{1}{2}$ mfd.; $L=0.022$ henry, $g=0.1$. In the equation $z=c_1e^{\alpha t}+c_2e^{\beta t}+c_3e^{\gamma t}$ we first determine α, β, γ as the roots of the cubic in D , viz. $\alpha=-2352.7$ sec.⁻¹, $\beta=-16005.9$, $\gamma=-39530.7$. We next obtain c_1, c_2, c_3 from the equations

$$c_1 + c_2 + c_3 = 0, \quad c_1\alpha + c_2\beta + c_3\gamma = 0,$$

$$c_1\alpha^2 + c_2\beta^2 + c_3\gamma^2 = \frac{(P+R)(S-s)}{g(Q+S-s)} f = \frac{144000}{31} f;$$

the result is

$$\log\left(\frac{c_1}{f}\right) = \bar{6}.96148, \quad \log\left(-\frac{c_2}{f}\right) = \bar{5}.16024, \quad \log\left(\frac{c_3}{f}\right) = \bar{6}.72519.$$

The current

$$z = c_1\alpha e^{\alpha t} + c_2\beta e^{\beta t} + c_3\gamma e^{\gamma t}, \quad \text{and} \quad \log\left(-\frac{c_1\alpha}{f}\right) = \bar{2}.33304,$$

$$\log\left(\frac{c_2\beta}{f}\right) = \bar{1}.36452, \quad \log\left(-\frac{c_3\gamma}{f}\right) = \bar{1}.32212.$$

We can then easily show that the current in the galvanometer is zero (and then reversed) after 1.728×10^{-4} sec., and that in this time the flow is 5.19×10^{-6} coulomb. At the end of 10^{-3} sec. this has been reduced to 0.87×10^{-6} , and after 10^{-2} sec. the aggregate flow (in the direction of the arrow in the figure of § 2) is only 5.5×10^{-16} . We have here rather exaggerated the inductance of the galvanometer; if we take $\frac{1}{100}$ henry instead of $\frac{1}{10}$, we have

$$\alpha = -2349.3, \quad \beta = -27076.8, \quad \gamma = -234011;$$

$$\log\left(\frac{c_1}{f}\right) = \bar{7}.90897, \quad \log\left(-\frac{c_2}{f}\right) = \bar{7}.95799,$$

$$\log\left(\frac{c_3}{f}\right) = \bar{8}.98631;$$

and the flow after 10^{-3} sec. is only 0.77×10^{-6} , instead of 0.87×10^{-6} . Thus if the galvanometer is one which gives a throw of 200 mm. per micro-coulomb, with a period of 15 secs., we may say that after so short a time as $\frac{1}{1500}$ of the period all unsteadiness of the currents has sensibly vanished. The conclusion seems to be that far too much has been made of the importance of a continuous balance, and that unsteadiness of the needle must be otherwise explained. In cases where an ordinary condenser is employed, an ample explanation is provided by the phenomena often referred to as "residual charge." In experiments where an air-condenser (or no condenser at all) is used, there is still something analogous to the ordinary condenser. It is certain that the capacity of the connecting wires is not always as thoroughly negligible as is usually assumed, especially when twisted leads are employed; and it seems not impossible that these may in some instances play a similar part in preventing the operator from securing a satisfactory balance.

LVII. *The Pulse Theory of X Rays, γ Rays, and Photoelectric Rays, and the Asymmetric Emission of β Rays.* By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield*.

IT is well known that when a beam of X rays or ultra-violet rays falls upon a thin sheet of metal, the values for the number and velocity of the β rays produced are greater for the emergence β rays than for the incidence ones. The explanation of this fact on the wave theory is generally considered to be attended by difficulties so serious as to necessitate the abandonment of the pulse theory in favour of a corpuscular hypothesis. Practically the same arguments which support the corpuscular theory for X rays also support it for ultra-violet light, so that if we abandon the wave theory for one, we are almost forced to abandon it for the other. In the following paper I have endeavoured to show to what extent the want of symmetry in the expulsion of β rays may be reconciled with the pulse theory, and also to discuss certain other points concerned with the properties of X rays, &c.

There are two views which we may take as to the origin of the β rays which an electromagnetic train releases. They may come from those free electrons which exist between the molecules of the metal, or they may be torn out of the atoms.

* Communicated by the Author.

There is an important difference between the two views. The second is the one which leads to the most satisfactory explanation of the phenomena observed, but as the first view presents some interesting features, and as it is the simpler of the two, I shall commence by discussing it. I shall, when possible, relegate to an appendix mathematical matter which, though necessary, may nevertheless be omitted in following the general trend of the arguments.

(1) *Action of a wave-train on the free electrons.*—When a beam of electromagnetic waves, travelling along the axis of x , encounters a free electron, the motion which the train produces is generally treated as being wholly transverse to the direction of the beam. This is, however, not quite true. The magnetic field of the electromagnetic train acts on the moving electron with a force parallel to the line of motion of the beam, and, in the case of a free electron, this force is such that the total velocity which it has produced since it started to act is always in the direction of the advancing wave, so that the electron will move in the direction of the wave as well as in the transverse direction, as will be seen from the following discussion.

We shall suppose our electromagnetic train to be of some finite length which it will not be necessary for us to specify. The electron shall be situated initially at $x=0$. $X Y Z$, $\alpha \beta \gamma$ shall refer to the electric and magnetic forces respectively, all expressed in electromagnetic units, and we shall mathematically specify our wave as follows:—

$$\text{For } t < 0 \text{ and } x > 0 \dots, \quad X=Y=Z=\alpha=\beta=\gamma=0. \quad . \quad (1)$$

$$\text{For } t > 0 \text{ and } ct > x > 0 \dots, \quad X=0, \quad Y=Y_0\phi(ct-x), \quad Z=0. \quad (2)$$

$\phi(ct-x)$ being an arbitrary function of $ct-x$. Such a function satisfies the electromagnetic equations, which are of the type

$$\frac{1}{c^2} \frac{\partial X}{\partial t} = \frac{\partial \gamma}{\partial y} - \frac{\partial \beta}{\partial z}, \quad -\frac{\partial \alpha}{\partial t} = \frac{\partial Z}{\partial y} - \frac{\partial Y}{\partial z}, \text{ etc.,} \quad . \quad (3)$$

and corresponds to a wave travelling in the positive direction along the x axis with the velocity c , which represents the velocity of light. It may readily be verified from the electromagnetic equations that the values of $\alpha \beta \gamma$, corresponding to the above values of $X Y Z$, are

$$\alpha \beta \gamma = 0.0. \frac{Y_0}{c} \phi(ct-x). \quad . \quad . \quad . \quad (4)$$

(1), (2), and (4) satisfy the condition that XYZ , $\alpha\beta\gamma$ are continuous on the two sides of the advancing wave-front, provided that $\phi(0)=0$, a condition which would be satisfied by a sine function, for example.

The equations of motion of our electron, neglecting damping (see Appendix, problem 1), are

$$\frac{m}{e} \frac{d^2 y}{dt^2} = Y_0 \phi(ct-x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{m}{e} \frac{d^2 x}{dt^2} = X + \gamma \frac{dy}{dt} = \frac{Y_0}{c} \cdot \frac{dy}{dt} \phi(ct-x). \quad . \quad . \quad (6)$$

By eliminating $\phi(ct-x)$ between (5) and (6) we obtain

$$\frac{1}{c} \frac{dy}{dt} \cdot \frac{d^2 y}{dt^2} = \frac{d^2 x}{dt^2},$$

which we can integrate to the form

$$\frac{dx}{dt} - q_1 = \frac{1}{2c} \left\{ \left(\frac{dy}{dt} \right)^2 - q_2^2 \right\}, \quad . \quad . \quad . \quad . \quad (7)$$

q_1 and q_2 being the values of \dot{x} and \dot{y} just before the train strikes the electron. If the electron is at rest at $t=0$ so that $\dot{x} = \frac{1}{2c} \dot{y}^2$, we see that \dot{x} must always be positive.

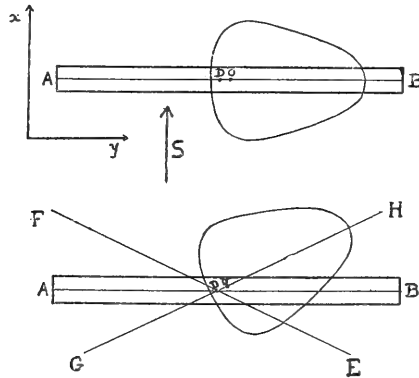
This method of viewing the matter seems more direct than one which involves considerations of the pressure of radiation, which are always a little vague when applied to an electron.

We may suppose that before the electron was hit by the train it was travelling with too small a speed to enable it to leave the metal. If the velocity which it receives from the pulse, however, is sufficiently great it will be able to get away. Except for extremely large values of \dot{y} , \dot{x} is of course only a small fraction of \dot{y} ; so that if the beam of waves is travelling normally on to a metal plate, the electrons will start off practically parallel to the surfaces. It will only be by swinging round some of the atoms that an electron will be able to get out; and when it does so, the main part of its velocity will be controlled by the \dot{y} part. The existence of the velocity \dot{x} destroys the symmetry on the two sides of the plate in a way which may perhaps best be discussed as follows:—

First, we notice that q_1 and q_2 , which correspond to velocities comparable with those of temperature agitation, are so small compared with the velocities of the β rays produced

by X rays that we may neglect them, though it would not complicate matters much if we did not. Neglecting q_1 and q_2 , however, we have $\dot{x}/\dot{y} = \dot{y}/2c$. If we consider the case of the β rays ejected by X rays, which have a velocity of the order 6×10^9 cm./sec., we see that for these rays $\dot{x}/\dot{y} = 1/10$. Now suppose that a metallic film with its plane perpendicular to the plane of the paper is represented in section by AB (fig. 1), the train of waves being incident in

Fig. 1.



the direction of the arrow S. If \dot{x} were zero the rays would start out in all directions parallel to the plane AB, if the train were unpolarized, or in two opposite directions if it were plane polarized. Consider an electron which at D receives a velocity \dot{y} in the positive direction of y . Its chances of deflexion in any direction by the first atom O which it meets may be represented in the valuable manner suggested by Professor Bragg, by the radius vector of an egg-shaped surface, the radius vector being drawn from the point O. This oval would obviously be symmetrical about the plane AB, so there would be symmetry with respect to this plane in the number and velocities of the β rays escaping on the two sides of the film. If \dot{x} is not zero, however, the deflexion oval will be symmetrical, not about the line AB, but about a line GH or EF, according as \dot{y} is positive or negative, the inclination θ of these lines to AB being such that $\tan \theta = \dot{x}/\dot{y}$. If dn is the number of electrons sent off from an element ds at D per second in the direction DH, the fraction of these which are deflected within a given solid angle $d\Omega$ measured from O will be proportional to $r d\Omega$, where r is the radius vector corresponding to $d\Omega$, and consequently the number passing through the plane through O parallel to AB (which is practically the same as the plane AB) in the forward direction is to the number passing

through in the backward direction as $\int rd\Omega$ for the portion of the egg-shaped surface in front of AB is to $\int rd\Omega$ for the portion behind AB. The same conclusion would obviously apply if the waves were not polarized, so that the electrons started off in several different directions. We must remark that by as much as the number of β rays sent forward is increased by the existence of \dot{x} by so much is the number sent backward decreased, so that although we cannot without knowledge of the shape of the deflexion oval, and of the coefficient of absorption for the rays, calculate the exact want of symmetry produced, it is obvious that the value $\dot{x}/\dot{y}=1/10$ is of an order of magnitude sufficient to account for the want of symmetry observed both in number and velocity, at any rate in certain cases of β rays ejected by X rays*. A casual glance at the deflexion oval would make it appear that we might expect a large number of β rays to be emitted in directions such as DH inclined at a considerable angle to the normal to the film; but we must remember that those which move to any extent parallel to the surface of the film have a much smaller chance of getting out than those which are deflected normally to the film. We have thus seen that, provided that the train of waves can give an electron a velocity of the order 6×10^9 , this velocity will automatically carry with it a want of symmetry in the number and velocity of the right order for β rays; but we must now inquire what order of magnitude the field in the wave must have in order to account for such velocities. It will be convenient to assume $\phi(ct-x)$ to be of the form $\sin \frac{2\pi}{\lambda}(ct-x)$, and to determine the motion of the electron.

A solution of (5) and (6) with $\sin \frac{2\pi}{\lambda}(ct-x)$ written for $\phi(ct-x)$ is (see Appendix, problem 2) to the degree of accuracy to which we require it:

$$\frac{dx}{dt} = \frac{1}{2c} \left(\frac{Y_0 e \lambda}{cm\pi} \right)^2 \sin^4 \frac{\pi c}{\lambda} t, \quad . \quad . \quad . \quad (8)$$

$$\frac{dy}{dt} = \frac{Y_0 e \lambda}{cm\pi} \sin^2 \frac{\pi c}{\lambda} t. \quad . \quad . \quad . \quad (9)$$

We thus see that \dot{x} and \dot{y} are always positive.

If we imagine the wave-train to end with XYZ, $\alpha\beta\gamma$

* On considering probable shapes of the deflexion oval it will be seen that a value of \dot{x}/\dot{y} equal to 0.1 will account for much more than a 10 per cent. want of symmetry in the numbers of electrons ejected.

all zero, which is equivalent to supposing it to contain a whole number of half waves, as it must do if the conditions of continuity at the front and rear of the wave-train are to be satisfied, we see that after the train has passed, \dot{x} and \dot{y} have either their maximum values or zero values, according as the number of half wave-lengths in the train is odd or even. The maximum values of \dot{x} and \dot{y} are consequently the only values with which we have to deal. They are:

$$\dot{x} = \frac{1}{2c} \left(\frac{Y_0 e \lambda}{cm\pi} \right)^2 \quad \cdot = \frac{Y_0 e \lambda}{cm\pi} \quad \dots \quad (10)$$

If we prefer to consider a damped train of waves, ending with zero amplitude, as is done in the Appendix (problem 3), rather than a train ending with finite amplitude, the only difference which is introduced is that the velocities have the above values, except for an extra factor in the denominator of \dot{y} , which becomes squared in the denominator of \dot{x} , and which for cases of very great damping results in \dot{y} being proportional to the frequency of the waves (see Appendix, problem 3).

Taking the case of X rays, for which we shall assume

$\dot{y} = 6 \times 10^9$ and $\lambda = 5 \times 10^{-9}$ cm., since $\frac{e}{m} = 1.8 \times 10^7$ we have

$Y_0/c = 2 \times 10^{11}$. The average electric energy per c.c. of the wave is $Y_0^2/16\pi c^2 = 8 \times 10^{20}$, and the total energy per c.c. is 16×10^{20} ergs per c.c.

It must be noticed that we have been compelled, on the present theory, to assume this enormous energy density, not merely to account for the want of symmetry, but to account for the main part of the electron's velocity. A field which will give a velocity of 6×10^9 cm./sec. automatically carries with it a want of symmetry of the order we have discussed. We can form an idea as to the possibility or absurdity of the existence of this enormous energy density by calculating the dimensions of a pulse which would contain energy of this density, and which would contain a certain total assigned amount of energy. Using (10) in conjunction with the expression for the energy per c.c., we can readily show that

$y^2 = \frac{8E\lambda^2 e^2}{la\pi m^2}$, where E is the total energy of the pulse, l the

length, and a the cross-sectional area, so that, for example, if we take l as $\lambda/2$ and E as the amount of energy in the Planck unit, *i. e.* $6.5 \times 10^{-27} c/\lambda$ erg, we find $a = 10^{-20}$, so that the diameter of the pulse would be about 10^{-10} cm., or

about one-hundredth of the diameter of an atom*. The energy in the Planck unit for $\lambda = 5 \times 10^{-9}$ cm. amounts to 4×10^{-8} erg, and that of the electron is about 2×10^{-8} , so that the electron will take about half the energy of the pulse.

If we were to imagine a pulse containing a much larger amount of energy but of the same energy density—*i. e.*, a pulse of greater diameter—the same actual amount of energy would be absorbed by the electron, but this energy would then only be a small fraction of the total amount. The real gain in concentrating the energy in a narrow beam is that we then get an appreciable fraction of it absorbed by the electron. This fact is not as obvious as it may at first sight appear, and its reason, as we see, is more deep-seated than can be explained by an attempt to account for it by considerations of the relative widths of the pulse and of the electron.

There is another method in which we may increase the fraction of the energy which is absorbed from the wave-trains without increasing the energy density so much by narrowing the pulses—*viz.*, by splitting the pulses up into a large number carrying altogether the same total amount of energy, but following each other more or less at random, with the restriction that at the advancing wave-front $\frac{\partial Y}{\partial x}$

is of the same sign for each pulse. Each of the pulses in passing over the electron communicates an amount of momentum in the y direction, of which the velocity factor is equal either to zero or to $\frac{Y_0 e \lambda}{cm\pi}$, according as the number of

half wave-lengths is even or odd. The average velocity given during the passage of s pulses is thus $\frac{s Y_0 e \lambda}{2cm\pi}$ †. It

may be noted that this expression is true even if the pulses follow each other so rapidly that they overlap, since it is easy to see that (neglecting the movement of the electron in the x direction during the passage of a single pulse) we may look upon each pulse as producing its own contribution to the y momentum of the electron, independently of the others.

* If we calculate the distance the electron travels in the y direction by the time \dot{y} attains its maximum, we shall find it to be 2.5×10^{-10} cm., which is rather greater than the width of the pulse: but to overcome this difficulty it is only necessary to take a rather different value of λ , or to assume that the pulse contains more than a single Planck unit.

† Similar remarks with regard to damped trains apply as in the last problem.

Thus to produce a given value of \dot{y} it is necessary to have $\frac{Y_0}{c} = \frac{2m\pi}{se\lambda} \dot{y}$, i. e. only $\frac{2}{s}$ of the value which was necessary in the case of the single pulse. Truly there are s pulses, but since the energy-density is proportional to $\left(\frac{Y_0}{c}\right)^2$ the energy in the s pulses is much less than in the single pulse, provided that the pulses do not overlap, and this is not an effect which could be brought about by simply adding the pulses end on end and looking upon them as one long pulse, for, in the first place, they would not join up into a continuous pulse, since, if there are an odd number of half wave-lengths in each, the value of $\frac{\partial Y}{\partial x}$ at the tail of one pulse would be opposite in sign to the value at the head of the next; and, in the second place, we see from (9) that the electron attains its maximum velocity during the passage of the first half-wave.

The value of the energy-density in the pulses is $\frac{\pi m^2 \dot{y}^2}{2s^2 e^2 \lambda^2}$. If $\frac{\lambda}{2}$ is the length of each pulse and a the cross-sectional area, and if the total energy in the s pulses is equal to E , we have $a = \frac{16\lambda E s e^2}{\pi \dot{y}^2 m^2}$. It will be obvious that if we imagine a sufficiently large number of pulses containing a total amount of energy E , it is possible to make a as large as we please. It is even possible to make it so large that the pulse expands into a hemisphere about the origin. As to the magnitude which ought to be assigned to s and E in the present theory, there is little to guide us, unless we make some special assumption as to the mode of origin of the X rays, such, for example, as the assumption that in the original discharge-tube each electron on striking the anode suffers a number of separate retardations, the effect of all the electrons suffering these retardations at slightly different times being to produce a series of pulses of the kind we have imagined. If in the discharge-tube the electrons strike the anode not absolutely continuously, but in little splashes, each splash containing a large number of electrons, the result will be that the pulses will come off in groups, the members of each group following each other very closely, but the separate groups being more or less widely separated. If there are r such groups per second, each containing s pulses of wave-length 5×10^{-9} , and if the

whole X-ray tube emits about 10^5 ergs per second*, in order that a shall correspond to the area of a hemisphere of say 20 cm. radius, we must, if $\dot{y} = 6 \times 10^9$ have $\frac{s}{r} = 10^{10}$. The number r might possibly, though not necessarily, be associated with the frequency of oscillation in the discharge-tube, so that if it is of the order 100 we have $s = 10^{12}$. The s pulses would take at least 10^{-7} second to pass an electron, and this of course introduces the difficulty that during this time the electron would suffer many collisions, and even if this were not so, it would travel several metres while the pulses were passing over it.

Of course, the above is extremely speculative, and my object in bringing it forward is not to suggest it as a theory (indeed, I do not believe that it is the explanation of the phenomenon at all), but rather to examine what can be done in the way of explaining the origin of the β rays as arising from the free electrons between the molecules. The main points so far may thus be summarized as follows:—

(a) If the electrons are ejected by the pulses with velocities of the order 6×10^9 they will certainly show a want of symmetry, both in velocity and number, approaching the amount experimentally found.

(b) The energy required to eject the electrons with the necessary velocity seems at first sight to be enormous, or rather the energy-density appears to be enormous, so that it would appear necessary to concentrate the energy in thin filaments in order to obtain a large energy-density in places without a large total quantity. On examining the matter more closely, however, it is found that the concentration of the energy becomes no longer necessary when we imagine the radiation to take place in a large series of pulses. Under these conditions, even on the assumption of spherical pulses, the velocities produced in the electrons are quite consistent with the radiation of a reasonably small amount of energy from the X-ray bulb, but difficulties are encountered in this case owing to the movement of the electron during the comparatively long time in which it is receiving its velocity. The want of symmetry is just as pronounced as if the velocity had been produced by a single pulse, since, in the case of a free electron, no matter how \dot{y} is produced, so long as it is produced by electromagnetic waves we always have $\dot{x} = \frac{1}{2c} \dot{y}^2$. The concentration of the

* Rutherford and McClung, Phil. Trans. A. vol. cxvii. p. 25 (1901).

energy in thin filaments is introduced not so much to explain the want of symmetry and the magnitude of the velocities produced as to account for the fact that only one electron here and there appears to be affected as the rays pass through the metal, and the further equally curious fact that the velocity of the ejected electrons is independent of the distance from the source of the X rays.

Some of the main difficulties associated with the theory which attempts to explain the production of the β rays from the free electrons between the molecules are, in addition to those already mentioned :—

(a) The theory, though accounting for the necessary want of symmetry in the case of the β rays ejected by X rays, gives far too small a want of symmetry for photoelectric electrons, which travel with much smaller velocities (velocities of the order 5×10^7 cm./sec.).

(b) The theory gives no explanation of the variation for different metals in the want of symmetry in the β rays produced by X rays.

(c) It does not readily lead to an explanation of the law relating the velocity of photoelectric electrons and the frequency of the light, though there are one or two ways in which it may be made to do so—*e. g.*, the view suggested on p. 539.

A much more powerful theory evolves when we consider the ejected electrons to come, not from the free electrons, but from the electrons inside the atoms.

(2) *Action of a wave-train on the electrons in the atoms.*—We shall consider the case where a train of electromagnetic waves passes over an atom. Some of the electrons in the atom will have a natural period equal to that of the waves, and these will absorb energy rapidly from the waves. When the electron has got a sufficiently large amount of energy it will be able to get away, and we shall find that when it escapes the ratio of \dot{x} , the velocity in the direction in which the wave is moving, to \dot{y} , the velocity transverse to the direction of propagation of the wave, is no longer dependent only on \dot{y} , and other facts with regard to the relationship between the velocity of ejection, frequency, want of symmetry, &c. will evolve.

Let V_e be the potential energy of the electron. The equations of motion are :—

$$\frac{m}{e} \frac{d^2 y}{dt^2} + \frac{\partial V}{\partial y} = Y_0 \phi(ct - x), \quad . \quad . \quad . \quad . \quad (11)$$

$$\frac{m}{e} \frac{d^2 x}{dt^2} + \frac{\partial V}{\partial x} = \gamma \frac{dy}{dt} = \frac{Y_0}{c} \frac{dy}{dt} \phi(ct - x) : \quad . \quad (12)$$

from (11) and (12) we derive

$$\frac{1}{c} \left\{ \frac{dy}{dt} \cdot \frac{d^2y}{dt^2} + \frac{e}{m} \frac{\partial V}{\partial y} \cdot \frac{dy}{dt} \right\} = \frac{d^2x}{dt^2} + \frac{e}{m} \frac{\partial V}{\partial x} \quad (13)$$

We do not wish, until we are compelled to do so, to confine ourselves to a case where the restoring force is proportional to the displacement, and so we shall at first take the more general case where V is of the form $V_x + V_y$, where V_x is a function only of x and V_y is a function only of y . It will be seen that for the cases we are going to consider this assumption will be justified. (13) then integrates to

$$\frac{1}{c} \left\{ \frac{1}{2} \left(\frac{dy}{dt} \right)^2 + \frac{e}{m} V_y \right\} = \frac{dx}{dt} + \frac{e}{m} \int V_x dt, \quad (14)$$

the constant of integration being zero if we take a case where when t is zero $\dot{x} = \dot{y} = x = y = 0$.

Now suppose we imagine any atom with an electron in the position A (fig. 2). It will be obvious that a pulse moving in the direction of the arrow would have a much better chance of ejecting this electron than an electron at B, since the natural period of B's tangential motion would be much longer than that of the pulse, so that resonance could not come into play in the case of B. In the case of electrons such as A, we see that for small displacements V_x will be practically zero, or at any rate this will be so for certain arrangements of electrons in the atom, such an arrangement, for example, in which there is a positive sphere with only two electrons situated along a diameter*. In such cases we shall have

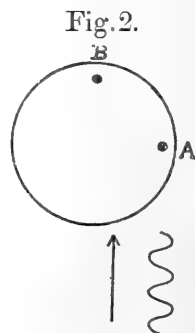


Fig. 2.

$$\dot{x} = \frac{1}{c} \left\{ \frac{1}{2} \dot{y}^2 + \frac{e}{m} V \right\}^\dagger \quad (15)$$

$\frac{1}{2} \dot{y}^2 + \frac{e}{m} V$ is $\frac{1}{m}$ times the energy E which the electron has absorbed from the wave, or practically so. If ω is the

* This is not intended to represent more than a rough picture of the phenomenon. It would perhaps be better to say that where an electron is to be found capable of free motion parallel to the x axis, for small displacements, that electron will have a better chance of being ejected than any other.

† In the Appendix (problem 4) the problem where V_x is not zero is considered.

energy which the electron must have in order to get away, directly E becomes equal to ω the electron will escape.

We may picture the electron at the beginning of its $(p-1)$ th oscillation with just too little energy to get away. At the p th oscillation it will get away carrying with it the extra amount of energy which it obtained in the p th oscillation, or rather as much of it as was left over after paying the extra little bit necessary to make the energy of the $(p-1)$ th oscillation up to the amount ω .

If u and v are the average values of \dot{x} and \dot{y} with which the electron is shot out of the atom, the value of $\frac{1}{2}v^2$ is thus of the order $\frac{1}{m}$ times the energy given to the electron in the p th oscillation, while u is $\frac{1}{c}$ times the much larger quantity representing $\frac{1}{m}$ times the total energy, kinetic and potential, given to the electron in the p oscillations. In fact, if ω is sufficiently large, u may, as we shall see, be greater than v . It may even mask v entirely so that the whole velocity of the ejected electron is in the x direction, being given by $u = \frac{\omega}{mc}$.

If we imagine that the electron absorbs one Planck unit of energy before it escapes, we shall have $\omega = 6.5 \times 10^{-27} c/\lambda$, and since $m = 10^{-27}$ we have

$$u = \frac{6.5}{\lambda} \dots \dots \dots (16)$$

If $\lambda = 2 \times 10^{-5}$ cm., as for example in the case of ultra-violet light, we find $u = 3 \times 10^5$, which is much smaller than the velocity of photoelectric electrons. We might rectify this difficulty by imagining that in the case of photoelectric electrons ω corresponds not to a single Planck unit, but to N such units, N being approximately the same for all atoms, but we shall find that for values of λ as large as 2×10^{-5} there are difficulties in the assumptions necessary to insure that u is large compared with v , and moreover in this case (16) corresponds to too great an asymmetry for photoelectric electrons, so that tempting as the formula is, in that it shows the velocity to be proportional to the frequency, I think that we can hardly reconcile ourselves to the belief that it contains the true explanation of the photoelectric effect. Perhaps after all this is no matter for great regret in view of the fact that modern measurements seem to show that the maximum velocity is not proportional to the frequency at all, but

to the square root of the frequency*, a law which we shall see can be made to follow from a slightly modified form of the above theory in which the main part of the electron's velocity exists in the y component.

Although (16) cannot be the explanation of the photo-electric effect, it is a formula to which the results should approximate for very large values of ω , and consequently very small values of λ , at any rate when we introduce a factor N to allow for the absorption of more than one Planck unit, so that it is well fitted to represent the facts for X or γ rays. Suppose, for example, we take $\lambda = 5 \times 10^{-9}$ for X rays, and N as small as unity, we find $u = 1.3 \times 10^9$, a value approaching the right magnitude, and we shall presently see that for these velocities the value of v would probably be quite insignificant, though even if it were as great as u it would not alter the order of magnitude of the velocity found.

It must be particularly remarked that our theory does not involve a unitary structure for light, nor indeed does it necessitate the introduction of the Planck unit at all. It merely involves the idea that the electron requires a definite amount of energy to set it free. The association of this amount of energy with the Planck unit is not essential.

On a view which considers that practically the whole initial velocity of the electrons set free by X rays or by γ rays takes place in the direction of the advancing wave, the difficulty becomes, not to explain the want of symmetry in the expulsion of the β rays, but the existence of any symmetry at all, to explain in fact why any rays come out against the train. The difficulty may at once be met by assuming that the β rays, though they are all originally started in the same direction, are scattered by the material of the plate; and it is a significant fact that in a substance like lead, which we know scatters β rays much more than substances of low atomic weight, a want of symmetry of only 15 per cent. is found, for the β rays ejected by γ rays, *i. e.* the scattering of the β rays is almost complete, while in a light atom like carbon the ejected β rays come out almost entirely in the direction of the emergent γ rays. It would be interesting to see whether, in the case of very thin films of substances of heavy atomic weight, there was a more prominent asymmetry than in the case of thicker films. We should expect this, since if the film is very thin the scattering will be diminished.

(3) *Case where v is not small compared with u .*—Let us now turn to a consideration of the case where the velocity with which the electrons emerge from the atom is not

* Richardson and Compton, *Phil. Mag.* xxiv. p. 575, Oct. 1912.

wholly in the x direction, but where u is only a fraction of v . We shall in this way be led to a theory more in accordance with the facts of the photoelectric effect. There are two ways in which we may proceed. We may accept as a hypothesis that the electron absorbs energy in Planck units, either because the pulses themselves carry it in these units, and are so narrow that they give up all their energy to the electron when they pass it, or because the mechanism of the atom is such that the energy becomes absorbed in units. On the other hand, we may attempt to derive the result in a manner which is perhaps more satisfying to the mind, that is to say, by considering the actual effect of the wave on the electron, in which case we are unfortunately obliged to make some assumptions with regard to the relationship between the restoring forces and the displacements.

The first method leads to a result very quickly. If N is the smallest number of whole Planck units necessary to free the electron, the quantity represented by E on p. 544 becomes

equal to $\frac{6.5cN}{\lambda m} \times 10^{-27}$. If ω is the actual amount of energy

necessary $\frac{6.5 Nc}{\lambda m} \times 10^{-27} - \omega$ will be of the order of a single

Planck unit, and we may take half this quantity as very fairly representing $\frac{1}{2}mv^2$. Thus we see that v^2 is proportional to the frequency c/λ , and is such that

$$v^2 = \frac{6.5 c}{m\lambda} \times 10^{-27} = \frac{6.5c}{\lambda}, \quad \therefore \quad \dots \quad (17)$$

so that if in (15) we put

$$\frac{1}{2}\dot{y}^2 + \frac{e}{m}V = \frac{6.5Nc}{m\lambda} \times 10^{-27} = \frac{6.5Nc}{\lambda},$$

we find

$$\dot{x} = u = \frac{6.5 N}{\lambda} \quad \text{and} \quad \frac{u}{v} = \frac{Nv}{c}. \quad \dots \quad (18)$$

Thus in the case of photoelectric effects where $\lambda =$ say 2×10^{-5} , we find $v = 10^8$, which is of the correct order of magnitude. In order to obtain a want of symmetry of the order {expressed by $\frac{u}{v} = 1/15$, which is about the correct value, it would be necessary to have $N = 20$.

Adopting the second method of procedure, in which we do not make use of the Planck unit, we must, following the usual practise in such cases, imagine the electrons to be constrained by forces proportional to the displacement; and

though we must admit that this law cannot hold right up to the point at which the electron gets free, we must imagine our actual atom replaced by a kind of hypothetical atom in which the law does hold. We shall assume a case where there is resonance between the light-waves, and the oscillations parallel to the y axis, and our equations of motion become approximately

$$\ddot{y} + 4\pi^2 n^2 y = \frac{Y_0 e}{m} \sin 2\pi n t, \quad . \quad . \quad . \quad (19)$$

leading to

$$\ddot{x} + 4\pi^2 \mu^2 x = \frac{Y_0 e}{mc} \dot{y} \sin 2\pi n t, \quad . \quad . \quad . \quad (20)$$

$$\frac{1}{c} \left\{ \frac{1}{2} \dot{y}^2 + 2\pi^2 n^2 y^2 \right\} = \dot{x} + 4\pi^2 \int \mu^2 x dt, \quad . \quad . \quad (21)$$

n and μ being the natural frequencies of the electron parallel to the y and x axes respectively.

We have already, on p. 544, given reasons for supposing that for the cases in which we are concerned μ is small. In the Appendix (problem 4) we shall consider the case where μ is not absolutely zero, *i. e.* where the electrons are not entirely free along the x axis, an assumption which leads to a theory very similar to that given below, in which we take the simpler case where μ is zero.

The solution of (19) subject to $y = \dot{y} = \ddot{y} = 0$, when $t = 0$, is

$$y = \frac{Y_0 e}{4\pi m n} \left\{ \frac{1}{2\pi n} \sin 2\pi n t - t \cos 2\pi n t \right\}, \quad . \quad (22)$$

giving

$$\dot{y} = \frac{Y_0 e}{2m} t \sin 2\pi n t. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Unless p is as small as one or two, at the p th maximum (measured in the positive direction only) the value of \dot{y} is very approximately

$$(\dot{y})_p = \left(\frac{p + 0.25}{n} \right) \frac{Y_0 e}{2m} = \frac{1}{2} \frac{p}{n} \frac{Y_0 e}{m} \text{ approximately.}$$

If ω is the minimum energy which the electron must have in order to get away, the first integer p which makes

$$\frac{1}{4} \frac{p^2}{n^2} \left(\frac{Y_0 e}{m} \right)^2 > \frac{2\omega}{m}$$

will result in the electron becoming free. If at the $(p-1)$ th maximum the electron has nearly enough energy to escape, it will after the p th maximum get away with practically the

whole of the energy given to it in the p th oscillation. Its velocity \dot{y}_1 will be such that

$$\frac{1}{2}m\dot{y}_1^2 = \frac{1}{2}m\{p^2 - (p-1)^2\} \left(\frac{Y_0e}{2mn}\right)^2 \text{ is } \dot{y}_1^2 = \frac{(2p-1)}{4} \left(\frac{Y_0e}{mn}\right)^2. \quad (24)$$

On the other hand, if at the p th maximum the electron has only barely enough energy to escape, it will just succeed in crawling away with practically zero velocity. The average value of the velocity with which the electron escapes will thus be of an order given by

$$v^2 = \frac{(2p-1)}{8} \left(\frac{Y_0e}{mn}\right)^2 \quad (25)$$

From (20) we have

$$\ddot{x} = \frac{1}{2c} \left(\frac{Y_0e}{m}\right)^2 t \sin^2 2\pi nt,$$

leading on integration between the limits zero and t to

$$\dot{x} = \frac{1}{8c} \left(\frac{Y_0e}{m}\right)^2 \left\{ t^2 - \frac{t}{2\pi n} \sin 4\pi nt + \frac{1}{4\pi^2 n^2} \sin^2 2\pi nt \right\}.$$

After a few oscillations the first term becomes all important, and at the p th maximum of \dot{y} we have

$$u = (\dot{x})_p = \frac{(p+0.25)^2}{8c} \left(\frac{Y_0e}{mn}\right)^2 = \frac{p^2}{8c} \left(\frac{Y_0e}{mn}\right)^2 \text{ approximately.} \quad (26)$$

Thus from (25) and (26)

$$\frac{u}{v} = \frac{p}{2c} v. \quad (27)$$

The energy E which has been absorbed is approximately the energy which the electron has absorbed in the p oscillations, *i. e.* the kinetic energy of the electron at its p th maximum is

$$E = \frac{m}{8} \left(\frac{pY_0e}{mn}\right)^2, \quad (28)$$

so that we have from (25)

$$v^2 = \frac{2E}{mp} = \frac{2\omega}{mp} \text{ approximately.} \quad (29)$$

Suppose we take ω for a certain electron as corresponding to the energy absorbed by the ionic charge in a fall through

100 volts, we find $\omega = 10^{-10}$ erg. Taking the case of photo-electric electrons for which $v =$ say 5×10^7 , we find that the necessary value of p is 80. Using this value we find from (27) that $\frac{u}{v} = \frac{1}{15}$, which is just about of the right order of magnitude for photoelectric effects. Greater values of ω would of course correspond to greater values of $\frac{u}{v}$. It may be mentioned that for X rays where v is of the order 6×10^9 , $\frac{u}{v}$ would become equal to unity for $p = 5$, and for large values of p , u would completely mask v , as we pointed out on p. 546*.

So far in the present problem it has not been necessary to introduce the idea of the Planck unit; if, however, we do so at this stage we arrive at conclusions which though rather speculative are nevertheless interesting. Suppose we consider E the total energy which the atom absorbs before the electron is allowed to escape as equivalent to N Planck units, so that from (29) $v^2 = \frac{2hNn}{mp}$, where h is Planck's constant. If v^2 is to be proportional to the frequency n we must have p independent of n . Using (25) in conjunction with the expression for the energy per c.c., we find, if a is the cross-sectional area of the pulse, since $p\lambda a$ is the volume of the p wave-lengths,

$$v^2 = 2\pi p \lambda^2 \frac{e^2}{m^2} \frac{U}{p\lambda a} = 2\pi \lambda \frac{e^2}{m^2} \frac{U}{a}, \quad . \quad . \quad . \quad (30)$$

where U is the total energy in the p wave-lengths of the pulse.

If the diameter of the pulse is to be such that the whole of the energy of the p wave-lengths is to be absorbed, we must have $E = U$. As a matter of fact, since the energy absorbed per oscillation is proportional to the number of the oscillations, in order that the p th wave-length shall have enough energy we must have $U = 2E$, so that since from (29)

$E = \frac{mp}{2} v^2$ we find that on substituting in (30)

$$a = \frac{2\pi \lambda e^2 p}{m} . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

* Of course it is not *necessary* for the application of the theory to X rays that u should mask v .

Since p is to be independent of λ , (31) requires that a shall be proportional to λ . Taking the value of p which we have chosen in the example above, we find $a = 8.4 \times 10^{-11} \lambda$, so that for $\lambda = 2 \times 10^{-5}$ we find $a = 17 \times 10^{-16}$, corresponding to a diameter of 4×10^{-8} cm.* In the present case each electron requires about 10^{-10} erg to set it free. Even if 10^{10} electrons were emitted per second, which would correspond to a photoelectric current of 10^{-10} c.g.s. unit, the actual energy required from the source of light would be only 1 erg per second, so that if we imagine 100 ergs to be supplied from the source per second in the form of ultra-violet energy, we could afford to widen the cross-sectional area of the pulse 100 times, so that the diameter would be of the order 4×10^{-7} cm. In fact the extreme narrowness of the pulses is not necessitated so much by energy considerations as by the fact that so few electrons are liberated, though there are other ways of accounting for this, *e. g.* by considering that only a comparatively small number of atoms contain electrons of the appropriate frequencies.

It must be pointed out that since from (26) and (28)

$$u = \frac{E}{cm} \text{ independently of the value of } p, \text{ while from (29)}$$

$$v^2 = \frac{2E}{mp}, \text{ even in the case of photoelectric effects we can}$$

make u represent the whole of the velocity of the ejected electron, provided that we admit a sufficiently large value of E (a value of the order corresponding to a fall of the ionic charge through 1000 volts). It will be seen that this is so, since by taking a sufficiently large value of p , v^2 becomes reduced to insignificance. Postulating a large value of p is equivalent to assuming a small value for the energy density, as may be seen from (26); it is also equivalent to assuming a large value of a , as may be seen from (31). Indeed, if p were 10^{15} , a would be about 1 sq. cm., but the pulse would then take about a second to pass, and there are other objections to such large values of p , as may be seen from a consideration of problem 4 in the Appendix.

It is an interesting point in connexion with the pulses,

* It can be shown from (28) that in virtue of the constancy of p , Y_0^2 and consequently the energy-density is proportional to the cube of the frequency. It is interesting to notice, that if we associate hard X rays with large densities, they must correspond to high frequencies, and consequently to high velocities for the electrons emitted, with the result that there will be but little scattering. It is a significant fact that the electrons ejected by hard X rays show a much greater want of symmetry than those ejected by soft rays.

that the narrower the pulse the greater the fraction of the energy which becomes absorbed, and we have seen on p. 550 that in order that half the energy of the pulse which has passed over the electron shall be absorbed, we must have $a = \frac{2\pi\lambda e^2 p}{m}$. Provided that the pulse has a sufficiently small

diameter, the electron will take practically every bit of the energy which the pulse sends to it. It will allow none to pass until it has got enough to enable it to fly away, leaving the beheaded pulse to pass on and produce similar effects in other electrons, until eventually there is nothing of it left. We can see why it is that on this view a definite kind of X ray or photoelectric train may produce a β ray of definite velocity without that X ray being looked upon as carrying a definite total amount of energy. The question as to whether the β ray so ejected will, when it enters another atom, give rise to a pulse of the same frequency as that which liberated it, is one which it would take too long to discuss here.

It is sometimes thought that the existence of filamentary pulses is inconsistent with the electromagnetic theory. It must be pointed out, however, that no filamentary structure of the æther is necessarily implied, all that is required is that the *energy* shall travel out in streaks from the vibrating electron; and if it be objected that no electromagnetic solution corresponding to such a state of affairs can be found, we may reply that if we place a source of light at the focus of a lens, we know that the energy comes out in a parallel beam, and yet we know that if we take cognizance of all the electrons, &c. in the glass which forms the lens, the true electromagnetic solution would bring out the parallel nature of the beam. Truly there is slight spreading at the edges due to diffraction, but this effect only becomes appreciable when the beam is comparable in width with the wave-length of the light. In the case of X rays the wave-length is extremely small, and is comparable with the widths of pulses, which are so thin that they would give up practically the whole of their energy to the absorbing electrons as they passed them. The difficulties with regard to interference phenomena may to some extent be met by supposing that the energy from a single electron is radiated not along a single streak, but along several: in this way it is possible to get light from a source giving interference with its image if there are enough streaks to insure that in the case of each electron streaks come to the observer direct, and also after reflexion from the mirror. It may be pointed out that we do not require absolute parallelism in the pulses, for nobody has tested the variation

of quality of the X rays with distance over distances of more than a metre or so. Indeed, absolute parallelism would lead us into difficulties with regard to the interference of light from distant bodies like the stars, since, unless the streaks from each electron were practically infinite in number, no electron in the star would succeed in sending more than one streak to our planet at most, so that we could not get interference. The slightest spreading, however, releases us from our difficulty. In fact, all that is needed is sufficiently little spreading to account for X-ray phenomena over the distances to which they have been tested, and sufficiently great spreading to insure that when the source of light is so far from the observer that the number of streaks coming from each electron is too small to account for interference, the spreading of the streaks makes up for the difficulty.

It may be suggested that the electromagnetic solution of the problem of an accelerated electron shows that the pulses *are* spherical, but I would submit that this is not necessarily the case. If the proof of the problem be examined, it will be found that it is only in virtue of the simplicity of the assumptions with regard to the electron itself that the spherical pulse is obtained. Quite apart from this, however, it is quite conceivable that the atom in which the electron is accelerated exerts some kind of focussing action on the radiation. In fact, when we think of the atom with its spherical boundary, its electrons inside it, and possibly with its positive electricity gathered together into little nuclei which as a whole constitute the hypothetical positive sphere, the picture of our electron inside it is, in the case of such short wavelengths as those of X rays, electromagnetically not very unlike that of a source of light inside a glass globe, which to the electromagnetic eye is nothing more than conglomeration of electrons.

Summary.—(1) The action of an electromagnetic train on the free electrons in a metal is considered. The order of magnitude of the want of symmetry in the expulsion of the β rays is calculated. The question of the energy of the pulses is examined, and a method of avoiding the assumption of filamentary pulses is discussed. The main facts are summed up on p. 543.

(2) The case where the electrons are ejected from the atoms is considered. A formula is deduced which corresponds to a case where the electrons are ejected from the atom entirely in the direction in which the waves are travelling. The formula agrees with observations for X rays, the fact that some β rays come out against the wave-train

being explained as due to scattering. Although the formula shows the velocity to be proportional to the frequency, there are reasons why it should not apply for photoelectric effects.

(3) A modified form of the last theory is discussed applicable to photoelectric effects, explaining the want of symmetry &c., and becoming identical with the above theory for X rays. The theory is first developed making use of the Planck unit, and afterwards without utilizing this idea. In the Appendix (problem 4) a theory is developed which is in some respects more complete than the others. The paper concludes with some remarks on filamentary pulses, and a calculation of a possible relation between the widths of the pulses and the wave-lengths.

APPENDIX.

Problem (1). The question of damping due to radiation.

The equation of motion of an electron, allowing for radiation, is of the form

$$m\ddot{y} \left\{ 1 + \frac{2}{3} \frac{e^2}{mc\dot{y}} \cdot \ddot{y} \right\} = Ye. \quad . \quad . \quad . \quad (32)$$

Putting Y in the approximate form $Y = Y_0 \sin \frac{2\pi}{\lambda} t$ we see that approximately

$$\ddot{y} = \frac{Ye}{m}, \quad \text{and} \quad \dot{y} = -\frac{e}{m} \frac{\lambda}{2\pi c} Y_0 \cos \frac{2\pi c}{\lambda} t.$$

Hence $\frac{2}{3} \frac{e^2}{mc\dot{y}} \ddot{y}$ is of the order $\frac{4}{\lambda} \frac{e^2}{m}$. Even when λ is as small as 10^{-9} the term will only amount to 6×10^{-4} , which is insignificant compared with unity, so that damping may be neglected.

Variation of mass with the velocity may also be neglected to the degree of accuracy to which we are working, since it depends on terms of the order \dot{y}^2/c^2 .

Problem (2). Integration of equations (5) and (6).

In the first case we may notice that, provided that we do not apply our results over too many periods of the waves, we may replace $\sin \frac{2\pi}{\lambda} (ct - x)$ by $\sin \frac{2\pi c}{\lambda} t$, so that our

equations of motion become

$$\frac{m}{e} \ddot{y} = Y_0 \sin \frac{2\pi c}{\lambda} t, \quad . \quad . \quad . \quad . \quad (33)$$

$$\frac{m}{e} \ddot{x} = \frac{Y_0}{c} \dot{y} \sin \frac{2\pi c}{\lambda} t. \quad . \quad . \quad . \quad . \quad (34)$$

(33) and (34) lead, as we have seen, to

$$\dot{x} = \frac{1}{2c} \dot{y}^2, \quad . \quad . \quad . \quad . \quad (35)$$

for a case where $\dot{x} = \dot{y} = 0$ when $t = 0$.

By integrating (33) subject to $\dot{y} = 0$ when $t = 0$ we find

$$\dot{y} = \frac{Y_0 e \lambda}{c m \pi} \sin^2 \frac{\pi c}{\lambda} t,$$

and from (35)

$$\dot{x} = \frac{1}{2c} \left(\frac{Y_0 e \lambda}{c m \pi} \right)^2 \sin^4 \frac{\pi c}{\lambda} t.$$

Problem (3). The case of a damped train of waves.

The relation $\dot{x} = \frac{1}{2c} \dot{y}^2$ holds, as we have seen on p. 536, for the general form $Y = Y_0 \phi(ct - x)$. Let us specify our damped train of waves by

$$Y = Y_0 e^{-a(ct-x)} \sin \frac{2\pi}{\lambda} (ct - x).$$

We have to a sufficient degree of accuracy for our purpose

$$\ddot{y} = \frac{e}{m} Y_0 e^{-act} \sin \frac{2\pi}{\lambda} ct, \quad . \quad . \quad . \quad . \quad (36)$$

leading for a case where $\dot{y} = 0$ when $t = 0$ to

$$\dot{y} = \frac{Y_0 e \lambda}{2c m \pi \left(1 + \frac{\lambda^2 a^2}{4\pi^2} \right)},$$

the time being considered to be so great that the amplitude has sunk to zero.

It is interesting to notice that if a is so large that $\frac{\lambda^2 a^2}{4\pi^2}$ is large compared with unity

$$\dot{y} = \frac{2\pi Y_0 e}{m c \lambda a^2},$$

showing that if a is independent of λ , \dot{y} is proportional to the frequency.

We may point out that if the energy per unit cross-section of the wave be calculated it will contain a^2 in the denominator.

Problem (4). Solution of (19) and (20) when μ is not zero.

The solution of (19) subject to $y = \dot{y} = \ddot{y} = 0$ when $t = 0$ is still given by (22) leading to

$$\dot{y} = \frac{Y_0 e}{2m} t \sin 2\pi n t.$$

The solution of (20) subject to $x = \dot{x} = \ddot{x} = 0$ when $t = 0$ is

$$x = \frac{1}{c} \left(\frac{Y_0 e}{4\pi m} \right)^2 \left\{ \frac{t}{\mu^2} - \frac{2n^2(4n^2 - 3\mu^2)}{\pi\mu^3(4n^2 - \mu^2)} \sin 2\pi\mu t + \frac{t \cos 4\pi n t}{4n^2 - \mu^2} - \frac{2n \sin 4\pi n t}{\pi(4n^2 - \mu^2)^2} \right\}, \quad \dots \quad (37)$$

which on differentiation leads after a little reduction to

$$\frac{dx}{dt} = \frac{1}{4c} \left(\frac{Y_0 e}{m} \right) \left\{ \frac{4n^2 - 3\mu^2}{(4n^2 - \mu^2)^2} 2n^2 t^2 \frac{\sin^2 \pi\mu t}{\pi^2 \mu^2 t^2} - \frac{nt \sin 4\pi n t}{\pi(4n^2 - \mu^2)} + \frac{4n^2 + \mu^2}{2\pi^2(4n^2 - \mu^2)^2} \sin^2 2\pi n t \right\}. \quad \dots \quad (38)$$

When μ is absolutely zero this of course reverts to the expression found on p. 549. When μ is small compared with n but not necessarily zero, we have

$$\dot{x} = \frac{1}{8c} \left(\frac{Y_0 e}{\pi n m} \right)^2 \left\{ \frac{n^2}{\mu^2} \sin^2 \pi\mu t - \frac{\pi}{2} n t \sin 4\pi n t + \frac{1}{4} \sin^2 2\pi n t \right\} \quad \dots \quad (39)$$

After a few oscillations of the wave the last term becomes unimportant compared with the others. The first term must not be neglected however, since it is multiplied by the large factor $\frac{n^2}{\mu^2}$. In fact this term is all important until a time t has elapsed such that $\frac{\pi}{2} n t = \frac{n^2}{\mu^2}$, or until a number of oscillations p of the light-wave have taken place such that $p = \frac{2}{\pi} \frac{n^2}{\mu^2}$ (since p is of the order nt). For example, if $n = 30\mu$ it would not be until 600 oscillations had taken

place that the second term would become of the same order as the first. The first term is always positive, and while it is all important \dot{x} must always be positive. The second term is oscillatory in sign, however, and when it becomes so great as to mask the first term, \dot{x} may be positive or negative. We see, however, that there is time for plenty of oscillations before it becomes important.

In order that the theory in the form in which we have developed it on pp. 547 to 549 should strictly speaking apply, it is necessary for μ to be so small compared with n that $\frac{\sin^2 \pi \mu t}{\pi^2 \mu^2 t^2}$ is sensibly unity, in which case of course (38) reverts to the form given on p. 549.

To take an illustration, suppose that $\pi \mu t$ must not be more than $\frac{\pi}{4}$. We must have $\mu t < \frac{1}{4}$, and since $p = nt$ approximately, this means that we must have $\frac{\mu}{n} < \frac{1}{4p}$, i. e. in the problem considered on p. 550 $\frac{n}{\mu} > 320$.

Expressing the results of the theory in the form here developed, we have from (39), since $nt = p$ approximately,

$$\dot{x} = \frac{1}{8c} \left(\frac{Y_0 e}{\pi n m} \right)^2 \frac{n^2}{\mu^2} \sin^2 \frac{\pi \mu}{n} p, \text{ approximately, } \quad (40)$$

subject to the restriction that

$$\frac{\mu^2}{n^2} < \frac{\pi}{2p},$$

so that from (28) and (29), which still apply when μ is not zero,

$$u = \frac{1}{\pi^2 p^2 c} \cdot \frac{n^2}{\mu^2} \cdot \frac{E}{m} \sin^2 \frac{\pi \mu p}{n} \quad v^2 = \frac{2E}{mp} \dots \dots (41)$$

Thus
$$\frac{u}{v} = \frac{1}{2} \left(\frac{n^2}{\mu^2} \right) \frac{v}{\pi^2 c p} \sin^2 \frac{\pi \mu p}{n} \dots \dots (42)$$

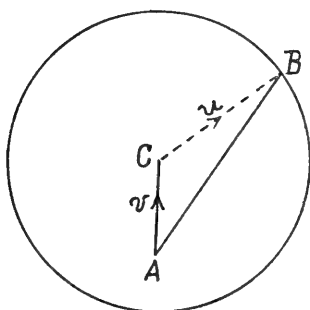
Physical Laboratory,
The University of Sheffield,
January 1, 1913.

LVIII. *Graphical Construction for Steering Course of a Ship.*
 By JOHN WYLIE, B.A., *Demonstrator of Physics, Queen's University, Belfast* *.

GIVEN a number of parallel belts of water, along any one belt the water flowing with constant velocity but the velocity varying from belt to belt, to find the minimum time path and the course a ship should steer going from a point in one belt to a point in some other belt.

1. For a single belt the true motion of the ship is the resultant of the two velocities, v that of the current, and u that of the ship in still water.

Fig 1.



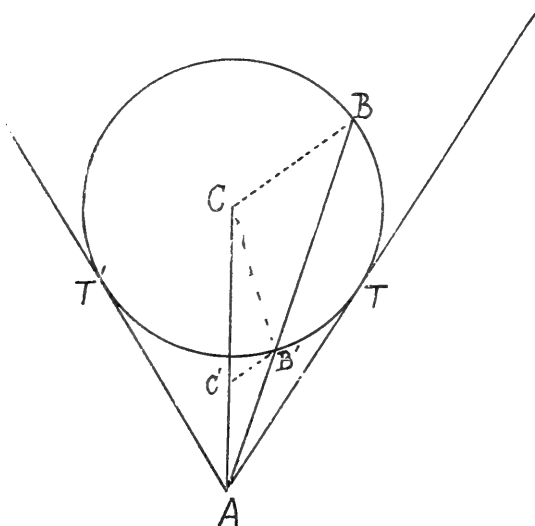
In fig. 1 let A be starting point. Draw AC to represent v , and on same scale describe a circle with centre C and radius u . Then if B be any point on this circle, the ship will go from A to B along line AB by steering in a direction parallel to CB. Since AB is a straight line, AB will be the minimum time path between A and B, and so long as A is inside the circle, that is v less than u , this holds from A to any point of the circle.

But if v be greater than u , then, as in fig. 2, AB, steering parallel to CB, will be a minimum time path; but AB', steering parallel to CB', will not be a minimum time path. AB' will be the minimum time path for steering course C'B' where C'B' is parallel to CB.

It is easily seen that if v is less than u it is possible for the ship to reach any point in plane space, but if v is greater than u she cannot get outside of the angle bounded by the tangents AT and AT'.

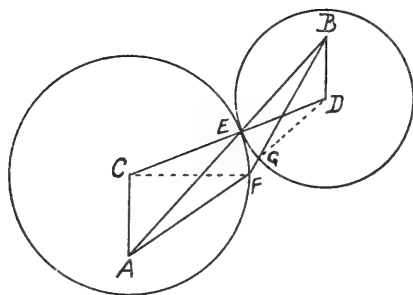
* Communicated by the Author.

Fig. 2.



Should it not be thought self-evident that the straight line joining two points is the minimum time path, consider fig. 3. AB is the straight line path from A to B. Let AFB be any

Fig. 3.



other path, AF and FB being straight lines. Take

$$AC : CF = v : u.$$

Then CF will be steering direction for AF. Let circle with C centre and CF radius cut AB in E. Produce CE to meet vertical through B in D. Describe circle with D centre and DE radius. This circle cuts FB in G, G lying between F and D. As in fig. 1

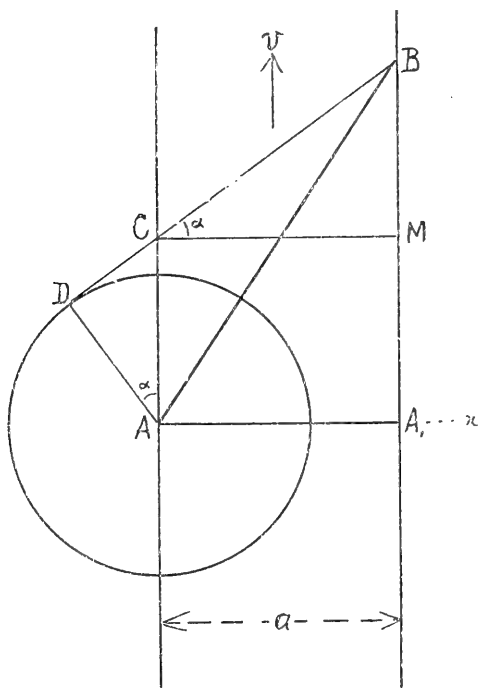
time along AE = time along AF,

and time along EB = time along GB,

therefore time along AB is less than time along AF and FB. Now AFB may be taken as three consecutive points on a

curved path, and by the above the time along the chord AB is less than the time along the arc AFB. This can be extended in the ordinary way to any size of an arc, so that finally we get the straight line law as above.

Fig. 4.



2. In all that follows, as in fig. 4, A, the starting point, is taken as origin of axes, and belts are all parallel to Ay .

Positive direction of currents is upwards.

Let $AC : CB = v : u$, fig. 4.

Then CB will be steering direction for minimum time path AB. Drop AD a perpendicular to CB produced, and CM a perpendicular to edge of belt through B. Let breadth of belt be a , and angle MCB be α .

Then

$$DA : MC = AC : CB,$$

or

$$DA : a = v : u,$$

$$\therefore DA = \frac{v}{u}a, \text{ a constant,}$$

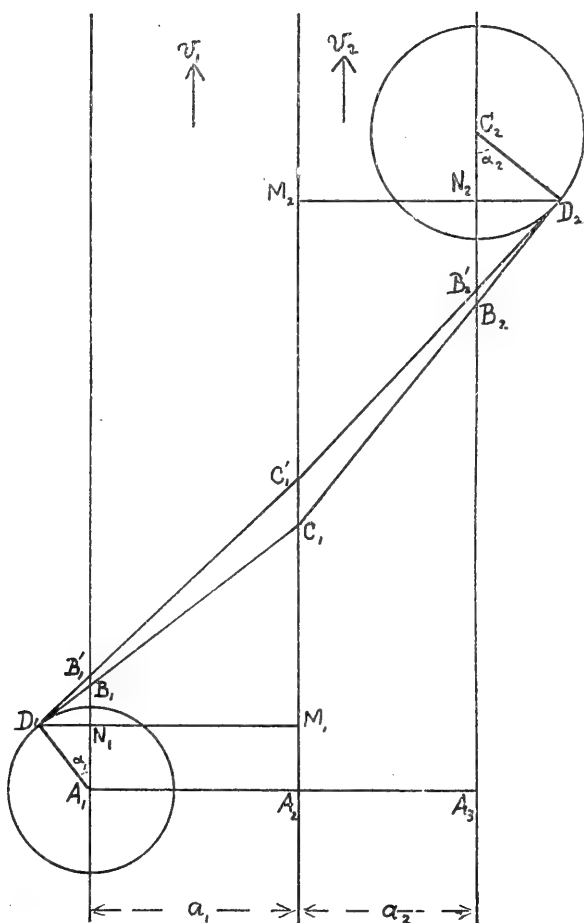
$$\therefore CB \text{ touches a circle centre } A \text{ and radius } \frac{v}{u}a.$$

So to go from A to any point B, the steering course is found by drawing from B a tangent to this circle. As two tangents can be drawn from B it is necessary to discriminate

between them. The one touching the upper half of the circle is used when v acts up, that touching the lower half when v acts down. The time of doing AB is the same as that taken to do AC with velocity v , or CB with velocity u ,

$$t = \frac{AC}{v} \quad \text{or} \quad \frac{CB}{u}.$$

Fig. 5.



3. For two belts, velocities v_1 and v_2 , and breadths a_1 and a_2 , fig. 5, to find minimum time path from A_1 in first belt to C_2 in second belt.

Describe circle centre A_1 and radius $\frac{v_1}{u}a_1$

and circle centre C_2 and radius $\frac{v_2}{u}a_2$.

Then for any path $A_1C_1C_2$ the steering directions are B_1C_1

and C_1B_2 these being the tangents to the circles, and touching at D_1 and D_2 .

$$\text{Time from } A_1 \text{ to } C_2 = \frac{A_1B_1}{v_1} + \frac{B_2C_2}{v_2}.$$

Let C_1' be a point in the common edge very near to C_1 , so that D_1C_1' and $C_1'D_2$ can be taken as the steering directions for path $A_1C_1'C_2$.

When $A_1C_1C_2$ is a minimum time path the times along these two paths will be the same,

$$\begin{aligned} \therefore \frac{A_1B_1'}{v_1} + \frac{C_2B_2'}{v_2} &= \frac{A_1B_1}{v_1} + \frac{C_2B_2}{v_2}, \\ \therefore \frac{B_1B_1'}{v_1} &= \frac{B_2B_2'}{v_2} \dots \dots \dots (1) \end{aligned}$$

Drop perpendiculars $D_1N_1M_1$ and $D_2N_2M_2$ on the edges of the belts.

Then by similar triangles

$$B_1B_1' : C_1C_1' = D_1N_1 : D_1M_1,$$

$$\begin{aligned} \therefore B_1B_1' &= C_1C_1' \times \frac{D_1N_1}{D_1M_1} = C_1C_1' \times \frac{\frac{v_1}{u} a_1 \sin \alpha_1}{\frac{v_1}{u} a_1 \sin \alpha_1 + a_1} \\ &= C_1C_1' \frac{v_1}{v_1 + \frac{u}{\sin \alpha_1}}. \end{aligned}$$

Similarly,

$$B_2B_2' = C_1C_1' \frac{v_2}{v_2 + \frac{u}{\sin \alpha_2}}.$$

Substituting into (1) gives

$$v_1 + \frac{u}{\sin \alpha_1} = v_2 + \frac{u}{\sin \alpha_2}, \dots \dots \dots (2)$$

which is the condition to be satisfied for a minimum time path.

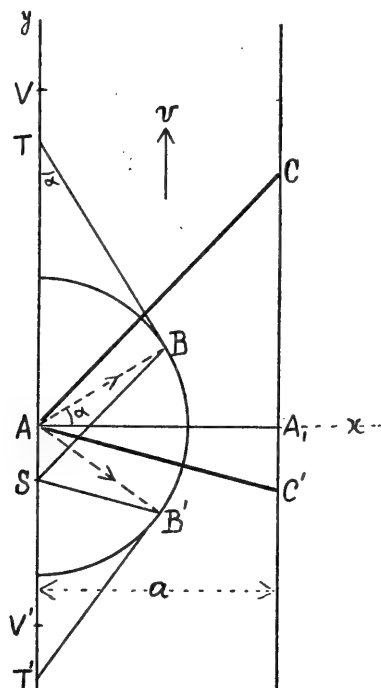
This condition is independent of the breadths of the belts. It may be called the "Law of Refraction" as regards the steering directions in passing from one belt to another flowing at a different velocity. α_1 and α_2 being the angles of incidence and refraction.

It follows at once that for any number of parallel belts

$$v_1 + \frac{u}{\sin \alpha_1} = v_2 + \frac{u}{\sin \alpha_2} = v_3 + \frac{u}{\sin \alpha_3} = \&c. = K \text{ say,}$$

the value of K depending on the direction chosen in the first belt but remaining constant throughout that path.

Fig. 6.



4. It is easy to represent the function $v + \frac{u}{\sin \alpha}$ geometrically, fig. 6. Describe a semicircle centre A and radius u . Draw a radius AB at angle α with Ax . Draw a tangent at B cutting Ay at T . Take TV , measuring up, equal v . Then

$$AT = \frac{u}{\sin \alpha} \text{ and } AV = v + \frac{u}{\sin \alpha} = K.$$

Also take AS , measuring down, equal v .

Join SB , and draw AC parallel to SB . AC will be true path where AB is steering direction. The dashed letters give the construction for a negative value of K . AC' being true path for steering direction AB' .

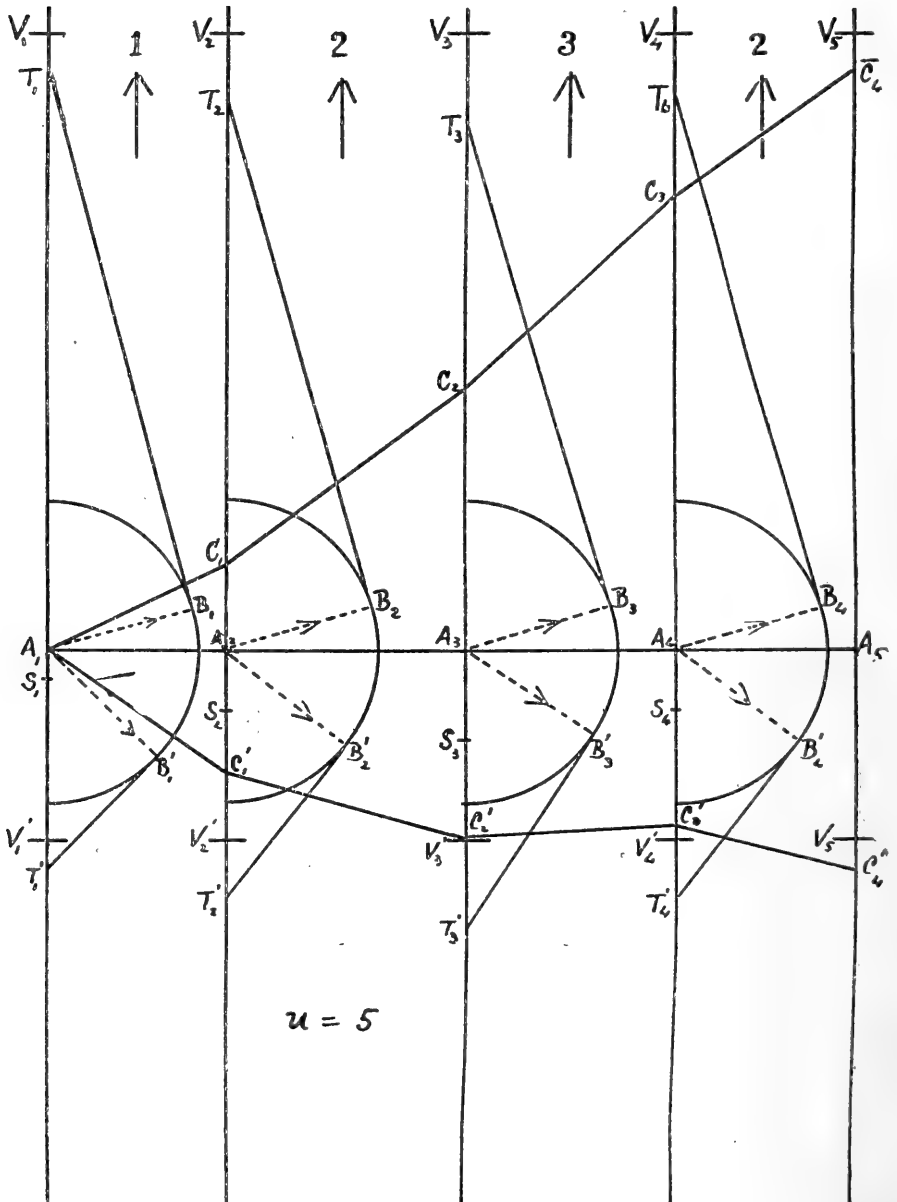
5. To apply this construction let there be a number of parallel belts, as in fig. 7 (p. 564), the velocities in the belts being 1, 2, 3, and 2 units, that of the ship u being 5.

Describe semicircles with centres A_1, A_2, A_3 , and A_4 , and radius 5.

Let A_1B_1 be steering direction in first belt. Draw tangent B_1T_1 and mark off $T_1V_1=v_1=1$. Then $A_1V_1=K$ the constant for this particular path. Cut off

$$A_2V_2=A_3V_3=A_4V_4=K.$$

Fig. 7.



Measure down

$$V_2T_2=2, V_3T_3=3, V_4T_4=2.$$

Draw the tangents T_2B_2 , T_3B_3 , T_4B_4 . Then A_2B_2 , A_3B_3 , A_4B_4 will be the corresponding steering directions, and taking

$$A_2S_2=2, A_3S_3=3, A_4S_4=2,$$

measuring down, the true path is got by drawing

A_1C_1 parallel to S_1B_1 ,

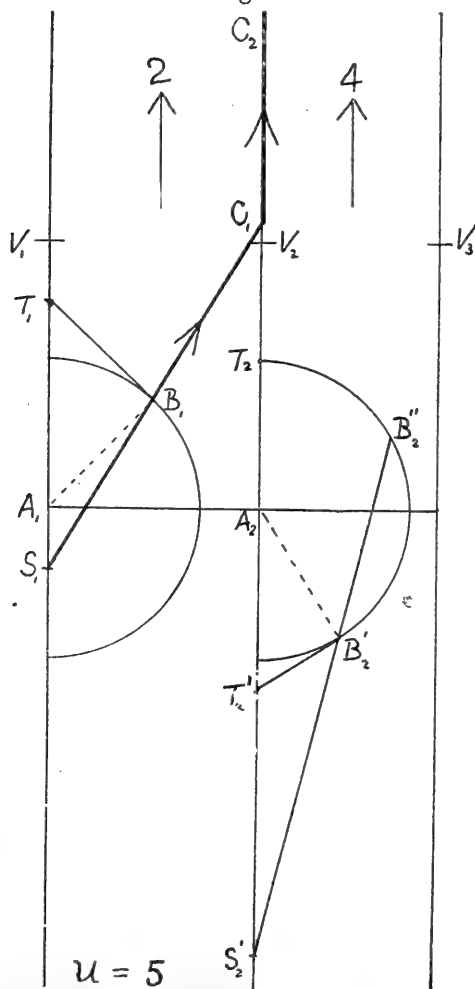
C_1C_2 parallel to S_2B_2 , and so on.

The dashed letters in the lower half of diagram give a path where K is negative. It is evident that if the first steering direction is positive, all the steering directions for that path are positive, and if the first is negative all are negative.

6. Regarding limiting values of K : (1) K positive. If v is negative, construction is always possible since T is always outside the circle.

But if v is positive, T must lie between V and the circle. Therefore K must not be less than $u + v$.

Fig. 8.

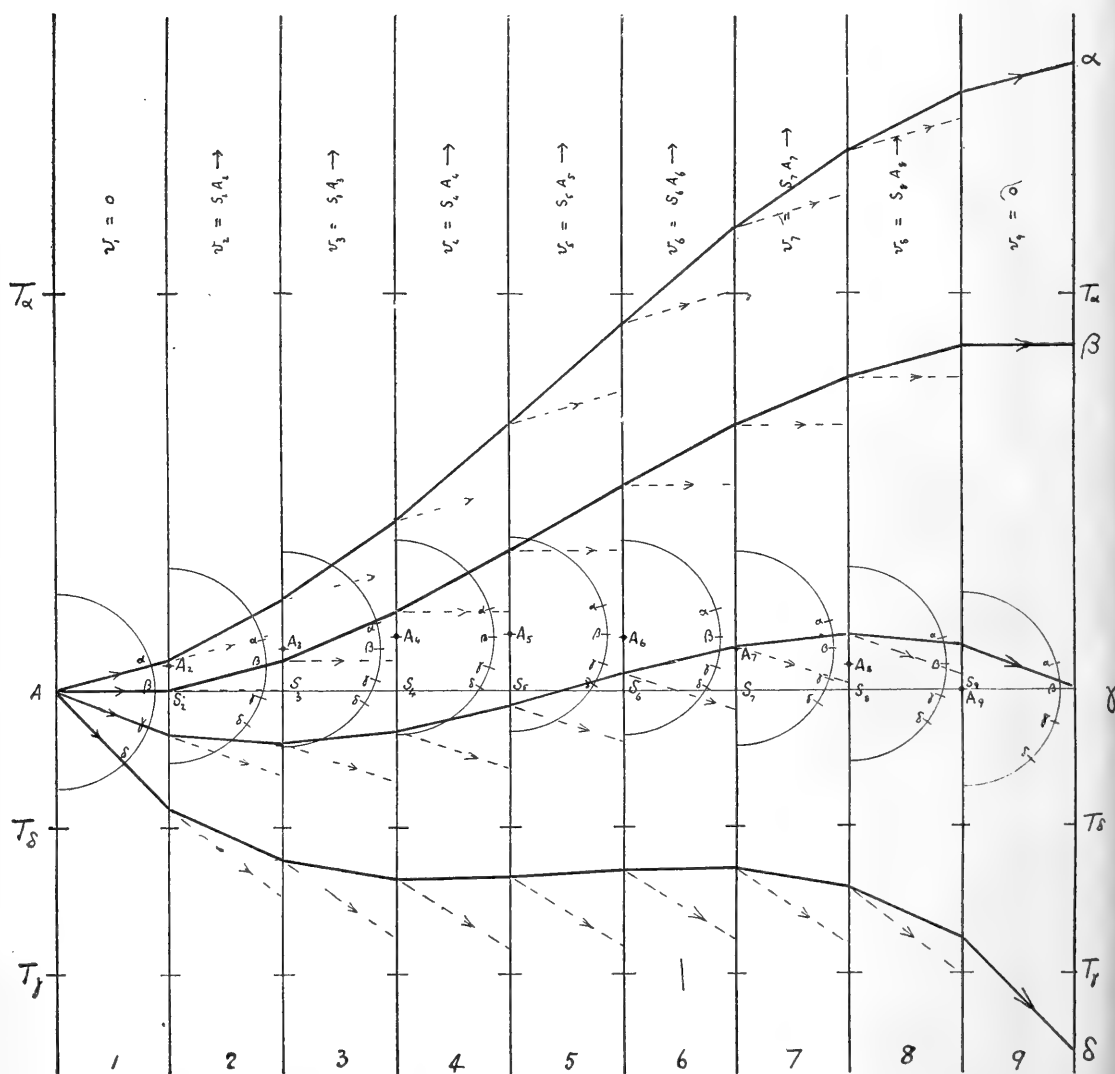


In fig. 8 velocities in belts are 2 and 4, $u=5$, limiting value of K is 9. $A_1C_1C_2$ is the true path for this value. K must be greater than 9 if the path is to cross the second

belt. Stated generally, if all the belts are to be crossed, K must not be less than u plus the greatest positive velocity.

Suppose the velocity in second belt so great as to bring the point T_2 down below the circle as at T_2' , the drawing of a tangent would be again possible. Then S_2' would be as in figure, and $S_2'B_2'$ produced would cut the circle again at B_2'' . That is A_2B_2' is steering direction for path parallel to $S_2'B_2'$. But it was pointed out in paragraph 1 that this is not a minimum time path at all. Hence T_2 cannot come below the circle. (2) Similarly, if K is negative K must not be less than u plus the greatest negative velocity.

Fig. 9.



7. Fig. 9 shows four minimum time paths, $A_1\alpha$, $A_1\beta$, $A_1\gamma$, and $A_1\delta$. The construction has been modified in a way which simplifies somewhat the drawing. The S points are

If $E=0$, and if the condenser be charged and then allowed to discharge through the circuit, Lord Kelvin first showed, that provided $\mu^2 > \lambda^2$, damped harmonic electric oscillations ensue whose period is equal to

$$\frac{2\pi}{\sqrt{\mu^2 - \lambda^2}},$$

which, if λ is small, is very approximately

$$= \frac{2\pi}{\mu} = 2\pi \sqrt{KL}.$$

In the sequel $2\pi/\mu$ will be called the natural period, and μ the natural frequency of the circuit; λ will be called the damping coefficient of the circuit, and a circuit such as the one here dealt with will be called an oscillating circuit.

2. If two inductively coupled circuits, that is, two oscillating circuits so placed that they act inductively on each other, have vibratory currents C_1 and C_2 circulating in them, and if M is the mutual inductance between the circuits whose other characteristics are identified by the subscripts 1 or 2, then the E.M.F. in circuit 1 is equal to $-MDC_2$, and in circuit 2 is equal to $-MDC_1$.

Hence by I., § 1,

$$\left. \begin{aligned} r_1 C_1 &= -MDC_2 \\ r_2 C_2 &= -MDC_1 \end{aligned} \right\} \dots \dots \dots (I.)$$

As $C_1 = K_1 DV_1$ and $C_2 = K_2 DV_2$, where V_1 and V_2 are the values at any instant of the P.D.s of the condensers, we find, after substituting for C_1 and C_2 in the above equations and integrating each once, that

$$\left. \begin{aligned} r_1 K_1 V_1 &= -MDK_2 V_2 \\ r_2 K_2 V_2 &= -MDK_1 V_1 \end{aligned} \right\} \dots \dots \dots (II.)$$

as the constant to be added in either case is obviously zero.

Eliminating C_1 or C_2 from equations I., or V_1 or V_2 from equations II., we find that C_1 , C_2 , V_1 , or V_2 will satisfy the differential equation

$$(r_1 r_2 - M^2 D^2) \phi = 0,$$

that is

$$\left\{ (D^2 + 2\lambda_1 D + \mu_1^2)(D^2 + 2\lambda_2 D + \mu_2^2) - \frac{M^2}{L_1 L_2} D^4 \right\} \phi = 0, \quad (III.)$$

which, when damping is neglected, reduces to

$$\left\{ (D^2 + \mu_1^2)(D^2 + \mu_2^2) - \frac{M^2}{L_1 L_2} D^4 \right\} \phi = 0. \quad (\text{IV.})$$

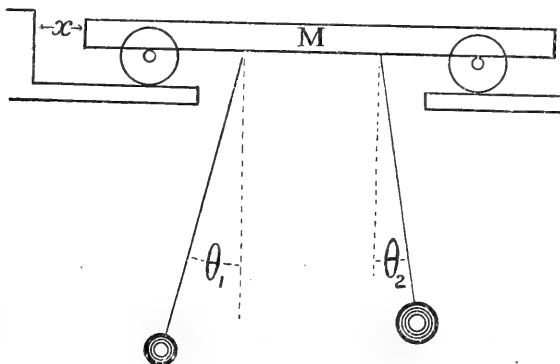
$M/\sqrt{L_1 L_2}$, usually spoken of as the coefficient of coupling, or the coupling, of the two circuits will be represented in what follows by $\sin \psi$, and ψ will be called the coupling angle, so that

$$\sin^2 \psi = \frac{M^2}{L_1 L_2}.$$

3. Consider now the motion of the following mechanical system when making small oscillations.

A horizontal beam of mass M is so supported that it can move freely in the direction of its length, and from it two simple pendulums of lengths l_1 and l_2 with bobs of masses m_1 and m_2 are suspended by means of V suspensions so arranged that the bobs are constrained to move in the vertical plane through the axis of the beam (see fig. 1).

Fig. 1.



Let the position of the beam be specified by x , the horizontal distance between its end and a fixed origin, and that of the pendulums by θ_1 and θ_2 , the angles they make with the vertical, θ_1 being measured towards the left and θ_2 towards the right; then if T be the kinetic and V the potential energy of the system when making small oscillations,

$$2T = M\dot{x}^2 + m_1(\dot{x} - l_1\dot{\theta}_1)^2 + m_2(\dot{x} + l_2\dot{\theta}_2)^2$$

$$2V = g(m_1 l_1 \theta_1^2 + m_2 l_2 \theta_2^2),$$

and as

$$\frac{d}{dt} \cdot \frac{dT}{d\dot{\phi}} + \frac{dV}{d\phi} = 0,$$

where ϕ is any one of the coordinates, we find that

$$\begin{aligned} (M + m_1 + m_2)\ddot{x} - m_1 l_1 \ddot{\theta}_1 + m_2 l_2 \ddot{\theta}_2 &= 0 \\ -\ddot{x} + l_1 \ddot{\theta}_1 + g\theta_1 &= 0 \\ \ddot{x} + l_2 \ddot{\theta}_2 + g\theta_2 &= 0. \end{aligned}$$

Eliminating \ddot{x} from the first and second, and also from the first and third of these equations, we obtain

$$\text{and} \quad \left. \begin{aligned} (D^2 + \mu_1^2)\theta_1 &= -p_1 D^2 \theta_2 \\ (D^2 + \mu_2^2)\theta_2 &= -p_2 D^2 \theta_1, \end{aligned} \right\} \quad \dots \quad (\text{I.})$$

where

$$\left. \begin{aligned} \mu_1^2 &= \frac{M + m_1 + m_2}{M + m_2} \frac{g}{l_1}, & \mu_2^2 &= \frac{M + m_1 + m_2}{M + m_1} \frac{g}{l_2}, \\ p_1 &= \frac{l_2}{l_1} \frac{m_2}{M + m_2}, & p_2 &= \frac{l_1}{l_2} \frac{m_1}{M + m_1}. \end{aligned} \right\} \quad (\text{II.})$$

Equations II., § 2, connecting the P.D.s of the condensers in the coupled circuits can, when damping is neglected, be written in the identical form of equations I. of this paragraph, and the values of the constants for the electrical case are given by

$$\left. \begin{aligned} \mu_1^2 &= \frac{1}{K_1 L_1}, & \mu_2^2 &= \frac{1}{K_2 L_2}, \\ p_1 &= \frac{K_2}{K_1} \frac{M}{L_1}, & p_2 &= \frac{K_1}{K_2} \frac{M}{L_2}. \end{aligned} \right\} \quad (\text{III.})$$

Hence the angular displacements of the two pendulums in the mechanical system are mutually connected by equations identical in form with those which connect the P.D.s of the condensers in the electrical system, and as $C_1 = K_1 D V_1$, $C_2 = K_2 D V_2$, the angular velocities of the pendulums are similarly analogous to the currents in the two electrical circuits.

If in the proposed system the strings of the second pendulum become rigid and be rigidly attached to the beam, then $D^2 \theta_2 = 0$, and the equation of motion of the first pendulum becomes

$$(D^2 + \mu_1^2)\theta_1 = 0,$$

that is, the motion is simple harmonic of frequency μ_1 .

Hence, to determine the quantity relating to the mechanical

system that is analogous to the "natural period" of the primary electric circuit, we have simply to place the bob of the second pendulum on the beam and then measure the period of the first by observation in the usual way. Similarly the natural period, as we shall call it, of the second pendulum is determined.

Returning to equations I. above, if we eliminate θ_1 or θ_2 between them we find that either θ_1 or θ_2 will satisfy the differential equation

$$\{(D^2 + \mu_1^2)(D^2 + \mu_2^2) - p_1 p_2 D^4\} \theta = 0,$$

which is identical in form with equation IV., § 2, which is satisfied by the variables in the coupled circuit system.

It is evident that the "coupling" of the pendulum system or the value of $\sin \psi$ for the latter is equal to

$$\sqrt{p_1 p_2} = \sqrt{\frac{m_1 m_2}{(M + m_1)(M + m_2)}}.$$

Hence all the variables either of the mechanical or of the electrical system satisfy the differential equation

$$\{\cos^2 \psi D^4 + (\mu_1^2 + \mu_2^2) D^2 + \mu_1^2 \mu_2^2\} \phi = 0, \quad . \quad (\text{IV.})$$

where μ_1 and μ_2 are the natural frequencies, and ψ the coupling angle in either case.

4. In order to follow up this analogy, it is necessary to know fully the details of the motion in either system arising from analogous initial conditions. We shall therefore obtain the solution when for the electrical system the initial conditions are

$$V_1 = E, \quad V_2 = 0, \quad C_1 = 0, \quad C_2 = 0, \quad \text{when } t = 0,$$

the usual initial conditions to a disturbance in a Marconi transmitter, and when for the mechanical system the initial conditions are

$$\theta_1 = E, \quad \theta_2 = 0, \quad \dot{\theta}_1 = 0, \quad \dot{\theta}_2 = 0, \quad \text{when } t = 0.$$

Let us put a for μ_1^2 and b for μ_2^2 in equation IV. § 3, and it becomes

$$\{\cos^2 \psi D^4 + (a + b) D^2 + ab\} \phi = 0.$$

Proceeding with the solution of this differential equation in the usual way by obtaining the factors of the operator

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 considered as a simple quadratic function, we find that

$$D^2 = \frac{-(a+b) \pm \sqrt{(a+b)^2 - 4ab \cos^2 \psi}}{2 \cos^2 \psi}$$

$$= \frac{-(a+b) \pm \sqrt{a^2 + b^2 - 2ab \cos 2\psi}}{2 \cos^2 \psi}.$$

If, now, a and b be taken as the two sides of a triangle whose included angle is 2ψ , then as

$$\cos \psi = \sqrt{\frac{s(s-c)}{ab}},$$

where c is the third side and $a+b+c=2s$, the roots of the quadratic are equal to

$$-\frac{s-c}{\cos^2 \psi} = -\frac{ab}{s}$$

and

$$-\frac{s}{\cos^2 \psi} = -\frac{ab}{s-c}.$$

Hence if

$$\omega_1^2 = \frac{ab}{s}, \quad \omega_2^2 = \frac{ab}{s-c}, \quad . \quad . \quad . \quad . \quad (I.)$$

the differential equation is reduced to

$$(D_2 + \omega_1^2)(D^2 + \omega_2^2)\phi = 0, \quad . \quad . \quad . \quad (II.)$$

which shows that the resultant motion is that due to two superposed harmonic motions whose individual frequencies are ω_1 and ω_2 .

It will be seen in the sequel that the above method of presenting the solution for the resultant frequencies by aid of a triangle (which we shall call *the triangle*) simplifies many of the considerations relating to coupled circuits. It at once enables us to follow the variations in the resultant frequencies due to variations either of the coupling or of the natural frequencies of the two circuits.

Thus if the natural frequencies of the circuits be constant while the coupling varies from very loose coupling when ψ is small to very tight coupling when ψ approximates to a right angle, and consequently the angle 2ψ included between a and b becomes nearly 180° , the squares of the reciprocals of the frequencies are given by

$$\frac{1}{\omega^2} = \frac{a+b}{2ab} \pm \frac{c}{2ab},$$

c gradually changing from $a-b$, its value for infinitely loose coupling, to $a+b$, its value for infinitely tight coupling.

Again, if the natural periods of the circuits are equal, the triangle is isosceles, and it is easy to show that the resultant periods τ for any value $\sin \psi$ of the coupling are always given by the formula

$$\tau = \sqrt{2} t \sin \left(\frac{\pi}{4} \pm \frac{\psi}{2} \right),$$

where t is the natural period of either circuit.

Similar statements will obviously apply to the coupled pendulums.

5. Dealing with the electrical system, the general solution of equation II. § 4 for the currents is

$$C_1 = A_1 \cos \omega_1 t + B_1 \sin \omega_1 t + P_1 \cos \omega_2 t + Q_1 \sin \omega_2 t$$

$$C_2 = A_2 \cos \omega_1 t + B_2 \sin \omega_1 t + P_2 \cos \omega_2 t + Q_2 \sin \omega_2 t,$$

where A_1, B_1 , &c., are constants to be determined. But C_1 and C_2 are connected by the equation (see I. § 2)

$$L_1(D^2 + a)C_1 + MD^2C_2 = 0,$$

in which a , one side of the triangle, represents μ_1^2 as before.

Hence

$$\frac{A_2}{A_1} = \frac{B_2}{B_1} = \frac{L_1(a - \omega_1^2)}{M\omega_1^2} = \frac{L_1}{M} \cdot \frac{s-b}{b},$$

$$\frac{P_2}{P_1} = \frac{Q_2}{Q_1} = \frac{L_1(a - \omega_2^2)}{M\omega_2^2} = -\frac{L_1}{M} \cdot \frac{s-a}{b}.$$

Substituting from these equations for A_2, B_2, P_2 , and Q_2 in the expression for C_2 , we find that

$$C_2 = \frac{L_1}{bM} \left\{ (s-b)(A_1 \cos \omega_1 t + B_1 \sin \omega_1 t) - (s-a)(P_1 \cos \omega_2 t + Q_1 \sin \omega_2 t) \right\}.$$

Now as $C_1 = C_2 = 0$ when $t=0$, it follows that

$$A_1 = 0 \quad \text{and} \quad P_1 = 0,$$

hence

$$C_1 = B_1 \sin \omega_1 t + Q_1 \sin \omega_2 t$$

$$C_2 = \frac{L_1}{bM} \left\{ (s-b)B_1 \sin \omega_1 t - (s-a)Q_1 \sin \omega_2 t \right\}$$

and as $K_1 V_1 = D^{-1} C_1$, $K_2 V_2 = D^{-1} C_2$,

$$K_1 V_1 = -\frac{B_1}{\omega_1} \cos \omega_1 t - \frac{Q_1}{\omega_2} \cos \omega_2 t$$

$$K_2 V_2 = -\frac{L_1}{bM} \left\{ (s-b) \frac{B_1}{\omega_1} \cos \omega_1 t - (s-a) \frac{Q_1}{\omega_2} \cos \omega_2 t \right\}.$$

But when $t=0$, $V_1=E$ and $V_2=0$, therefore

$$\frac{B_1}{\omega_1} + \frac{Q_1}{\omega_2} = -K_1 E$$

$$(s-b) \frac{B_1}{\omega_1} - (s-a) \frac{Q_1}{\omega_2} = 0,$$

which give us

$$\frac{B_1}{\omega_1} = -\frac{s-a}{c} K_1 E, \quad \frac{Q_1}{\omega_2} = -\frac{s-b}{c} K_1 E,$$

where a , b , c , and s refer to the triangle.

Hence for the initial conditions $V_1=E$, $V_2=0$, $C_1=C_2=0$ when $t=0$, the complete solution is given by

$$\left. \begin{aligned} V_1 &= \frac{E}{c} \left\{ (s-a) \cos \omega_1 t + (s-b) \cos \omega_2 t \right\} \\ V_2 &= p_2 a \frac{E}{c} \left\{ \cos \omega_1 t - \cos \omega_2 t \right\} \\ C_1 &= -K_1 \frac{E}{c} \left\{ \omega_1 (s-a) \sin \omega_1 t + \omega_2 (s-b) \sin \omega_2 t \right\} \\ C_2 &= p_2 a K_2 \frac{E}{c} \left\{ -\omega_1 \sin \omega_1 t + \omega_2 \sin \omega_2 t \right\}, \end{aligned} \right\} \text{(I.)}$$

where

$$p_2 = \frac{K_1 M}{K_2 L_2} = b K_1 M = \frac{b}{a} \frac{M}{L_1}$$

(see equation III. § 3).

The complete solution for the pendulum system for analogous initial conditions is obviously given by the same equations. Thus, if when $t=0$, $\theta_1=E$, $\theta_2=0$, $\dot{\theta}_1=0$, $\dot{\theta}_2=0$,

$$\theta_1 = \frac{E}{c} \left\{ (s-a) \cos \omega_1 t + (s-b) \cos \omega_2 t \right\}$$

$$\theta_2 = p_2 a \frac{E}{c} \left\{ \cos \omega_1 t - \cos \omega_2 t \right\},$$

where

$$p_2 = \frac{l_1}{l_2} \frac{m_1}{M + m_1}$$

(see equations II. § 3).

The motion of the beam is also the resultant of two superposed harmonic motions of frequencies ω_1 and ω_2 , and can easily be obtained from the consideration that during the motion, when the initial conditions are those assumed above, the centre of mass of the system must remain fixed, hence

$$(M + m_1 + m_2)x - l_1 m_1 \theta_1 + l_2 m_2 \theta_2 = \text{constant}.$$

6. It is interesting to consider the analogies between the constants of the two systems.

Taking as the starting point the correspondence between V and θ , then as the energy expressions must be equivalent, that is

$$\frac{1}{2} K_1 V_1^2 \quad \text{and} \quad \frac{1}{2} m_1 g_1 l_1 \theta^2,$$

therefore

$$K_1 \propto m_1 l_1 g_1$$

$$K_2 \propto m_2 l_2 g_2$$

where the symbol \propto means analogous to.

Again, as

$$C_1 = K_1 D V_1$$

$$C_1 \propto m_1 l_1 g \dot{\theta}_1$$

$$C_2 \propto m_2 l_2 g \dot{\theta}_2.$$

As the frequency must be the same thing in both systems,

$$\frac{1}{K_1 L_1} \propto \frac{M + m_1 + m_2}{M + m_2} \cdot \frac{g}{l_1},$$

hence

$$L_1 \propto \frac{1}{g^2} \frac{M + m_2}{m_1 (M + m_1 + m_2)}$$

$$L_2 \propto \frac{1}{g^2} \frac{M + m_1}{m_2 (M + m_1 + m_2)}.$$

The coupling must be the same for both systems, so that

$$\frac{M^2}{L_1 L_2} \propto \frac{m_1 m_2}{(M + m_1)(M + m_2)},$$

hence

$$M \propto \frac{1}{g^2 (M + m_1 + m_2)}.$$

As a test of the accuracy of these conclusions it is easy to show that T , the kinetic energy of the pendulum system given in § 3, can be easily reduced, by aid of the relation at the end of § 5, to the form

$$\frac{1}{2}L_1C_1^2 + MC_1C_2 + \frac{1}{2}L_2C_2^2$$

(the expression for the kinetic energy of the circuits), where the symbols in this expression represent their analogous quantities given above. It is also easy to show that if T be the kinetic and V the potential energy of either system, then

$$2T = K_1E^2 \left\{ \frac{s-a}{c} \sin^2 \omega_1 t + \frac{s-b}{c} \sin^2 \omega_2 t \right\}$$

$$2V = K_1E^2 \left\{ \frac{s-a}{c} \cos^2 \omega_1 t + \frac{s-b}{c} \cos^2 \omega_2 t \right\}.$$

7. It should now be admitted that the mechanical system or model proposed is a perfect analogue to the coupled circuits of a Marconi transmitter. The model should therefore be useful in demonstrating many of the properties and much of the behaviour of such coupled circuits.

Its construction is so simple that anyone can design a suitable apparatus for himself if he takes sufficient care to minimize friction. A description of the model that I have found satisfactory may, however, be desirable.

The beam consists of a square brass tube 1 in. \times 1 in. \times 18 in., to the two opposite sides of which are screwed and sweated four short steel straight edges to act as runners, two near each end with their running edges projecting below the lower face of the beam. The bearing edges of these runners are all carefully scraped so as to be straight and to all lie in a plane parallel to the upper surface, and to the axis of the beam. The pair of runners at each end now rest on the cylindrical steel spindle $\frac{3}{16}$ in. in diameter joining two light but rigid brass disk wheels each $2\frac{1}{2}$ in. in diameter. Great care was taken to have the surfaces of the spindles and the rims of the wheels coaxial, and to have the diameters of the wheels and spindles that support one end of the beam exactly equal to those of the wheels and spindle that support the other end.

The wheels run on a bed made of a strip of good plate glass 30 in. \times 3 in. firmly supported so as to prevent any tendency towards flexure, about 3 feet above a table, and carefully levelled.

To the upper side of the beam are attached two cross

rods of wood, one near each end, and both perpendicular to the axis of the beam. In each of these rods two holes, equidistant from the beam, are drilled, through which the upper ends of the thread forming the V suspension of each pendulum pass. Ordinary binding screws on the upper surface of the rods serve to make fast the strings and render quick adjustment of length easy. The distance between the holes in each rod should, of course, be sufficient to enable the V of string supporting each bob to clear the bed and its supports, the bobs of the pendulums being vertically under the beam and bed, and able to move only in a vertical plane parallel to the axis of the beam.

To the upper side of the beam opposite the runners at either end are attached two platforms, on which the masses used to vary the coupling can be placed. It was shown in § 3 that the square of the coupling or $\sin^2 \psi$ is equal to

$$\frac{m_1 m_2}{(M + m_1)(M + m_2)}$$

where M is the total mass of the beam, so by increasing the load on the beam, M in the above will be increased and the coupling diminished.

Equal masses should be placed on each platform, and the platforms should be directly over the bearing spindles when the system is at rest, in order to reduce to a minimum any tendency the loads might have to bend the beam.

8. In order to exemplify the use of the model for the purpose of illustrating the properties of coupled circuits, I will describe some experiments on the relation of the resultant periods to the natural periods and the coupling.

Adjust the pendulums to be of about the same length, say 2 ft. 6 in. or 3 ft., put different masses for the bobs, say make one twice as heavy as the other, and make the coupling loose by arranging that the mass of the beam shall be at least ten times the mean of the masses of the bobs.

Determine by observation the natural period of each pendulum. As has already been explained, this is done for the first by placing the bob of the second on its platform and counting the number of swings made by the first in a given time in the usual way: similarly, determine the natural period of the second pendulum. The natural periods can now be computed by means of the formulæ in § 3 if the masses and lengths have been measured.

To the actual mass of the beam and its load must be added a correction for the wheels to obtain the value of M in the

formulæ referred to. It is easy to show that if the wheels or rollers are constructed as I have described, this correction is equal to

$$2 \frac{\mu R^2 + I}{(R + r)^2},$$

where μ is the mass and I the moment of inertia of each complete roller, R the radius of a wheel, and r the radius of a spindle.

The agreement between the observed and computed natural periods will enable one to judge of the perfection of the model.

Now impart motion to the system, the initial conditions being those already specified in §§ 4, 5.

To do this, first bring the system to rest, then steady the beam with one hand and with the other hold the bob of the first pendulum slightly deflected, and then let bob and beam go simultaneously.

It will be seen that the second pendulum begins to swing and continues with increasing amplitude, while the amplitude of the first at the same time diminishes. This goes on to a certain point when the reverse takes place, and the transfer of energy forwards and backwards many times between the two pendulums is strikingly demonstrated.

From this motion the resultant frequencies ω_1 and ω_2 can easily be obtained by observation.

For the motion of the second pendulum is given by

$$\begin{aligned} \theta_2 &= p_2 a \frac{E}{c} \left\{ \cos \omega_1 t - \cos \omega_2 t \right\} \\ &= 2p_2 a \frac{E}{c} \sin \frac{\omega_2 - \omega_1}{2} t \sin \frac{\omega_2 + \omega_1}{2} t, \end{aligned}$$

which shows that it is a vibration whose amplitude

$$2p_2 a \frac{E}{c} \sin \frac{\omega_2 - \omega_1}{2} t$$

varies harmonically with a frequency

$$= \frac{1}{2}(\omega_2 - \omega_1),$$

while the oscillations of the pendulum have a frequency of

$$\frac{1}{2}(\omega_2 + \omega_1).$$

Hence, if we count the number of double swings the

pendulum makes ($=n$ say) between 11 points of rest, that is during 5 periods of amplitude change, then

$$\frac{n}{5} = \frac{\omega_2 + \omega_1}{\omega_2 - \omega_1},$$

giving the ratio of ω_1 to ω_2 .

Now measure in the usual way the period of the individual swings of the second pendulum, which is equal to

$$\frac{4\pi}{\omega_2 + \omega_1}.$$

From these two results ω_1 and ω_2 can be deduced, and the values so obtained can be compared with those computed by means of the triangle formulæ given in § 4.

In this connexion it is interesting to note that if the pendulums are of the same length l , and have bobs of equal mass m , then one of the resultant frequencies is always the same as that of an ordinary simple pendulum of length l with a rigid point of suspension, that is, it is equal to $\sqrt{g/l}$, no matter what the coupling may be.

For in this case (see § 3)

$$\sin \psi = \sqrt{p_1 p_2} = \frac{m}{M+m}$$

and

$$a = b = \frac{M+2m}{M+m} \frac{g}{l} = (1 + \sin \psi) \frac{g}{l},$$

and as the "triangle" is isosceles,

$$s = a(1 + \sin \psi), \quad s - c = a(1 - \sin \psi)$$

but

$$\omega_1^2 = \frac{ab}{s}, \quad \omega_2^2 = \frac{ab}{s-c},$$

hence

$$\omega_1^2 = \frac{g}{l}, \quad \omega_2^2 = \frac{1 + \sin \psi}{1 - \sin \psi} \frac{g}{l},$$

for all values of $\sin \psi$, the coupling.

9. The surging of the energy forwards and backwards between two coupled circuits is very well illustrated by the model.

When the P.D. of the condenser in a circuit is at the full amplitude for a particular oscillation, the current in that circuit is zero, and all the energy in the circuit at the instant

is $\frac{1}{2}KV^2$ where K is the capacity and V the P.D. of the condenser. Hence the square of the amplitude of the condenser P.D. at any time may be taken as proportional to the energy in the circuit at that time. The analogous statement for the pendulums is obvious.

Let us consider the surging of the energy between two coupled circuits (or coupled pendulums) that have been tuned so that their natural frequencies are equal.

Then $a=b$, $s-a=s-b=\frac{1}{2}c$, and the equations I. of § 5 giving the V 's or θ 's become

$$V_1 = \frac{1}{2}E(\cos \omega_1 t + \cos \omega_2 t),$$

$$V_2 = \frac{1}{2}E\sqrt{\frac{p_2}{p_1}}(\cos \omega_1 t - \cos \omega_2 t)$$

where

$$\begin{aligned}\frac{p_2}{p_1} &= \frac{K_1}{K_2} = \frac{L_2}{L_1} \text{ for the circuits,} \\ &= \frac{l_1 m_1}{l_2 m_2} \text{ for the pendulums.}\end{aligned}$$

These equations can be written as

$$V_1 = E \cos \frac{\omega_2 - \omega_1}{2} t \cos \frac{\omega_2 + \omega_1}{2} t,$$

$$V_2 = E\sqrt{\frac{p_2}{p_1}} \sin \frac{\omega_2 - \omega_1}{2} t \cos \left(\frac{\omega_2 + \omega_1}{2} t - \frac{\pi}{2} \right),$$

showing (1) that the amplitudes vary harmonically and have a constant phase difference of $\frac{\pi}{2}$, that is, when one waxes the other wanes; (2) that the oscillations also have a constant phase difference of $\frac{\pi}{2}$, their frequency being $\frac{1}{2}(\omega_2 + \omega_1)$.

From the values for $\sqrt{\frac{p_2}{p_1}}$ given above it will be seen that

$$\sqrt{\frac{p_2}{p_1}} E,$$

the amplitude of the amplitude or the maximum amplitude of V_2 , is independent of the coupling when $a=b$, but that

this maximum amplitude is only attained in the time t given by

$$\frac{\omega_2 - \omega_1}{2} t = \frac{\pi}{2},$$

and as the "triangle" is isosceles it is easy to deduce that

$$t = \frac{\cos \psi}{\sin \psi/2} \cdot \frac{T}{4}$$

where $T = \frac{2\pi}{\sqrt{a}}$ = the natural period of either circuit.

It will be seen from this expression for t that as the coupling ($\sin \psi$) diminishes the time t required for V_2 to attain its maximum amplitude increases, and when the coupling is zero (*i. e.* when $\psi = 0$) it requires an infinite time for the maximum to be reached.

The above can be very effectively demonstrated by the model, the coupling being regularly reduced by loading the beam and if necessary diminishing the masses of the bobs.

From the remarks at the beginning of this paragraph, we may write the energies in the two circuits at the time t as being equal to

$$\frac{1}{2} K_1 E^2 \cos^2 \frac{\omega_2 - \omega_1}{2} t$$

and

$$\frac{1}{2} K_1 E^2 \sin^2 \frac{\omega_2 - \omega_1}{2} t \text{ respectively.}$$

These expressions show that $\frac{1}{2} K_1 E^2$, the whole of the energy in the system, passes from either circuit to the other and back to the original one in the time t_s given by

$$\frac{\omega_2 - \omega_1}{2} t_s = \pi,$$

so that t_s , which we shall call the period of the surges, is given (easily by the triangle) by

$$t_s = \frac{\cos \psi}{\sin \psi/2} \frac{T}{2},$$

where T is the natural period of either circuit.

On the other hand, we have seen that the frequency of the resultant oscillations in either circuit is $\frac{1}{2}(\omega_2 + \omega_1)$, and if t_0 be their period, we easily find by geometry that

$$t_0 = \frac{\cos \psi}{\cos \psi/2} T.$$

Hence the number of oscillations in one surge is

$$\frac{t_s}{t_0} = \frac{1}{2} \cot \frac{\psi}{2},$$

which increases and finally becomes infinity as the coupling is loosened.

Now the efficiency of the secondary circuit as a radiator depends both on the energy of each oscillation and on the number of oscillations that follow each other in a train, and we have seen that when $a=b$ the maximum amplitude, and hence the average energy of an oscillation during one complete surge, is independent of the coupling. Hence the best arrangement is to make the coupling as loose as is consistent with the oscillations attaining the maximum amplitude before damping and radiation have reduced them too much. Thus is explained the advantage of the loose coupling in the Marconi transmitter.

10. In the general case, when the circuits are not tuned to the same natural frequency, we have (see § 5)

$$V_1 = \frac{E}{c} \left\{ (s-a) \cos \omega_1 t + (s-b) \cos \omega_2 t \right\},$$

which may be transformed to

$$\begin{aligned} V_1 &= \frac{E}{c} \sqrt{(s-a)^2 + (s-b)^2 + 2(s-a)(s-b) \cos(\omega_2 - \omega_1)t} \\ &\quad \times \cos\left(\frac{\omega_2 + \omega_1}{2}t + \delta\right) \\ &= E \sqrt{1 - 4 \frac{ab}{c^2} \sin^2 \psi \cdot \sin^2 \frac{\omega_2 - \omega_1}{2}t} \cos\left(\frac{\omega_2 + \omega_1}{2}t + \delta\right) \end{aligned}$$

where

$$\tan \delta = \frac{b-a}{c} \tan \frac{\omega_2 - \omega_1}{2}t,$$

and

$$V_2 = p_2 \frac{a}{c} E (\cos \omega_1 t - \cos \omega_2 t)$$

which may be transformed to

$$V_2 = 2E \sqrt{\frac{K_1}{K_2}} \cdot \frac{\sqrt{ab}}{c} \sin \psi \cdot \sin \frac{\omega_2 - \omega_1}{2}t \cos\left(\frac{\omega_2 + \omega_1}{2}t - \frac{\pi}{2}\right),$$

showing that in this case ($a \neq b$) both the amplitude and the phase of the oscillations of V_1 vary with the time, and that

the amplitude of V_1 does not become zero every surge as when $a=b$, its minimum value being

$$E\sqrt{1 - 4\frac{ab}{c^2}\sin^2\psi}$$

which $=0$ as it ought when $a=b$.

The energies in the two circuits are now (see § 9)

$$\frac{1}{2}K_1E^2\left(1 - 4\frac{ab}{c^2}\sin^2\psi\sin^2\frac{\omega_2 - \omega_1}{2}t\right),$$

$$\frac{1}{2}K_1E^2 \times 4\frac{ab}{c^2}\sin^2\psi\sin^2\frac{\omega_2 - \omega_1}{2}t,$$

showing that the energy which surges into and out of each circuit is equal to

$$\frac{1}{2}K_1E^2 \times \frac{4ab}{c^2}\sin^2\psi = S \text{ (say).}$$

If at the instant when S has all entered the radiating circuit for the first time the primary circuit be broken, then S will have to remain in the radiating circuit, which will now proceed to vibrate with its own natural frequency, and the vibrations will persist until damping and radiation have used up the energy S .

This is the theory of the quenched spark which can be very strikingly demonstrated by means of the pendulum model.

In doing so, it is obviously impossible to perform on the first pendulum the action analogous to breaking the primary circuit without disturbing the motion of the remainder of the system. Instead of placing the bob on its platform, the result desired can be very approximately obtained by taking it in the hand so as to slacken its strings.

11. The "triangle" with its associated equations will be useful as a means for solving many questions dealing with the tuning or adjustment of the circuits.

As examples, three cases will be briefly considered. Many such cases will present themselves or arise in practice.

(1) Let us investigate the conditions for obtaining the greatest maximum amplitude of V_2 , the P.D. of the secondary condenser, for a given initial value E of V_1 .

By equations 1. § 5 the max. amp. of V_2 is equal to

$$\frac{b}{c} \cdot \frac{M}{L_1} E.$$

For this to be a maximum, if M/L_1 be given, b/c must be a maximum.

Let the coupling be given also, so that the conditions now are that the ratios

$$M : L_1 : L_2 \text{ are given.}$$

When the coupling is known the angle included between a and b is fixed, and it is easy to show that in the triangle the ratio b/c will be a maximum when the angle opposite b is a right angle. Hence, in this case, when the max. amp. of V_2 is a maximum,

$$a = b \cos 2\psi ;$$

and the max. max. value of V_2 is easily shown to be equal to

$$\frac{1}{2 \cos \psi} \sqrt{\frac{L_1}{L_2}} \cdot E,$$

which as L_1/L_2 is given obviously increases as ψ , and hence as the coupling becomes closer.

Hence, if T_1 and T_2 be the natural period of the circuits,

$$\text{as } T_1 = \frac{2\pi}{\sqrt{a}}, \quad T_2 = \frac{2\pi}{\sqrt{b}},$$

the tuning, or mistuning, should be done in accordance with the law

$$T_2 = T_1 \sqrt{\cos 2\psi},$$

after making the coupling as close as is desirable.

(2) Again, to find the tuning so that the energy that surges into the radiator circuit may be a maximum.

In § 10 we have shown that the maximum energy in the secondary is equal to.

$$\frac{1}{2} K_1 E^2 \frac{4ab}{c^2} \sin^2 \psi,$$

and for this to be a maximum if K_1 and E are given,

$$\frac{4ab}{c^2} \sin^2 \psi$$

must be a maximum.

But

$$\frac{4ab}{c^2} \sin^2 \psi = \frac{4(s-a)(s-b)}{c^2} = 1 - \left(\frac{a-b}{c} \right)^2,$$

which is a maximum when $a=b$, that is when the natural periods of the two circuits are equal.

(3) Again, to investigate the tuning so that the max. amp. of the current C_2 in the secondary may be a maximum.

From equations I. § 5,

$$C_2 = p_2 K_2 \frac{a}{c} E \left\{ -\omega_1 \sin \omega_1 t + \omega_2 \sin \omega_2 t \right\},$$

whose resultant amplitude is equal to

$$p_2 K_2 \frac{a}{c} E \sqrt{\omega_1^2 + \omega_2^2 - 2\omega_1 \omega_2 \cos (\omega_2 - \omega_1) t},$$

whose greatest value is equal to

$$p_2 K_2 \frac{a}{c} E (\omega_1 + \omega_2),$$

which after a few reductions becomes

$$\frac{1}{M} \frac{\sin^2 \psi}{\cos \psi} \frac{\sqrt{s} + \sqrt{s-c}}{c} E.$$

Let one condition under which we find this to be a maximum be that $M = \text{constant}$, then as

$$\frac{\sin^2 \psi}{\cos \psi}$$

increases with ψ within the possible range of the latter, we will determine when

$$\frac{\sqrt{s} + \sqrt{s-c}}{c}$$

is a maximum for a fixed value of $\sin \psi$, the coupling.

Now

$$\frac{\sqrt{s} + \sqrt{s-c}}{c} = \frac{1}{\sqrt{s} - \sqrt{s-c}},$$

and, remembering that

$$c^2 = a^2 + b^2 - 2ab \cos 2\psi,$$

we find that $\sqrt{s} - \sqrt{s-c}$ is a minimum when

$$b = a \cos^2 \psi,$$

and that its minimum value is

$$\sqrt{a} \cdot \sin \psi,$$

which gives for the max. max. amp. of C_2 when M and the coupling are given, the value

$$\frac{\tan \psi}{\sqrt{a}} \cdot \frac{1}{M} E,$$

which increases as the coupling is increased. Hence when M is given the max. max. amp. of C_2 is obtained when the tuning is done in accordance with the law

$$T_2 = T_1 \sec \psi,$$

after making the coupling $\sin \psi$ as close as is desirable.

12. If initial conditions, different from those we have up to the present assumed, be given to the motion, either of the circuits or of the pendulums, different results will ensue, and one case is sufficiently interesting to be briefly discussed here.

When $t=0$, let

$$\begin{aligned} V_1 \text{ or } \theta_1 &= E_1, & V_2 \text{ or } \theta_2 &= E_2, \\ C_1 \text{ or } \dot{\theta}_1 &= 0, & C_2 \text{ or } \dot{\theta}_2 &= 0, \end{aligned}$$

that is, both condensers are charged or both pendulums are deflected at the instant at which motion begins.

Proceeding as in § 5, we find that the motion that ensues is given by

$$\begin{aligned} V_1 \text{ or } \theta_1 &= \frac{1}{c} \left[\{ (s-a)E_1 + p_1 b E_2 \} \cos \omega_1 t + \{ (s-b)E_1 - p_1 b E_2 \} \cos \omega_2 t \right], \\ V_2 \text{ or } \theta_2 &= \frac{1}{p_1 b c} \left[(s-b) \{ (s-a)E_1 + p_1 b E_2 \} \cos \omega_1 t - (s-a) \{ (s-b)E_1 - p_1 b E_2 \} \cos \omega_2 t \right] \\ &\quad \text{with} \quad C_1 = K_1 D V_1, \quad C_2 = K_2 D V_2, \end{aligned}$$

all the symbols having the same significations as before.

Now if the initial P.D.s or deflexions be such that

$$(s-a)E_1 + p_1 b E_2 = 0,$$

the component whose frequency is ω_1 disappears, and the resultant motion is a pure harmonic motion in both circuits whose common frequency is ω_2 , the higher of the two resultant frequencies of the system. In the pendulum system this motion is unstable, and it is therefore probably unstable in the coupled circuits.

Again, if the initial values E_1 and E_2 be such that

$$(s-b)E_1 - p_1 b E_2 = 0,$$

the component whose frequency is ω_2 disappears, and the resultant motion is a pure harmonic motion in both circuits

whose common frequency is ω_1 , the lower of the two resultant frequencies of the system.

In the pendulum system this motion is stable, and it is therefore probably stable in the electrical system. Its stability increases if the friction of the beam is increased; in fact if there is much frictional resistance to the motion of the beam, any kind of motion of the pendulums even when they differ much in length quickly degenerates into this motion.

This suggests that the pendulum model might be used to illustrate some of the problems that arise in the paralleling of alternators.

Substituting from the equation of condition,

$$(s-b)E_1 - p_1 b E_2 = 0,$$

in the general expressions for V_1 and V_2 , we find that the equations of motion take the simple forms

$$\begin{aligned} V_1 &= E_1 \cos \omega_1 t, & V_2 &= E_2 \cos \omega_1 t, \\ C_1 &= -\omega_1 K_1 E_1 \sin \omega_1 t, & C_2 &= -\omega_1 K_2 E_2 \sin \omega_1 t. \end{aligned}$$

Thus there is no transfer of energy from one circuit to the other, and it can be shown that

$$\begin{aligned} \frac{1}{2} L_1 C_1^2 + M C_1 C_2 + \frac{1}{2} L_2 C_2^2 &= \frac{1}{3} (K_1 E_1^2 + K_2 E_2^2) \sin^2 \omega_1 t, \\ \frac{1}{2} K_1 V_1^2 + \frac{1}{2} K_2 V_2^2 &= \frac{1}{2} (K_1 E_1^2 + K_2 E_2^2) \cos^2 \omega_1 t. \end{aligned}$$

13. The model can be modified so as to be the exact analogue to the coupled circuits of a wireless receiver when receiving signals.

The first pendulum, instead of being a simple one, is now a compound one, triangular in shape. The base of the triangle is fitted with knife-edges which rest on suitable planes on the upper surface of the beam, while the vertex of the triangle hangs downwards.

The disturbance arriving at the receiver is imitated by a periodic pure couple transmitted to this pendulum *from the beam* by means of a simple electromagnet device which can be energized through light and very flexible wires. A suitable arrangement is to attach to the pendulum a short permanent bar-magnet, above and perpendicular to its knife-edge, and to fix vertically to the beam two short straight electromagnets, one under each pole of the permanent magnet, and with their windings in the same direction.

There are well-known methods of obtaining an alternating current of small and adjustable frequency, suitable to operate

the pendulum; and when the electromagnets are energized by such a current the mutual stress between the beam and the pendulum will be approximately a pure couple.

14. If the mutual stress between the beam and the pendulum be the periodic couple $P = p \cos \alpha t$, the equations of motion of the system can easily be shown to be

$$\begin{aligned} (M + m_1 + m_2) \ddot{x} - m_1 h \ddot{\theta}_1 + m_2 l_2 \ddot{\theta} &= 0 \\ -\ddot{x} + \frac{k^2 + h^2}{h} \ddot{\theta}_1 + g \theta_1 &= \frac{P}{m_1 h} \\ \ddot{x} + l_2 \ddot{\theta}_2 + g \theta_2 &= 0, \end{aligned}$$

where m_1 is the mass of the first pendulum as before, k its radius of gyration round its centre of mass, and h the distance of its centre of mass below the knife-edges.

Putting l_1 for $\frac{k^2 + h^2}{h}$, the length of the simple pendulum equivalent to the compound one, and proceeding exactly as in § 5, we obtain the following equations connecting θ_1 , θ_2 , and P ,

$$\left. \begin{aligned} (D^2 + \mu_1^2) \theta_1 &= -p_1 D^2 \theta_2 + y P, \\ (D^2 + \mu_1^2) \theta_2 &= -p_2 D^2 \theta_1, \end{aligned} \right\} \quad \text{. . . . (I.)}$$

where

$$\mu_1^2 = \frac{M + m_1 + m_2}{(M + m_1 + m_2) l_1 - m_1 h} g, \quad p_1 = \frac{m_2 l_2}{(M + m_1 + m_2) l_1 - m_1 h},$$

$$\mu_2^2 = \frac{M + m_1 + m_2}{M + m_1} \frac{g}{l_2}, \quad p_2 = \frac{m_1}{M + m_1} \frac{h}{l_2},$$

$$y = \frac{1}{m_1 h} \frac{M + m_1 + m_2}{(M + m_1 + m_2) - m_1 h}.$$

[*Note.* θ_1 must always be kept less than the angle of friction between the knife-edge and the plane on which it bears.]

15. If a periodic E.M.F. $= P = p \cos \alpha t$ act on the receiving circuit of a wireless receiver, the equations for the currents in the circuits are (see §§ 1, 2)

$$r_1 C_1 = -M D C_2 + P,$$

$$r_2 C_2 = -M D C_1,$$

and for the P.D.s of the condensers in the circuits are

$$r_1 K_1 V_1 = -MK_2 DV_2 + D^{-1}P,$$

$$r_2 K_2 V_2 = -MK_1 DV_1;$$

and as

$$r_1 = L_1 \frac{D^2 + \mu_1^2}{D}, \quad r_2 = L_2 \frac{D^2 + \mu_2^2}{D},$$

(damping being neglected), the latter become

$$\left. \begin{aligned} (D^2 + \mu_1^2)V_1 &= -p_1 D^2 V_2 + \frac{P}{L_1}, \\ (D^2 + \mu_2^2)V_2 &= -p_2 D^2 V_1, \end{aligned} \right\} \dots \dots (I.)$$

where

$$\begin{aligned} \mu_1^2 &= \frac{1}{K_1 L_1}, & \mu_2^2 &= \frac{1}{K_2 L_2}, \\ p_1 &= \frac{K_2 M}{K_1 L_1}, & p_2 &= \frac{K_1 M}{K_2 L_2}, \end{aligned}$$

as before in § 3.

Thus, as the differential equations in § 14 connecting the pendulum deflexions are identical in form with the differential equations, given in this paragraph, connecting V_1 and V_2 for the receiver coupled circuits when receiving, and as the equations connecting the angular velocities of the one system are also identical in form with those connecting the currents in the other system; and as all the variables and initial conditions for one system can be expressed by the same symbols as the analogous variables and initial conditions for the other system, the modification of the mechanical model proposed is an exact analogue to the coupled circuits of a wireless receiver when receiving.

16. When damping is taken into account, the different variables in the case of the coupled circuits of a transmitter satisfy the following differential equation (see § 2),

$$\{\cos^2 \psi D^4 + 2(\lambda_1 + \lambda_2)D^3 + (a + b + 4\lambda_1 \lambda_2)D^2 + 2(b\lambda_1 + a\lambda_2)D + ab\}\phi = 0, \quad (I.)$$

where $a = \mu_1^2, \quad b = \mu_2^2, \quad \sin^2 \psi = \frac{M^2}{L_1 L_2},$

$$2\lambda_1 = \frac{R_1}{L_1}, \quad 2\lambda_2 = \frac{R_2}{L_2}.$$

We will now proceed to investigate this case when squares and higher powers of the damping coefficients are neglected.

Let the operator in (I.) above, after neglecting $4\lambda_1\lambda_2$, be identified with

$$\cos^2 \psi (D^2 + 2n_1 D + \omega_1^2)(D^2 + 2n_2 D + \omega_2^2),$$

when we find that

$$\left. \begin{aligned} \cos^2 \psi (\omega_1^2 + \omega_2^2) &= a + b, \\ \cos^2 \psi \omega_1^2 \omega_2^2 &= ab, \\ \cos^2 \psi (n_1 + n_2) &= \lambda_1 + \lambda_2, \\ \cos^2 \psi (\omega_2^2 n_1 + \omega_1^2 n_2) &= b\lambda_1 + a\lambda_2. \end{aligned} \right\} \quad \text{(II.)}$$

The first two of these relations give ω_1^2 and ω_2^2 , and show that the values of the latter in terms of the triangle are the same as before, namely,

$$\omega_1^2 = \frac{ab}{s}, \quad \omega_2^2 = \frac{ab}{s-c}.$$

From the last two the resultant damping coefficients n_1 and n_2 are at once obtained when we remember the easily proved relations

$$\omega_1^2 \sin^2 \frac{A}{2} + \omega_2^2 \cos^2 \frac{A}{2} = a,$$

$$\omega_1^2 \sin^2 \frac{B}{2} + \omega_2^2 \cos^2 \frac{B}{2} = b,$$

where A and B are angles of the triangle.

Thus we find that

$$\left. \begin{aligned} n_1 \cos^2 \psi &= \lambda_1 \sin^2 \frac{B}{2} + \lambda_2 \sin^2 \frac{A}{2}, \\ n_2 \cos^2 \psi &= \lambda_1 \cos^2 \frac{B}{2} + \lambda_2 \cos^2 \frac{A}{2}. \end{aligned} \right\} \quad \text{(III.)}$$

Hence V_1 , V_2 , C_1 , and C_2 are each the resultant of two damped harmonic oscillations, whose damping coefficients are n_1 and n_2 respectively, and whose frequencies are $\sqrt{\omega_1^2 - n_1^2}$, $\sqrt{\omega_2^2 - n_2^2}$, which, when the second power of the damping coefficients is neglected, are ω_1 and ω_2 respectively, and n_1 , n_2 , ω_1 , ω_2 are determined by the above relations in terms of the constants of the individual circuits of the transmitter and of their coupling.

17. When $a=b$, that is, when the natural frequencies of the two circuits are equal, it is easy to show that

$$n_1 = \frac{a}{2s} (\lambda_1 + \lambda_2) = \frac{\omega_1^2}{2a} (\lambda_1 + \lambda_2),$$

$$n_2 = \frac{a}{2(s-c)} (\lambda_1 + \lambda_2) = \frac{\omega_2^2}{2a} (\lambda_1 + \lambda_2);$$

hence

$$\frac{n_1}{n_2} = \frac{\omega_1^2}{\omega_2^2}.$$

As the product of wave-length into frequency is constant, and as ω_1 is less than ω_2 ,

$$\frac{\omega_1^2}{\omega_2^2} \text{ being equal to } \frac{s-c}{s},$$

we see that the oscillation with greatest wave-length is the least damped.

The same is true in general, as can be seen by putting equations III. § 16 in the form

$$2n_1 \cos^2 \psi = \lambda_1 + \lambda_2 - (\lambda_1 \cos B + \lambda_2 \cos A),$$

$$2n_2 \cos^2 \psi = \lambda_1 + \lambda_2 + (\lambda_1 \cos B + \lambda_2 \cos A).$$

18. The general solution of

$$(D^2 + 2n_1 D + \omega_1^2)(D^2 + 2n_2 D + \omega_2^2)\phi = 0$$

is of the form

$$\phi = A_1 e^{-n_1 t} \cos(\omega_1 t + \chi_1) + A_2 e^{-n_2 t} \cos(\omega_2 t + \chi_2),$$

where A_1 , A_2 , χ_1 , χ_2 are constants; and ϕ may represent V_1 , V_2 , C_1 , or C_2 , the constants having different values for each.

In order to obtain the complete solution for given initial conditions, use must be made of one of the four relations, similar to

$$(D_2 + 2\lambda_1 D + a)V_1 = -p_1 D^2 V_2,$$

obtainable from the early part of this paper (see §§ 1, 2, 3) in the same way as in § 5.

It will be found, if the first power only of the damping is taken account of, and if when $t=0$, $V_1=E$, $V_2=0$, $C_1=0$,

$C_2=0$, that the complete solution is given by

$$\begin{aligned} V_1 &= \frac{E}{c} \left\{ (s-a)e^{-n_1 t} \cos(\omega_1 t + \alpha_1) + (s-b)e^{-n_2 t} \cos(\omega_2 t + \alpha_2) \right\}, \\ V_2 &= p_2 a \frac{E}{c} \left\{ e^{-n_1 t} \cos(\omega_1 t + \beta_1) - e^{-n_2 t} \cos(\omega_2 t + \beta_2) \right\}, \\ C_1 &= -\frac{K_1 E}{c} \left\{ \omega_1 (s-a)e^{-n_1 t} \sin(\omega_1 t + \gamma_1) + \omega_2 (s-b)e^{-n_2 t} \sin(\omega_2 t + \gamma_2) \right\}, \\ C_2 &= p_2 a \frac{K_2 E}{c} \left\{ -\omega_1 e^{-n_2 t} \sin(\omega_1 t + \delta_1) + \omega_2 e^{-n_2 t} \sin(\omega_2 t + \delta_2) \right\}, \end{aligned}$$

where $p_2 = \frac{K_1 M}{K_2 L_2} = b K_1 M$ as before, and

$$\gamma_1 = 4 \frac{s-b}{c^2 \omega_1} \zeta, \quad \gamma_2 = -4 \frac{s-a}{c^2 \omega_2} \zeta,$$

$$\delta_1 = 2 \frac{a-b}{c^2 \omega_1} \zeta, \quad \delta_2 = 2 \frac{a-b}{c^2 \omega_2} \zeta,$$

in which $\zeta = a\lambda_2 - b\lambda_1$

and
$$\alpha_1 = \gamma_1 - \frac{n_1}{\omega_1}, \quad \alpha_2 = \gamma_2 - \frac{n_2}{\omega_2},$$

$$\beta_1 = \delta_1 - \frac{n_1}{\omega_1}, \quad \beta_2 = \delta_2 - \frac{n_2}{\omega_2}.$$

LX. *On the Refraction and Dispersion of Gaseous Compounds, and the Cause of the Divergence from Additive Relations.* By CLIVE CUTHBERTSON*.

IT is well known that the refractivities of simple gaseous compounds do not follow an additive rule so closely as those of solids or liquids. The refraction equivalents of Gladstone and Dale and their followers were found to be fairly constant, at any rate for the same class of compound. But, in gases, the discrepancies observed are much wider; and this appears the more surprising since, in other fields of research, the gaseous state has proved peculiarly favourable for the discovery of simple relations.

With the object of investigating the cause of these apparent anomalies the writer has, with the help of others, measured the refraction and dispersion of a number of

* Communicated by Prof. A. W. Porter, F.R.S.

elements and simple compounds in the gaseous state between $\lambda\lambda$ 6708 and 4800; and, though the field of investigation is still somewhat restricted, sufficient *data* have now been collected to warrant the formulation of an hypothesis which seems to explain, in a qualitative way, the changes in refraction, dispersion, and absorption which are observed when gaseous compounds are formed from elements.

In the experimental work the refractivity of each substance was first determined for the green mercury line $\lambda=5461$, and reduced to a standard density, viz. that of hydrogen at 0° C. and 760 mm. multiplied by the ratio of the theoretical molecular weight to that of hydrogen. The dispersion was then found by measuring the refractivity at seven other wave-lengths, $\lambda\lambda$ 6708, 6438, 5790, 5770, 5209, 5085, 4800, relatively to the value obtained for λ 5461.

The eight values of the refractivity were generally found to fall on a smooth curve, which can be fitted by an equation of Sellmeyer's form

$$\frac{\mu^2 - 1}{2} = \mu - 1 \text{ (approx.)} = \frac{C}{n_0^2 - n^2},$$

where n_0^2 is the square of the frequency of the free vibration in the molecule (assuming there to be only one), and n^2 is the square of the frequency of the light, and is equal to

$$\frac{V^2}{\lambda^2} = \frac{9 \times 10^{20}}{\lambda^2} \text{ (in cms.)}.$$

In the following table (p. 594) are given the values of the constants of this equation, calculated from the experimental results, for those elements and compounds which will be referred to below.

In this table column 4 gives, for convenience, the value of λ_0 corresponding to that of n_0^2 in column 3. Column 5 gives the value of $\mu - 1$ for infinite waves found by equating it to C/n_0^2 . Column 6 shows, in the case of compounds, the additive value of the refractivity, *i. e.* that obtained by adding those of its constituents. In this calculation the refractivity of a single atom of an element is taken as half that found for biatomic molecules, and similarly for polyatomic molecules.

The last column shows the difference between the additive and experimental refractivities of compounds.

The modern theory of dispersion indicates that an intimate relation exists between dispersion and absorption. The refractivity should be abnormally high on the less refrangible

Substance.	$C \times 10^{-27}$.	$n_0^2 \times 10^{-27}$.	$\lambda_0 \times 10^8 (\text{A.U.})$.	$(\mu_\infty - 1) \times 10^6$.	Additive value for compounds.	Change on combination; p.c. of additive value.
(5) Helium (H_1)	1.21238	34992	507	34.648		
(5) Neon (Ne_1)	2.59826	38916	481	66.767		
(5) Argon (A_1)	4.71632	17009	726	275.97		
(5) Krypton (Kr_1)	5.3446	12768	840	418.59		
(5) Xenon (X_1)	6.1209	8978	1001	681.77		
(1) Hydrogen (H_2)	1.692	12409	851.6	136.35		
(1) Nitrogen (N_2)	5.0345	17095	725.6	294.5		
(1) Oxygen (O_2)	3.3970	12804	838.4	265.3		
(1) Sulphur (S_8)	14.424	4600	1398.8	3135.6		
(1) Phosphorus (P_4)	15.22	6534	1173.6	2329.4		
(2) Fluorine (F_2)	195 (D line)		
(3) Chlorine (Cl_2)	7.3131	9629.4	966.8	759.46		
(3) Bromine (Br_2)	4.2838	3919.2	1515.4	1093		
(3) Iodine (I_2)	λ_{6438} 2100		
				λ_{6100} 2160		
Compounds.						
(3) Steam (H_2O)	2.6270	10697	917.27	245.6	269	- 8.1
(4) Hydrogen sulphide (H_2S)	4.834	7808	1073.6	619.1	659	- 6.1
(4) Sulphur dioxide (SO_2)	5.728	8929	1004	641.5	788	- 18.6
(3) Hydrogen chloride (HCl)	4.6425	10664	918.67	435.34	448	- 2.8
(3) Hydrogen bromide (HBr)	5.1446	8668.4	1018.9	593.5	615	- 3.5
(3) Hydrogen iodide (HI)	5.7900	6556.4	1372.7	883.1	918?	- 3.8
(3) Ammonia (NH_3)	2.9658	8135.3	1051.8	364.6	352	+ 3.6
(3) Nitric oxide (NO)	3.5210	12216	858.3	288.2	280	+ 3.0
(3) Nitrous oxide (N_2O)	5.6685	11416	887.9	496.5	427	+ 16.3
(3) Ozone (O_3)	2.0703	4281.4	1449.9	483.6	398	+ 21.5

(1) C. & M. Cuthbertson, Proc. Royal Soc. lxxxiii. p. 151 (1909).

(2) C. Cuthbertson and E. B. R. Prideaux, Phil. Trans. 205 A, p. 319 (1905),

(3) C. & M. Cuthbertson. See a paper recently presented to the

Royal Society, but not yet printed.

(4) C. & M. Cuthbertson, Proc. Royal Soc. lxxxiii. p. 171 (1909).

(5) C. & M. Cuthbertson, Proc. Royal Soc. lxxxiv. p. 13 (1910).

side of an absorption band, and abnormally low on the more refrangible side. It may, therefore, be expected that the changes of position of absorption bands in the spectra of elements or compounds should corroborate the conclusions to be drawn from the variations of refraction and dispersion.

We are, thus, able to obtain three kinds of evidence from which to infer the physical meaning of the changes which take place. If, in the equation given above, C is altered by the act of combination, the whole scale of the figures is proportionally affected. If the free frequency is changed the value of n_0^2 will differ from that which it would have had on an additive hypothesis. If the absorption spectrum of the compound differs from that of its constituents, we have a clue to the identification of that portion of the refractivity which is connected with it.

The experimental results shown in the table above, and the concurrent changes in absorption, so far as they are known, may be summarized as follows:—

A. (1) In hydrochloric, hydrobromic, hydriodic acids, hydrogen disulphide, and sulphur dioxide, the refractivity of the compound is less than the sum of the refractivities of its constituents, and the dispersive power of the compound lies between those of its constituents.

(2) In the spectra of chlorine, bromine, iodine, and sulphur, strong absorption bands occur in the violet and near ultra-violet, which disappear in the compound.

B. (1) In nitrous oxide, nitric oxide, ammonia, and ozone, the refractivity of the compound is greater than the sum of the refractivities of the constituents, and the dispersive power is greater than that of either constituent.

(2) In the spectra of nitrous oxide, nitric oxide, and ozone, absorption-bands appear in the ultra-violet which are not present in the spectra of the elements.

To explain these results I propose the following hypothesis:—

(1) That the refractivity of a gaseous element (except those whose molecules are monatomic) or compound is mainly made up of two portions which may be called the atomic and the interatomic. The former is due to vibrations of parts of the *same* atom relatively to one another (on the electromagnetic theory of electrons relatively to the rest of the atom). The free frequency lies in the extreme violet ($\lambda=1000$ A.U. approximately), and the dispersion curve is very flat in the visible region. The refractivity due to this

mode of vibration is roughly $\cdot 8$ or $\cdot 9$ of the whole refractivity measured in the visible. The absorption connected with it is that which lies in the Schumann region. The atomic refractivity, being due to vibrations governed by forces which have their seat exclusively in a single atom, may be assumed to remain nearly constant. The latter, or interatomic portion of the refractivity, is the result of the existence of free periods in the visible or neighbouring portions of the ultra-violet or infra-red, due to forces which have their seat in more than one atom of the same molecule. The absorption due to these vibrations is that which is observed in the spectrum of these regions. The interatomic refractivity of an atom of an element varies with the atom with which it is combined, and with the nature of the linkage.

(2) When two elements combine to form a compound the observed changes of refraction, dispersion, and absorption are due to the disappearance of the interatomic portions of their refractivities and the appearance of new interatomic free frequencies.

An example will make the hypothesis clearer. Gaseous chlorine is characterized by high refractivity, moderately high dispersive power, and strong continuous absorption in the ultra-violet. Hydrogen has low refractive and dispersive power and exhibits no trace of absorption up to the limits of the Schumann region. The resulting compound (HCl) has a refractivity 2·8 per cent. less than the sum of the refractivities of $\frac{1}{2}(\text{Cl}_2) + \frac{1}{2}(\text{H}_2)$, a dispersive power intermediate between those of chlorine and hydrogen, and an absence of absorption, so far as is known, in the ultra-violet.

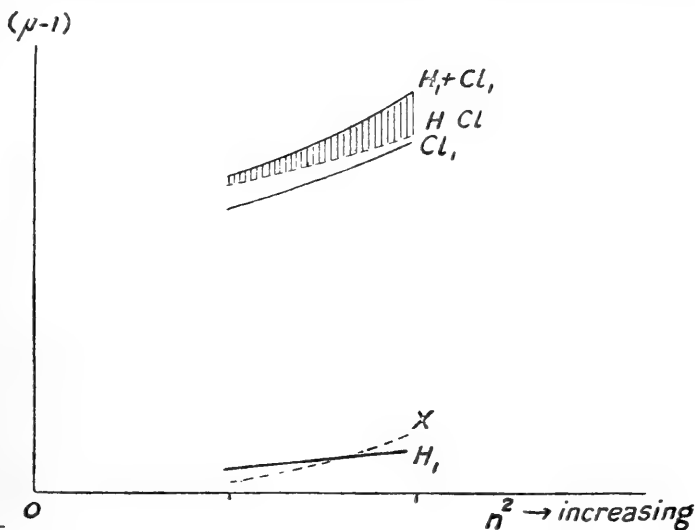
In the first place it appears highly probable that both the chlorine and the hydrogen atom carry into the compound the main portion of their refractivity. The additive rule fails, no doubt, to go further than a first approximation, even in the most favourable instances; but no one who studies the figures for gases or the work of Gladstone and Dale on solids and liquids can avoid the conviction that this rule must be the starting point of the explanation.

We have, then, to account for a small change in the sum of the refractive powers of the two elements, coupled with a considerable change in the dispersive power, which is indicated by the increase of n_0^2 from $9629\cdot 4 \times 10^{27}$ in Cl_2 to 10697×10^{27} in HCl, and the disappearance of an absorption band. This could be done by supposing that the refractivity of one of the elements (Cl_2) contains a term of which the absolute value is small but the slope steep, and that this term disappears when the molecule is broken up. The

curve which expresses such a term would rise rapidly, indicating an absorption band in the near ultra-violet, as is the case in chlorine, and the disappearance of this term would be accompanied by the disappearance of the absorption band, as we find is the case when hydrochloric acid is formed.

The inference that the forces which determine this free frequency have their seat in more than one atom is based on the fact that when the link which binds the atoms of chlorine together is broken the absorption band disappears.

In the figure these changes are exhibited graphically.



Plotting the refractivities against squares of frequencies, let Cl_1 denote the refractivity of gaseous chlorine divided by two, H_1 that of hydrogen divided by two, $H_1 + Cl_1$ the additive curve, and HCl the experimental curve for hydrogen chloride. What has to be accounted for is the disappearance of the portion indicated by vertical shading between $H_1 + Cl_1$ and HCl . Consider this portion as due to a distinct free frequency, and lay it down on the base-line as shown at X . It is evident that the curvature is great, since the ratio of the ordinates at the red and violet ends is greater than when the curve is bodily shifted higher, and it is natural to associate it with the absorption band which occurs in the near ultra-violet in chlorine.

It may be objected that no reason has been shown why the whole of the observed changes should be attributed to the chlorine molecule, and no allowance made for the disappearance of the interatomic refractivity of the hydrogen molecule or the appearance of a new interatomic effect for the molecule of hydrochloric acid. The criticism is just; and it must be admitted that some allowance ought to be

made for these changes. But reasons can be advanced for assigning to them less importance than is given to the change in the chlorine molecule. In the first place, the refractivity of hydrogen is less than one-fifth of that of chlorine, so that small changes in its refractivity due to similar causes would probably be in the same proportion. The same argument applies to hydrochloric acid, whose refractivity is about one-half that of chlorine. Again, neither hydrogen nor hydrochloric acid shows any absorption in the ultra-violet as chlorine does, so that, on the proposed hypothesis, the changes in their refraction and dispersion, due to the breaking up and formation of the molecules respectively, may also be expected to be small. Finally, the interatomic effects due to hydrogen and hydrochloric acid occur on different sides of the equation and tend to balance each other.

But the best test of the legitimacy of the hypothesis is to be found in the numerical results which are obtained from it.

The effect of the preceding analysis has been to split up the expression for the refractivity of chlorine into two parts, one of which, it is suggested, is due to the atomic and the other to the interatomic frequencies of the chlorine molecule. The values of the atomic refractivity are obtained by deducting the experimental values for $\frac{1}{2}(\text{H}_2)$ from those for HCl , while those for the interatomic refractivity of Cl_2 are found by deducting twice the resulting figure for (Cl_1) from the experimental values for (Cl_2) .

The first calculation gives eight values for the atomic refractivity, which are fitted by the curve given by

$$(\mu-1)_{\text{Cl}_1} = \frac{3.8787 \times 10^{27}}{10558 \times 10^{27} - n^2}, \quad . \quad . \quad . \quad (1)$$

while those for the interatomic refractivity are given by

$$(\mu-1)_{\text{Cl}_1-\text{Cl}_1} = \frac{.07302 \times 10^{27}}{2935 \times 10^{27} - n^2}. \quad . \quad . \quad . \quad (2)$$

The relations of the refraction, dispersion, and absorption of bromine and hydrobromic acid and iodine and hydriodic acid are exactly similar to those of chlorine and hydrochloric acid.

Adopting the same procedure as that given above we obtain for the atomic refractivities of bromine and iodine:—

$$(\mu-1)_{\text{Br}_1} = \frac{4.3566 \times 10^{27}}{8294 \times 10^{27} - n^2}, \quad . \quad . \quad . \quad (3)$$

$$(\mu-1)_{\text{I}_1} = \frac{5.1548 \times 10^{27}}{6325 \times 10^{27} - n^2}, \quad . \quad . \quad . \quad (4)$$

and for the interatomic

$$(\mu-1)_{\text{Br}_1-\text{Br}_1} = \frac{0.039018 \times 10^{27}}{713.4 \times 10^{27} - n^2}, \quad \dots \quad (5)$$

$$(\mu-1)_{\text{I}_1-\text{I}_1} = \frac{0.0893 \times 10^{27}}{456 \times 10^{27} - n^2}. \quad \dots \quad (6)$$

It will be noticed that the three expressions on the right-hand side of (1), (3), (4) form a series in which the numerators increase regularly with increasing atomic weight, and the denominators decrease. In this respect they resemble the expressions for the refractivity of the three inert gases argon, krypton, and xenon which I published two years ago* ; and, if the numerators of the six expressions are compared together by pairs, it is found that the numbers bear the same proportion to each other.

Comparison of the values of C in the expression $\mu-1 = C/n_0^2 - n^2$ for the halogens and inert gases.

	C'/C'' .	Ratio.
Chlorine	3.8787	$= .822,$
Argon	4.7163	
Bromine	4.3566	$= .815,$
Krypton	5.3446	
Iodine	5.1548	$= .842.$
Xenon	6.1209	

Since the numerical values of the refractivities of each triad are in the ratio of 2, 3, and 5 approximately, it follows that the denominators of the same formulæ, when compared in the same manner by pairs, bear approximately the same ratio.

Comparison of the values of n_0^2 for the halogens and inert gases.

	$n_0'^2/n_0''^2$.	Ratio.
Chlorine	10558	$= .621,$
Argon	17009	
Bromine	8294	$= .650,$
Krypton	12768	
Iodine	6325	$= .705.$
Xenon	8978	

* Phil. Mag. January 1911, p. 69.

The parallelism between these two sets of figures is unmistakable, and seems to afford strong evidence that this method of obtaining expressions for the refractivity of the halogen atoms is on the right track.

But it is possible to carry the comparison a step further. In the paper in the *Phil. Mag.* just referred to it was shown that, in the case of the four inert gases whose critical temperature has been determined, there is a constant ratio between the squares of the numerator of the dispersion formulæ (which, on Drude's theory, are proportional to the number of electrons in the atom which influence dispersion) and the critical temperatures. It, therefore, occurred to me to compare the critical temperatures of the halogens with those of the inert gases. Unfortunately, the determinations for bromine and iodine rest on the authority of only one observer; but, assuming their accuracy, the proportionality is evident.

Comparison of the critical temperatures of the
halogens and inert gases.

Element.	T _c . Absolute.	Ratio.	Observer.
Chlorine...	420	2.70	Knietzsch (419), Ladenberg (421). Ramsay and Travers.
Argon.....	155.6		
Bromine...	575	2.73	Nadeschdine. R. & T.
Krypton...	210.5		
Iodine ...	785	2.71	Radice. Patterson, Cripps & Whytlaw-Gray.
Xenon ...	289.6		

It follows that there is a constant ratio between the squares of the numerators of the expressions for the refractivities of the halogen atoms and their critical temperatures.

Turning now to the expressions assumed to be connected with the interatomic free frequencies (2), (5), (6), we can test the usefulness of the hypothesis by comparing the position of the calculated free frequency with that of the centre of the absorption band. The coincidences are not so striking as in the case just discussed, but, considering that we are here dealing with figures which are the differences between two nearly equal quantities and that the calculation takes no account of the influence of absorption on the value of the free frequency, the agreement is not unsatisfactory.

It will be observed that, in each case, the calculated free frequency is greater than the observed, and this is also true in the case of ozone and of nitrous oxide, nitric oxide, and even of oxygen, so far as can be judged without having observed the actual centre of the absorption-band of the latter element. It seems probable that the dispersion curve

Element.	Position of absorption band observed.	Wave-length of free vibrations (calculated).
Chlorine	3580—3020	1750
Bromine	{ visible—3832 2500—limits of ob. }	3352
Iodine	5000	4560

begins to be flatter than that which the simple theory demands a long way from the free frequency. It is unfortunate that we have no determinations of the coefficients of absorption in the case of these gases, by the use of which a closer approximation might be obtained.

In the case of the sulphur compounds H_2S and SO_2 we find that the evidence points in the same direction. Here, also, we have an element of high refractive, dispersive, and absorptive power united to one of low refractive and dispersive power, and free from absorption; and here again the resulting compound shows a decrease of refraction, a dispersive power intermediate between those of the two components, and a disappearance of the absorption band characteristic of the sulphur molecule. The same hypothesis as in the case of the halogens will account for the *direction* of these changes; but it must be admitted that it is not so successful in accounting for their magnitude. The expressions which I obtain for the atomic refraction of one atom of sulphur are

$$\frac{3.4168 \times 10^{27}}{7078 \times 10^{27} - n^2} \quad \text{and} \quad \frac{2.7780 \times 10^{27}}{7384 \times 10^{27} - n^2},$$

when calculated from H_2S and SO_2 respectively. But there is room for many important disturbing factors in the complexity of the molecules both of sulphur and of the compounds. A comparison of the cases of NO , N_2O and NH_3 shows that the number of atoms in the molecule has a considerable effect on the interatomic portion of the refractivity.

Turning now to the group of compounds in which the refractivity is higher than the sum of the refractivities of its constituents, we observe that they are composed of elements like hydrogen, nitrogen, and oxygen whose refractive and dispersive power is small, so that it might be expected, on our hypothesis, that, when their molecules break up, their loss of these powers would be slight, while, when they unite

into larger or less stable molecules, the new free frequencies introduced between the atoms of the compound would be slower than those between the atoms of the elements, with a correspondingly greater effect on the dispersion.

It should be noted that, in these cases, the only practicable test of our hypothesis is the converse of that which gives such promising results in the case of the halogens. There we neglected the interatomic refractivities of one element and the compound, and obtained a value for the atomic refractivity of the other element. Here we neglect the interatomic refractivities of both elements and obtain a value for the interatomic refractivity of the compound, and this, being the difference between two nearly equal quantities, is liable to much larger errors than the atomic.

In this group the most interesting results are obtained in the case of ozone. Here the refractivity is $21\frac{1}{2}$ per cent. higher than the value for three atoms of oxygen, and the dispersive power is much greater. If we deduct from the experimental values for the refractivity of ozone one and a half times the refractivity of oxygen, we obtain the following result:—

$$\lambda \times 10^8.$$

	6708	5461	4800
$[\mu-1]_{O_3} \times 10^8 \dots$	50764	52000	53290
$\frac{3}{2}[\mu-1]_{O_2} \times 10^8.$	<u>40428</u>	<u>40755</u>	<u>41049</u>
Difference $\times 10^8 \dots$	10336	11245	12241

The figures in the last line, which represent the increase in refractivity due to the interatomic effect in ozone, are fitted by the curve given by

$$[\mu-1]_{O_3-O_2} \times 10^8 = \frac{.12660 \times 10^{27}}{1424.8 \times 10^{27} - n^2}.$$

The wave-length which corresponds with $n_0^2 = 1424.8 \times 10^{27}$ is $\lambda = 2520$. The absorption spectrum of ozone has been most recently measured by Meyer (Drude's *Ann.* xii. p. 849 (1903)), who found a maximum of absorption at $\lambda 2580$.

One other fact with regard to this substance is worth mention. If we calculate the constants of the expression for the refractivity of ozone from the values given in the first line above for $\lambda 6708$ and $\lambda 4800$, we obtain a curve

which gives a value of 52080×10^{-8} at $\lambda = 5461$, instead of 52000 found experimentally. Hence the dispersion curve of ozone has greater curvature than can possibly be explained on the hypothesis of a single free frequency. At least two are required. The same effect was observed in a less degree in the case of chlorine.

For the three nitrogen compounds, ammonia, nitrous oxide, and nitric oxide, the refractivity of the compound is in excess and the dispersion curve becomes much steeper, suggesting the appearance of new free frequencies in the ultra-violet. But in the case of nitrous oxide the absorption spectrum has, apparently, not been examined. Nitric oxide has a band which begins about 3000 A.U. and increases to the limits of observation (Kreusler). The calculated band falls at $\lambda = 1940$. Ammonia is said by Soret to show an absorption band in the ultra-violet, but Hartley denies this.

The case of steam is a difficulty on the hypothesis now advanced; for though the dispersion curve has greater curvature than those of hydrogen and oxygen, the refractivity is notably less. This conjunction of changes is not impossible under the hypothesis, but it is less easily explicable.

In concluding this paper I wish to emphasize the fact that quantitative verification of the hypothesis is not claimed. The *data* are still too scanty, the range of observation too short, the gaps, both in mathematical theory and in observation, too many to permit this. All that it is desired to maintain is that the *direction* of the changes of refractivity, dispersion, and absorption consequent on the formation of compounds are consistent with the hypothesis that in every gaseous element (except those whose molecule is monatomic) and compound the refractivity is made up mainly of two portions. Of these one is governed by a free frequency in the far ultra-violet and is responsible for the bulk of the refractive power. Since it is always associated with the presence of an atom, it may be supposed to be due to forces which have their seat within the atom, and are hardly at all affected by neighbouring atoms. The other is due to a free frequency governed by forces which have their seat in more than one atom of the molecule, and which change with the linkage.

I think the numerical results obtained by the adoption of this hypothesis in the case of the simplest series of compounds known, the halogens and halogen acids, is strongly in its favour; and that the agreement between the observed and calculated positions of the absorption band in ozone is very remarkable.

But whatever value is attached to the numerical evidence by those competent to judge, the broad conclusion from the *direction* of the changes is unaffected.

I should like also to reply to one criticism which has been made. It is not necessary to the hypothesis that the atomic free frequency should be absolutely invariable throughout all chemical changes. If it were the case that a slight change (say 1 per cent.) in the atomic free frequency would account for all the observed changes of refractivity and dispersion, the criticism would have force. But any one who examines the figures in the table for (*e. g.*) hydrogen, nitrogen, and ammonia, will see that no slight change in a frequency can possibly account for the observed changes. For hydrogen $n_0^2 \times 10^{-27} = 12409$, for nitrogen 17095. For ammonia the number which expresses its average value is 8135, an enormous drop. At the same time the refractivity has gone up only $3\frac{1}{2}$ per cent. But if the number of vibrators had remained constant while the average free frequency decreased, the increase of the refractivity must have been much greater than this. Hence, to account for the observed changes, one must also assume that the number of vibrators (? electrons) has fallen off in about the same proportion as the frequency.

These two hypotheses seem much more improbable than that which is here put forward.

LXI. *The Laws of Deflexion of α Particles through Large Angles**. By Dr. H. GEIGER and E. MARSDEN †.

IN a former paper ‡ one of us has shown that in the passage of α particles through matter the deflexions are, on the average, small and of the order of a few degrees only. In the experiments a narrow pencil of α particles fell on a zinc-sulphide screen in vacuum, and the distribution of the scintillations on the screen was observed when different metal foils were placed in the path of the α particles. From the distribution obtained, the most probable angle of scattering could be deduced, and it was shown that the results could be explained on the assumption that the deflexion of a single α particle is the resultant of a large number of very small deflexions caused by the passage of the α particle through the successive individual atoms of the scattering substance.

* Communicated to *k. d.-k. Akad. d. Wiss. Wien*.

† Communicated by Prof. E. Rutherford, F.R.S.

‡ H. Geiger, Roy. Soc. Proc. vol. lxxxiii. p. 492 (1910); vol. lxxxvi. p. 235 (1912).

In an earlier paper *, however, we pointed out that α particles are sometimes turned through very large angles. This was made evident by the fact that when α particles fall on a metal plate, a small fraction of them, about 1/8000 in the case of platinum, appears to be diffusely reflected. This amount of reflexion, although small, is, however, too large to be explained on the above simple theory of scattering. It is easy to calculate from the experimental data that the probability of a deflexion through an angle of 90° is vanishingly small, and of a different order to the value found experimentally.

Professor Rutherford † has recently developed a theory to account for the scattering of α particles through these large angles, the assumption being that the deflexions are the result of an intimate encounter of an α particle with a single atom of the matter traversed. In this theory an atom is supposed to consist of a strong positive or negative central charge concentrated within a sphere of less than about 3×10^{-12} cm. radius, and surrounded by electricity of the opposite sign distributed throughout the remainder of the atom of about 10^{-8} cm. radius. In considering the deflexion of an α particle directed against such an atom, the main deflexion-effect can be supposed to be due to the central concentrated charge which will cause the α particle to describe an hyperbola with the centre of the atom as one focus.

The angle between the directions of the α particle before and after deflexion will depend on the perpendicular distance of the initial trajectory from the centre of the atom. The fraction of the α particles whose paths are sufficiently near to the centre of the atom will, however, be small, so that the probability of an α particle suffering a large deflexion of this nature will be correspondingly small. Thus, assuming a narrow pencil of α particles directed against a thin sheet of matter containing atoms distributed at random throughout its volume, if the scattered particles are counted by the scintillations they produce on a zinc-sulphide screen distance r from the point of incidence of the pencil in a direction making an angle ϕ with it, the number of α particles falling on unit area of the screen per second is deduced to be equal to

$$\frac{Qntb^2 \operatorname{cosec}^4 \phi/2}{16r^2},$$

where Q is the number of α particles per second in the

* H. Geiger and E. Marsden, Roy. Soc. Proc. vol. lxxxii, p. 495 (1909).

† E. Rutherford, Phil. Mag. vol. xxi, p. 669 (1911).

original pencil, n the number of atoms in unit volume of the material, and t the thickness of the foil. The quantity

$$b = \frac{2NeE}{mu^2},$$

where Ne is the central charge of the atom, and m , E , and u are the respective mass, charge, and velocity of the α particle.

The number of deflected α particles is thus proportional to (1) $\text{cosec}^4 \phi/2$, (2) thickness of scattering material t if the thickness is small, (3) the square of the central charge Ne of the atoms of the particular matter employed to scatter the particles, (4) the inverse fourth power of the velocity u of the incident α particles.

At the suggestion of Prof. Rutherford, we have carried out experiments to test the main conclusions of the above theory. The following points were investigated:—

- (1) Variation with angle.
- (2) Variation with thickness of scattering material.
- (3) Variation with atomic weight of scattering material.
- (4) Variation with velocity of incident α particles.
- (5) The fraction of particles scattered through a definite angle.

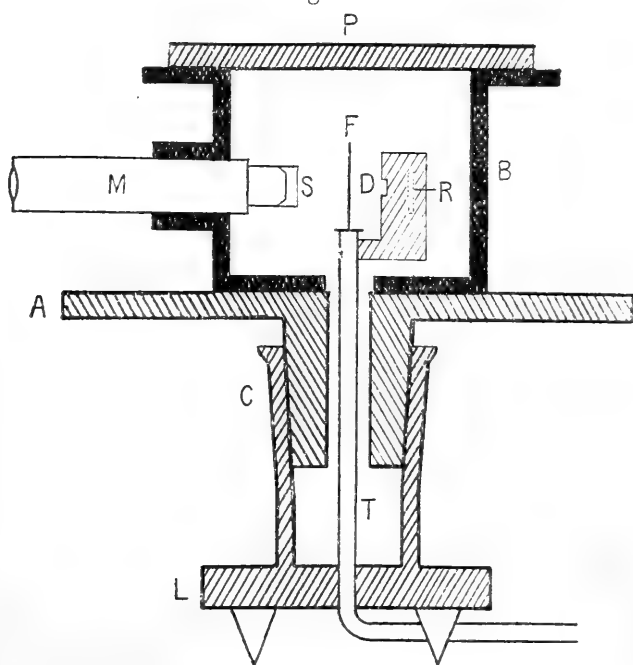
The main difficulty of the experiments has arisen from the necessity of using a very intense and narrow source of α particles owing to the smallness of the scattering effect. All the measurements have been carried out by observing the scintillations due to the scattered α particles on a zinc-sulphide screen, and during the course of the experiments over 100,000 scintillations have been counted. It may be mentioned in anticipation that all the results of our investigation are in good agreement with the theoretical deductions of Prof. Rutherford, and afford strong evidence of the correctness of the underlying assumption that an atom contains a strong charge at the centre of dimensions, small compared with the diameter of the atom.

(1) *Variation of Scattering with Angle.*

We have already pointed out that to obtain measurable effects an intense pencil of α particles is required. It is further necessary that the path of the α particles should be in an evacuated chamber to avoid complications due to the absorption and scattering of the air. The apparatus used is shown in fig. 1, and mainly consisted of a strong cylindrical metal box B, which contained the source of α particles R.

the scattering foil F, and a microscope M to which the zinc-sulphide screen S was rigidly attached. The box was fastened down to a graduated circular platform A, which could be rotated by means of a conical airtight joint C. By rotating the platform the box and microscope moved with it, whilst the scattering foil and radiating source remained in position, being attached to the tube T, which was fastened to the standard L. The box B was closed by the ground-glass plate P, and could be exhausted through the tube T.

Fig. 1.



The source of α particles employed was similar to that used originally by Rutherford and Royds* in their experiments on the nature of the α particle. It consisted of a small thin-walled glass tube about 1 mm. in diameter, containing a large quantity of well purified radium emanation. The α particles emitted by the emanation and its active deposit could pass through the glass walls without much reduction of range. For these experiments the unhomogeneity of the source, due to the different α particles from the emanation, Ra A and Ra C, does not interfere with the application of the law of scattering with angle as deduced from the theory, as each group of α particles is scattered according to the same law.

By means of a diaphragm placed at D, a pencil of α particles was directed normally on to the scattering foil F. By

* E. Rutherford and T. Royds, *Phil. Mag.* vol. xvii. p. 281 (1909).

rotating the microscope the α particles scattered in different directions could be observed on the screen S. Although over 100 millicuries of radium emanation were available for the experiments, the smallness of the effect for the larger angles of deflexion necessitated short distances of screen and source from the scattering foil. In some experiments the distance between the source and scattering foil was 2.5 cm., and the screen moved in a circle of 1.6 cm. radius, while in other experiments these distances were increased. Observations were taken in various experiments for angles of deflexion from 5° to 150° . When measuring the scattering through large angles the zinc-sulphide screen had to be turned very near to the source, and the β and γ rays produced a considerable luminescence on it, thus making countings of the scintillations difficult. The effect of the β rays was reduced as far as possible by enclosing the source in a lead box shown shaded in the diagram. The amount of lead was, however, limited by considerations of the space taken up by it, and consequently observations could not be made for angles of deflexion between 150° and 180° .

In the investigation of the scattering through relatively small angles the distances of source and screen from the scattering foil were increased considerably in order to obtain beams of smaller solid angle.

The number of particles scattered through different angles was found to decrease extremely rapidly with increase of angle, and as it is not possible to count with certainty more than 90 scintillations per minute or less than about 5 per minute, measurements could only be made over a relatively small range of angles at the same time. The number of α particles scattered through large angles was first measured, and as the emanation decayed it was possible to take measurements for smaller and smaller angles, and from the known decay of the emanation measurements taken at different times could be corrected for the decrease of activity.

Even when no scattering foil was used a few scintillations were always observed on the screen. They were obviously due to scattered radiation from the walls of the vessel and from the edge of the diaphragm limiting the beam. The effect was reduced as far as possible by lining the box with paper and by using a substance of low atomic weight, viz. aluminium, for the diaphragm. The number of stray α particles was determined for different positions of the microscope by removing the scattering foil so that the necessary corrections could be applied with certainty.

In order to make the best use of the emanation available,

measurements were made simultaneously with different foils. These foils were attached to frames which fitted into a slot in the tube T in such a way that they could be exchanged and accurately replaced in position. Table I. gives an example of a particular set of countings, when a silver foil was used to scatter the α particles.

TABLE I.—Variation of Scattering with Angle. (Example of a set of measurements.) Silver Foil. Time elapsed since filling of emanation tube, 51 hours. Correction for decay, 0.683.

Angle ϕ .	Scintillations per minute.				$\frac{1}{\sin^4 \phi/2}$.	$N \times \sin^4 \phi/2$.
	Without foil.	With foil.	Corrected for effect without foil.	Corrected for decay, N.		
150...	0.2	4.95	4.75	6.95	1.15	6.0
135 ..	2.6	8.3	5.7	8.35	1.38	6.1
120...	3.8	10.3	6.5	9.5	1.79	5.3
105...	0.6	10.6	10.0	14.6	2.53	5.8
75...	0.0	28.6	28.6	41.9	7.25	5.8
60...	0.3	69.2	68.9	101	16.0	6.3

In this set about 2500 scintillations were counted. After a few days had elapsed the measurements for the smaller angles were repeated and the range of angles extended. Proceeding in this way the whole range of angles was investigated in the course of a few weeks. When measuring relatively large angles of deflexion a wide beam of about 15° radius had to be used in order to obtain a suitable number of scintillations, but for the smaller angles the aperture of the diaphragm confining the beam was reduced considerably, so that the angle at which the scintillations were counted was always large compared with the angular radius of the beam. When changing over from one diaphragm to another comparative measurements for different angles were made so as to obtain an accurate value of the reduction constant.

Table II. gives the collected results for two series of experiments with foils of silver and gold. The thicknesses of the foils were in the first series equivalent to 0.45 and 0.3 cm. air, and in the second series 0.45 and 0.1 cm. air for silver and gold respectively. Col. I. gives the values of the

TABLE II.
Variation of Scattering with Angle. (Collected results.)

I. Angle of deflexion, ϕ .	II. $\frac{1}{\sin^4 \phi/2}$	III. SILVER. IV.		V. GOLD. VI.	
		Number of scintil- lations, N.	$\frac{N}{\sin^4 \phi/2}$	Number of scintil- lations, N.	$\frac{N}{\sin^4 \phi/2}$
150	1.15	22.2	19.3	33.1	28.8
135	1.38	27.4	19.8	43.0	31.2
120	1.79	33.0	18.4	51.9	29.0
105	2.53	47.3	18.7	69.5	27.5
75	7.25	136	18.8	211	29.1
60	16.0	320	20.0	477	29.8
45	46.6	989	21.2	1435	30.8
37.5	93.7	1760	18.8	3300	35.3
30	223	5260	23.6	7800	35.0
22.5	690	20300	29.4	27300	39.6
15	3445	105400	30.6	132000	38.4
30	223	5.3	0.024	3.1	0.014
22.5	690	16.6	0.024	8.4	0.012
15	3445	93.0	0.027	48.2	0.014
10	17330	508	0.029	200	0.0115
7.5	54650	1710	0.031	607	0.011
5	276300	3320	0.012

angles ϕ between the direction of the beam and the direction in which the scattered α particles were counted. Col. II.

gives the values of $\frac{1}{\sin^4 \phi/2}$. In Cols. III. and V. the

numbers of scintillations are entered which were observed for the silver and gold respectively. Corrections are made for the decay of the emanation, for the natural effect, and for change of diaphragm. For the smaller angles corrections have been applied (in no case exceeding 20 per cent.) owing to the fact that the beam of α particles was of finite dimensions and not negligible compared with the angle of deflexion. These corrections were calculated from geometrical considerations. In Cols. IV. and VI. the ratios of the numbers

of scintillations to $\frac{1}{\sin^4 \phi/2}$ are entered. It will be seen that

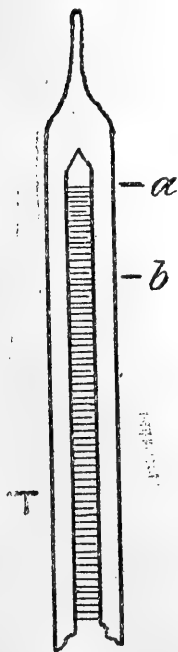
in both sets the values are approximately constant. The deviations are somewhat systematic, the ratio increasing with decreasing angle. However, any slight asymmetry in the apparatus and other causes would affect the results in a systematic way so that, fitting on the two sets of observations and considering the enormous variation in the numbers of scattered particles, from 1 to 250,000, the deviations from constancy of the ratio are probably well within the experimental

error. The experiments, therefore, prove that the number of α particles scattered in a definite direction varies as $\text{cosec}^4 \phi/2$.

Variation with Thickness of Material.

In investigating the variation of scattering with thickness of material, it seemed necessary to use a homogeneous source of α particles, for according to the theory the effect of the change of velocity with increasing thickness will be very appreciable for α particles of low velocity. In the experiments on "compound scattering" by one of us, a source was used consisting of Ra C deposited from radium emanation *in situ* in a small conical tube fitted with a mica window, the emanation being withdrawn when measurements were taken by expanding into a large volume connected to it. In our first experiments we used such a source, but the observations eventually showed it to be unsuitable. After expansion some emanation remains clinging to the walls of the glass tube. This emanation and the Ra A associated with it gives α particles of considerably lower velocity than the α particles of Ra C, and although the number of α particles so contributed was of the order of only a few per cent. of the number from the Ra C, yet owing to the fact that the amount of scattering increases very rapidly with decreasing velocity, the disturbances caused by the slower α particles were so large as to render the source unsuitable for the present work.

Fig. 2.

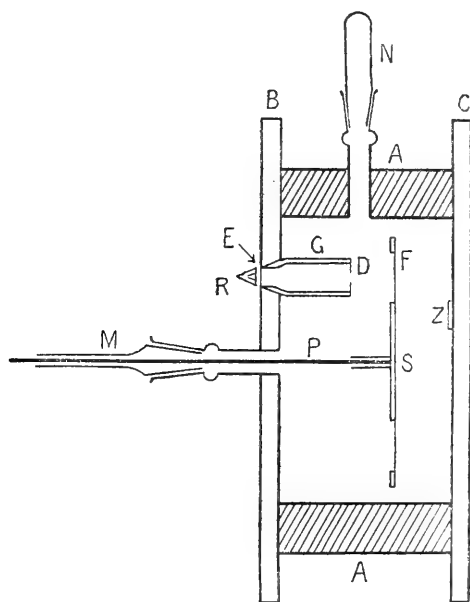


The source finally adopted was prepared as shown in fig. 2. About 80 millicuries of radium emanation were very highly purified and pressed into the conical end of the glass tube T of about 1 mm. internal diameter. After the emanation had remained in position for a sufficient time to attain equilibrium with Ra C, it was expanded into a bulb below, and a small part of the capillary tube was drawn off at *b*. About 1 mm. of the end of the tube which was coated with the Ra C was then cut off (at *a*) and freed from occluded emanation by washing with alcohol and by heating. The resulting source of Ra C was used in the experiments, and with due care its decay was found to be in agreement with theory, at least for the first 80 minutes.

The arrangement used for the comparison of the scattering

of different thicknesses of metal foils is shown diagrammatically in fig. 3. It consists essentially of a source of α radiation R, a diaphragm D, a scattering foil F, and a zinc-sulphide screen Z on which the scattered α particles were observed. The main part of the apparatus was enclosed in a cylindrical brass ring A, the ends of which were planed so that they could be closed airtight by the two glass plates B and C. The depth of the ring was 3.5 cm., and its internal and external diameters 5.5 and 7.5 cm. respectively. Two holes were drilled through the glass plate B, one in the centre and the other 1.65 cm. excentric. The source of radiation R was placed directly against a sheet of mica which was waxed over and closed the opening E. By placing the source outside the apparatus, any small amount of emanation associated with it was prevented from entering the chamber and disturbing the measurements.

Fig. 3.



By means of the diaphragm D a narrow pencil of α particles could be directed on to the scattering foil. The different foils were attached to the disk S and covered five of six holes drilled through it at equal distances from its centre. The uncovered opening was used to determine the natural effect. The disk could be fitted on to the rod P, which was fastened to the ground-glass joint M so that it could be rotated and the different foils brought in front of the diaphragm. The scattered α particles were observed by means of a microscope on the zinc-sulphide screen Z fixed inside the glass plate.

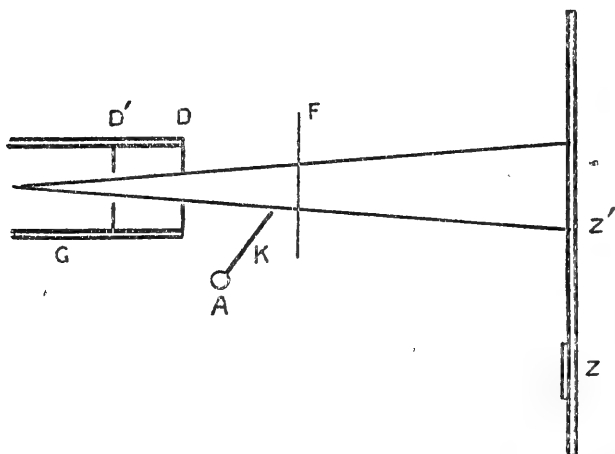
In making the observations the disk carrying the foils was placed in position about 1.2 cm. from the glass plate C. The apparatus was then completely exhausted through a tube not shown in the diagram, charcoal cooled by liquid air being used for the final exhaustion. After the source of radiation had been placed in position, the microscope was adjusted at that part of the zinc-sulphide screen where the scintillations appeared at a rate convenient for counting. With a source of 30 millicuries of Ra C this was usually the case for an angle of deflexion of from 20° to 30° . The area of the screen visible through the microscope was about 1 sq. mm., whilst the main beam of α particles covered an area of about 3 sq. mm.

As soon as the Ra A in the source had decayed completely (*i. e.* after 20 minutes) countings were commenced. Measurements were first taken with the layers of foils of smaller thickness, and as the source decayed they were extended to the thicker foils. From the known decay of the active deposit of radium the measurements could all be corrected for the variation in activity of the source, the results being verified by making observations on the same foils at different times. An experiment generally extended for about 80 minutes. After that time the decay corrections for the source were not always reliable owing to small quantities of radium emanation associated with it, as has been mentioned above. Owing to the relatively short time available in each experiment for the completion of the measurements, only about 100 to 200 scintillations could be counted with each foil.

As in the experiments on the variation of scattering with angle, some scintillations appeared on the zinc-sulphide screen even when no scattering foil was interposed. It was found that these scintillations were due to α particles which had been scattered from the edges of the diaphragm limiting the beam. Experiments were made with paper diaphragms and with aluminium diaphragms of only $\frac{1}{10}$ mm. thickness, whilst a diaphragm D' (fig. 4) was also introduced to prevent scattering from the inside of the glass tube G carrying the main diaphragm D. Even with these precautions the effect was still so large that accurate experiments with foils of low atomic weight would have been impossible. The difficulty was, however, successfully overcome by intercepting the stray α particles by a screen K, which could be turned by means of a ground-glass joint (N in fig. 3) about a vertical axis passing through A so as to be just outside the main pencil. The adjustment was made by observation of the scintillations produced by the main beam on the zinc-sulphide

screen Z, which was temporarily placed at Z'. The magnitude of the effect may be judged from the following figures obtained in a particular experiment with an aluminium diaphragm:—The number of scintillations without both the screen K and the scattering foil F was 60 per minute, whilst by bringing the screen K into position the number was reduced to 0.5 per minute. With the screen K in position and an aluminium foil equivalent to 0.5 cm. air as scattering foil, the number of scintillations was 14 per minute, or about one quarter the effect without screen or scattering foil.

Fig. 4.



In the following table the results of an experiment with gold foils are tabulated. Column I. gives the number of foils and column II. the thicknesses expressed as the stopping power of α particles in centimetres of air as determined by the scintillation method. The figures given in column III. represent the number of scintillations observed on the zinc-sulphide screen. These figures are corrected for the variation of activity with time of the source. A slight correction has been made due to the increase of scattering on account of the decrease of velocity of the α particles in passing through the foils. The magnitude of this correction could be calculated from the results given in the last section of the present paper, and amounted to 9 per cent. in this experiment for the thickest foil used. The last column of the table gives the ratio of the corrected number of scintillations to the thickness. The values are constant within the limits of the experimental error. The variations exhibited by the figures are well within the probability errors, owing to the relatively small number of scintillations which could be counted in the time available.

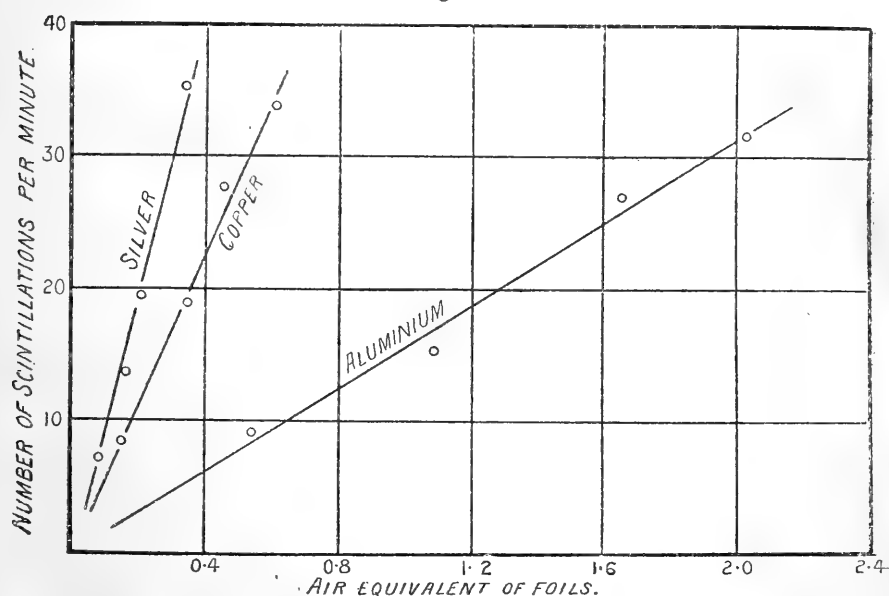
TABLE III.

Gold.—Variation of Scattering with Thickness.

I. Number of Foil.	II. Air equivalent. T in cm.	III. Number N of scintillations per minute.	IV. Ratio $\frac{N}{T}$.
1	0.11	21.9	200
2	0.22	38.4	175
5	0.51	84.3	165
8	0.81	121.5	150
9	0.90	145	160

Similar experiments were carried out with foils of tin, silver, copper, and aluminium. In each set about 1000 scintillations were counted. The results are plotted in fig. 5, where the abscissæ represent the thickness of the scattering foil expressed in centimetres of air equivalent and the ordinates the number of scattered particles. Similar corrections to the above have been introduced in each case.

Fig. 5.



For all the metals examined the points lie on straight lines which pass through the origin. The experiments therefore prove that for small thicknesses of matter the scattering is proportional to the thickness. If there is any appreciable

diminution in velocity of the α particles in passing through the foils, the number of scattered particles increases somewhat more rapidly than the thickness.

Variation with Atomic Weight.

Assuming that the magnitude of the central charge of the atom is proportional to the atomic weight A , Professor Rutherford has shown that the number of α particles scattered by different foils containing the same number of atoms should be proportional to A^2 . With the thin foils which had to be used experimentally, it was found impracticable to calculate the number of atoms per unit area by weighing the foils. It proved much more reliable to deduce the required number of atoms from the air equivalent as found by the reduction of the range of α particles by the scintillation method. This method had the advantage that the thickness was determined at the exact part of the foil which served to scatter the α particles, thus eliminating any errors due to variations in the thickness of the foils. Bragg and others have given numbers connecting the thicknesses of foils of various materials and their stopping power, and it has been shown that for different foils of the same air equivalent the numbers of atoms per unit area are inversely proportional to the square roots of the atomic weights. Consequently if the scattering per atom of atomic weight A is proportional to A^2 , the scattering per centimetre air equivalent will be proportional to $A^2 \times A^{-\frac{1}{2}}$, *i. e.* to $A^{3/2}$.

In the experimental investigation the same apparatus was used as in the previous experiments on the variation of scattering with thickness of material. The openings in the disk S were covered with thin foils of different materials, and their thicknesses chosen in such a way that they gave approximately the same effect of scattering. A number of different sets of experiments were made, the foils being varied in each experiment. The results in a particular experiment are given in Table IV. Columns I. and II. give the foils used and their respective atomic weights. In column III. the air equivalents of the foils are entered. Column IV. gives the number of scintillations observed after correction for the variation in activity of the source and the loss of velocity of the α particles in the foil. Column V. gives the number of scintillations per unit air equivalent of material. In column VI. the values of $A^{3/2}$ are given, and in column VII. the ratios of the numbers of scintillations to $A^{3/2}$ are calculated. The figures are constant within the experimental error.

TABLE IV.

Variation of Scattering with Atomic Weight. (Example of a set of measurements.)

I. Substance.	II. Atomic weight. A.	III. Air equivalent in cm.	IV. Number of scintillations per minute corrected for decay.	V. Number N of scintillations per cm. air equivalent.	VI $A^{3/2}$.	VII. $N \times A^{2/3}$.
Gold	197	·229	133	581	2770	0·21
Tin	119	·441	119	270	1300	0·21
Silver	107·9	·262	51·7	198	1120	0·18
Copper	63·6	·616	71	115	507	0·23
Aluminium..	27·1	2·05	71	34·6	141	0·24

The combined results of four experiments are given in Table V. In the last column are given the ratios of the numbers of scintillations per centimetre equivalent to $A^{3/2}$. This ratio should be constant according to theory. The experimental values show a slight increase with decreasing atomic weight.

TABLE V.

Variation of Scattering with Atomic Weight. (Collected results using Ra C.)

Substance.	Total number of scintillations counted for each material.	$A^{3/2}$.	Ratio of scintillations per cm. air equivalent to $A^{3/2}$ *.
Gold	850	2770	95
Platinum	200	2730	99
Tin	700	1300	96
Silver	800	1120	98
Copper	600	507	104
Aluminium	700	144	110

* *Note 1.*—Since these experiments were carried out, Richardson and one of us (Phil. Mag. vol. xxv. p. 184 (1913)) have determined the masses per unit area per cm. air equivalent for different metals, using the scintillation method. Introducing the results, and calculating the values of the ratio of the scattering per atom divided by A^2 , the following are obtained:—Au 3·4, Pt 3·2, Sn 3·3, Ag 3·6, Cu 3·7, Al 3·6. These numbers show better agreement than those in the last column above, which are calculated on the assumption of Bragg's law.

On account of the importance of these experiments further measurements were made under somewhat different conditions. The main difficulty in the previous experiments arose from the fact, that owing to the rapid decay of the source it was impossible to count in each case a sufficient number of scintillations to obtain a true average value. In the following set of measurements radium emanation in equilibrium with its active deposit was used as source of radiation. The source consisted of a conical glass tube (fig. 6) of about $1\frac{1}{2}$ mm. internal diameter at its widest part, the height of the cone being about 2.5 mm. The end of the tube was closed airtight by a sheet of mica of 0.62 cm. air equivalent. This tube was filled with about 30 milluries of highly purified emanation and placed at R (fig. 3, p. 612) directly against the mica window E, the air equivalent of which was also 0.62 cm.

Fig. 6.



The difficulty introduced by the employment of α particles of different velocities (emanation, Ra A, and Ra C) was eliminated by using foils of approximately the same air equivalent. The α particles therefore suffered the same reduction in velocity in each foil, and the numbers of scattered particles were therefore directly comparable. It was of course impossible to obtain foils of exactly the same air equivalent, but this difficulty was easily overcome by determining the scattering for two foils of the same material, one slightly smaller and the other slightly larger than a standard thickness of 0.6 cm. air equivalent.

Owing to the large variation with atomic weight of the amount of scattering, the foils could not be all directly compared with each other at the same angle. They were therefore compared in sets, the angle being chosen smaller for the sets of lower atomic weight. Column VI. in the following table gives the mean results of the ratio of the number of scattered particles to $A^{3/2}$.

The scattering of carbon was obtained by using thin sheets of paraffin wax which contained about 85.2 per cent. carbon and 14.8 per cent. hydrogen. The air equivalent of the carbon was calculated from Bragg's law to be about 78 per cent. of the whole stopping power, and on account of the low atomic weight of hydrogen all the scattering effect was assumed due to the carbon. The measurements of the scattering were made by comparison with that due to aluminium foils of the same air equivalent.

TABLE VI.

Variation of Scattering with Atomic Weight. (Collected results using Radium emanation.)

I.	II.	III.	IV.	V.	VI.
Substance.	Air equivalents of foils used.	Total number of scintillations counted for each substance.	Number N of scintillations at same angle and for same air equivalent.	$A^{3/2}$.	$N \times A^{2/3}$.
Gold	·52, ·68	1200	2400	2770	·85
Platinum	·54, ·625	1000	2900	2730	1·05
Tin	·51, 1·15	1400	1290	1300	·99
Silver	·38, ·435	600	1060	1120	·95
Copper	·495, ·61	1300	570	507	1·12
Aluminium ...	·45, ·52, 1·06	1600	151	144	1·05
Carbon	·55, ·57	400	57	41·6	1·37

Note 2.—Introducing the new data for the mass per unit area of foils of the same air equivalent, as in note 1, the following are the values for the ratio of the scattering per atom divided by A^2 :—Au 3·1, Pt 3·4, Sn 3·4, Ag 3·4, Cu 3·95, Al 3·4.

It will be seen from the table that, although the experimental conditions were very different from those in the previous experiments, the results are similar, and indicate the essential correctness of the assumption that the scattering per atom is proportional to the square of the atomic weight. The deviations from constancy of the ratio (see notes 1 and 2) are nearly within the experimental error.

The measurements have not so far been extended to substances of lower atomic weight than carbon. When the atomic weight is small and comparable with the mass of the α particle, the laws of scattering will require some modification to take into account the relative motion of the atom itself when a collision occurs.

Variation of Scattering with Velocity.

In order to determine the variation of scattering with velocity the apparatus was somewhat modified. A conical glass tube coated with active deposit was again used as source of radiation. This source was placed about 1 mm. from the mica window (E, fig. 3), so that it was possible to insert additional sheets of mica between the source and the window to reduce the velocity of the α particles. Mica sheets were used for this purpose on account of their uniformity of

thickness in comparison with metal foils. The micas were attached to a cardboard disk which could be rotated to bring the different sheets successively in position. The α particles were scattered by a foil of gold or silver, of stopping power about 3 mm. of air, which was attached to a rod passing through the ground glass N. This made it possible to turn the foil away from the main beam during an experiment in order to test the natural effect. The disk S, in this case, rotated in a plane very close to the glass plate C and carried sheets of mica of different thicknesses. By rotating the ground-glass joint the micas could be placed directly in front of the zinc-sulphide screen, making it possible to test the homogeneity of the α particles after they had been scattered.

The results are given in Table VII. Column I. gives the number of mica sheets which were interposed in addition to the mica window, and column II. the ranges of the α particles incident on the scattering foil. The values of the velocities v were calculated from these ranges R by use of the formula $v^3 = \alpha R$ previously found by one of us*. The relative values

TABLE VII.
Variation of Scattering with Velocity.

I. Number of sheets of mica.	II. Range R of α particles after leaving mica.	III. Relative values of $1/v^4$.	IV. Number N of scintillations per minute.	V. Nv^4 .
0	5.5	1.0	24.7	25
1	4.76	1.21	29.0	24
2	4.05	1.50	33.4	22
3	3.32	1.91	44	23
4	2.51	2.84	81	28
5	1.84	4.32	101	23
6	1.04	9.22	255	28

of $1/v^4$ are given in column III. The number of scintillations per minute N are entered in column IV., and in column V. relative values of $N \times v^4$ are given. Over the range examined the number of scintillations varies in the ratio 1:10, while it will be seen that the product Nv^4 remains sensibly constant. Several experiments were made, and in every case

* H. Geiger, Roy. Soc. Proc. A. vol. lxxxiii. p. 506 (1910).

the scattering was found to vary at a rate more nearly proportional to the inverse fourth power of the velocity than to any other integral power. Owing to the comparative uncertainty of the values of the velocity for small ranges, however, the error of experiment may be somewhat greater than appears from column V. of the table.

In these experiments it proved essential to use a source possessing a high degree of homogeneity. In earlier experiments, where we were not able to fulfil this condition, the scattering apparently increased much more rapidly than the inverse fourth power of the velocity of the Ra C α particles. Even with a source of Ra C with which only a small quantity of emanation was associated, the amount of scattering first rapidly increased on interposing the sheets of mica, then showed a slight decrease, and finally increased again. This irregularity was due to the α particles of the emanation and Ra A, which are of shorter range than those of Ra C, and therefore more easily scattered.

The measurements could not easily be extended to α particles of lower velocity than corresponds to a range of about 1 centimetre, owing to the difficulty of observing the faint scintillations at lower ranges. However, in one particular experiment, by adding sheets of mica to cut down the velocity the number of scattered α particles appearing on the screen was increased 25 times, showing how easily the α particles of low velocity are scattered.

The results of the examination of the homogeneity of the scattered α particles showed that at least in the case of gold they remained practically homogeneous after the scattering. Experiments of this nature in the case of scattering foils of low atomic weight would be very interesting, but are somewhat difficult.

Determination of Absolute Number of Scattered α Particles.

In the previous sections we have completely verified the theory given by Prof. Rutherford. Since, according to this theory, the large deflexion of an α particle is the result of a close encounter with a single atom of matter, it is possible to calculate the magnitude of the central charge of the atom when the fraction of α particles scattered under definite conditions is determined. We have made several attempts under different conditions to obtain a quantitative estimate of the scattered particles, but the results so far have only given us an approximate value. The main difficulty arises from the fact that the scattered particles consist of such a small

fraction of the original beam that different methods of measurement have to be employed in the two cases. The number of scattered α particles was determined from the number of scintillations observed on the zinc-sulphide screen, a correction being necessary owing to the fact that with the particular screens used only about 85 per cent. of the incident α particles produce scintillations. The number of α particles in the main beam was in one case in which an emanation tube was used (as shown in fig. 1, p. 607) determined directly by the scintillation method, several weeks being allowed to elapse, so that the emanation had decayed to a small value. In other experiments Ra C deposited on the inside of a conical glass tube (as in fig. 2, p. 611) was used, and the number of α particles was calculated from its γ -ray activity and the distance and area of the diaphragm determining the beam.

The results showed that, using a gold foil of air equivalent 1 mm. (actual thickness 2.1×10^{-5} cm.), the fraction of incident Ra C α particles ($v = 2.06 \times 10^9$ cm./sec.) scattered through an angle of 45° and observed on an area of 1 sq. mm. placed normally at a distance of 1 cm. from the point of incidence of the beam, was 3.7×10^{-7} . Substituting this value in the equation given at the commencement of this paper, it can be calculated that the value of the number of elementary electric charges composing the central charge of the gold atom is about half the atomic weight. This result is probably correct to 20 per cent., and agrees with the deduction of Prof. Rutherford from the less definite data given in our previous paper.

From the results of this and the previous sections it is possible to calculate the probability of an α particle being scattered through any angle under any specified conditions. For materials of atomic weight greater than that of aluminium, it is sufficiently accurate to put N equal to half the atomic weight in the equation given at the commencement of the paper.

It will be seen that the laws of "single scattering" found in this paper are quite distinct from the laws of "compound scattering" previously deduced by Geiger. It must be remembered, however, that the experiments are not directly comparable. In the present paper we are dealing with very thin sheets of matter, and are measuring the very small fraction of α particles which are deflected by single collisions through relatively large angles. The experiments of Geiger, however, deal with larger thicknesses of scattering foils and angles of deflexion of a few degrees only. Under these conditions the scattering is due to the combination of a large number of deflexions not only by the central charges of the

atoms, but probably also by the electronic charges distributed throughout the remainder of their volumes.

Summary.

The experiments described in the foregoing paper were carried out to test a theory of the atom proposed by Prof. Rutherford, the main feature of which is that there exists at the centre of the atom an intense highly concentrated electrical charge. The verification is based on the laws of scattering which were deduced from this theory. The following relations have been verified experimentally :—

(1) The number of α particles emerging from a scattering foil at an angle ϕ with the original beam varies as $1/\sin^4 \phi/2$, when the α particles are counted on a definite area at a constant distance from the foil. This relation has been tested for angles varying from 5° to 150° , and over this range the number of α particles varied from 1 to 250,000 in good agreement with the theory.

(2) The number of α particles scattered in a definite direction is directly proportional to the thickness of the scattering foil for small thicknesses. For larger thicknesses the decrease of velocity of the α particles in the foil causes a somewhat more rapid increase in the amount of scattering.

(3) The scattering per atom of foils of different materials varies approximately as the square of the atomic weight. This relation was tested for foils of atomic weight from that of carbon to that of gold.

(4) The amount of scattering by a given foil is approximately proportional to the inverse fourth power of the velocity of the incident α particles. This relation was tested over a range of velocities such that the number of scattered particles varied as 1 : 10.

(5) Quantitative experiments show that the fraction of α particles of Ra C, which is scattered through an angle of 45° by a gold foil of 1 mm. air equivalent (2.1×10^{-5} cm.), is 3.7×10^{-7} when the scattered particles are counted on a screen of 1 sq. mm. area placed at a distance of 1 cm. from the scattering foil. From this figure and the foregoing results, it can be calculated that the number of elementary charges composing the centre of the atom is equal to half the atomic weight.

We are indebted to Prof. Rutherford for his kind interest in these experiments, and for placing at our disposal the large quantities of radium emanation necessary. We are also indebted to the Government Grant Committee of the Royal Society for a grant to one of us, out of which part of the expenses has been paid.

LXII. *The Absorption of Heat produced by the Emission of Ions from Hot Bodies.* By H. L. COOKE, Assistant Professor of Physics, and O. W. RICHARDSON, Professor of Physics, Princeton University*.

IN 1903 † one of the writers pointed out that there should be a considerable stream of energy away from the surface of a hot body which is emitting electrons or ions. When the total thermionic current is i the rate of loss of energy is

$$i\left(\Phi + 2\frac{R}{e}\theta\right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Φ is the drop of potential through which an ion would have to fall in order to acquire the energy which is equal to the heat rendered latent when the ion is emitted by the substance, R is the gas constant for a single molecule, e is the charge on an ion, and θ is the temperature of the substance. Since i increases very rapidly with θ , the rate of loss of energy due to this cause should also increase very rapidly with increasing temperature.

In the paper referred to, the derivation of the formula which is equivalent to (1) is confined to the case of the emission of electrons, and is based upon the electronic theory of metallic conduction. The scope of the formula is, however, much wider than this. It can, in fact, be shown to hold for any case in which it is possible to have equilibrium between an external atmosphere of ions and the source of emission. Strictly speaking, these statements are only universally true provided the phenomenon of electron reflexion is disregarded. The modifications which may have to be introduced on this account cannot be large and will be referred to later.

Attempts to detect and measure this loss of energy have been made by Wehnelt and Jentzsch ‡ and by Schneider §. These investigators all used a lime-coated platinum wire as the source of electrons. They agree in observing a cooling effect which is generally larger than that given by the above theory. The discrepancy is most marked at the lower temperatures, where Wehnelt and Jentzsch believe their results to be most reliable. At the higher temperatures there is a considerable emission of gas from the heated wire, and this is ionized by collision with the escaping electrons; the

* Communicated by the Authors.

† O. W. Richardson, Phil. Trans. A, vol. cci. p. 502 (1903).

‡ *Ann. der Phys.* vol. xxviii. p. 537 (1909).

§ *Ibid.* vol. xxxvii. p. 569 (1912).

positive ions thus liberated bombard the hot wire and produce a heating effect which vitiates the measurements. At the lowest temperatures the measured effect was from five to ten times as large as the calculated. These discrepancies led Wehnelt and Jentzsch to the conclusion that the theory was insufficient completely to account for the phenomena which accompany the emission of electrons from hot conductors.

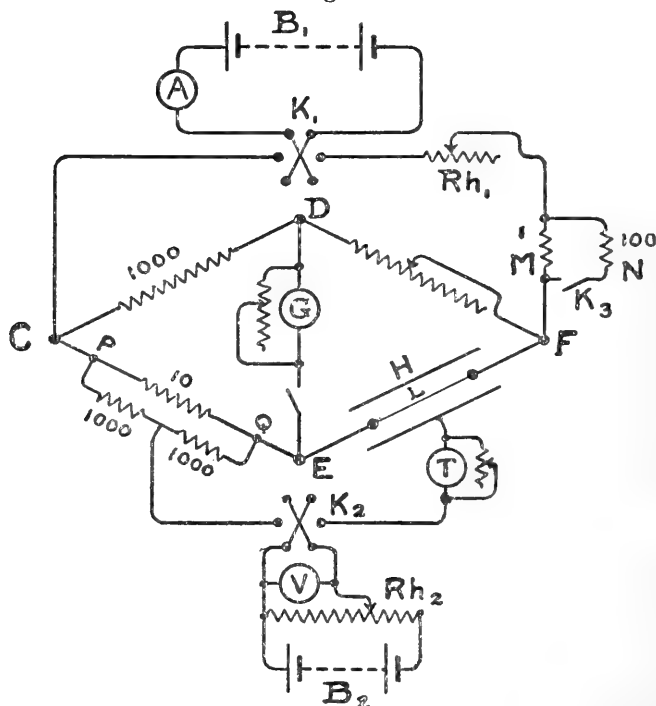
This may be so; but it seems to us possible that the source of the discrepancy is to be found in the method of experimenting. None of the investigators referred to have taken precautions to eliminate or allow for the direct disturbing action of the thermionic current on the galvanometer of the Wheatstone's bridge system, which is referred to in our papers* on the heat liberated during the absorption of electrons by metals. It is impossible to estimate the magnitude of this effect from the data given in the papers, but our own experience leads us to judge that it may well be much greater than the effect under investigation. We urge the possibility of this explanation with a certain amount of diffidence as we have not made experiments on lime-coated wires ourselves, and it is barely possible that there is something about the emission from lime that makes its behaviour exceptional.

All the experiments that we have made up to the present have been carried out with filaments of osmium as the source of emission. We are glad to be able to take this opportunity of thanking the Deutsche Gasglühlicht Actiengesellschaft of Berlin for presenting us with the material. The cooling effect was obtained by measuring the change of resistance of a heated filament which occurred when the thermionic current was turned on and off. The filament was heated by a direct current which was constant except for the disturbance produced by the thermionic current. The thermionic current was controlled by a suitable potential difference applied to a surrounding cylindrical electrode. It was started and stopped by reversing this potential difference. The change of resistance was compared with that produced by a known change in the main heating current, which thus supplied a known increment of energy to the system per unit time. If this increase in the rate of supply of energy is expressed in watts, the cooling effect per unit thermionic current may be obtained directly in equivalent volts by a comparison of the observed deflexions of the galvanometer of the Wheatstone's bridge.

* *Phil. Mag.* vol. xx. p. 173 (1910); vol. xxi. p. 404 (1911).

The method will be clearer after reference to fig. 1. This shows one of the two arrangements used which, for reasons which will be clear later, may be referred to as the "standard shunted" arrangement. The osmium filament L is placed

Fig. 1.



in the arm EF of the bridge. The adjacent arm CE carries a standard resistance of 10 ohms capable of taking a large current without heating. The resistance of the filament L was comparable with 4 ohms at the temperature of the experiments. The resistances CD and DF were 100 times CE and EF respectively, so that only one per cent. of the bridge current flowed along CDF . With this arrangement of resistances the same current may be used to actuate the bridge and to heat the filament, and on account of the large current flowing down the arms CEF very small changes of resistance may be detected. The main current was supplied by the battery B_1 of 12 or 24 volts, regulated by the rheostat Rh_1 , measured by the ammeter A and reversed by the reversing switch K_1 . It also passed through a standard 1 ohm resistance at NM . By means of the key K_3 this could be shunted by a standard 100 ohm resistance, thus producing a small known change in the heating current through L . The emitted electrons flowed from L to the surrounding cylinder H . They were driven by the high potential battery B_2 . This was placed

across a high resistance slide-rheostat Rh_2 , and various potential differences could be tapped off and read by the voltmeter V . The switch K_2 enabled this potential to be instantaneously reversed. From K_2 the electrons flowed to the middle point of a 2000 ohm resistance. In the standard shunted arrangement the ends PQ of this were connected to C and E respectively. This is equivalent electrically to making the thermionic current start from the middle of the arm CE of the bridge. In the "filament shunted" arrangement the ends PQ of the 2000 ohm resistance were connected respectively to E and F . This is equivalent electrically to a current starting from the centre of resistance of the filament and returning to its surface in the same proportion in various parts as the densities of the currents of (negative) electrons away from it bear to one another. If the emission of electrons is symmetrical about the centre of resistance, the thermionic current will produce no direct disturbance of the galvanometer in either of these cases. In the second case this will be true in any event, but in the first only provided the resistances are adjusted for no deflexion. The thermionic currents were measured by the microamperemeter T .

The method of carrying out a set of observations was as follows. The bridge current having been turned on, Rh_1 was adjusted until the thermionic current was of the desired value. After conditions had become steady the resistance in the arm DF was altered until the bridge was balanced, with the thermionic current stopped by opposing the potential supplied by the battery B_2 . A series of half-minute readings of the galvanometer G and the microammeter T were then taken with the thermionic current alternately on and off. Previous experiments had shown that half a minute allowed ample time for the new steady condition to be established and for effects due to the period of the galvanometer to have disappeared. Readings in opposite directions were taken in order to eliminate the steady drift due to fluctuations in the temperature of the filament arising from other causes. The mean of the successive deflexions was taken to represent the effect sought. Then, with the thermionic current off another set of half-minute readings on the galvanometer were taken, the key K_3 being now alternately closed and open. The mean of these gives the effect due to a known change in the energy supplied to the filament. The voltage of the battery B_1 and the reading of the ammeter A were then recorded. This constitutes one set of readings. A similar set was then taken with the key K_1 reversed. From these two sets, as we shall see, the value of Φ may be deduced. As a rule

the whole process was repeated with the 2000 ohm resistance connected across the filament instead of across the standard resistance CE. The new readings yield an independent value of Φ .

The galvanometer G was of the D'Arsonval type supplied by Nalder Brothers, London. It had a resistance of 225 ohms and gave 1 scale-division for 1.29×10^{-8} ampere. It was very heavily damped. The filaments used were 15 mm. long and .065 mm. in diameter. To saturate the thermionic current a potential difference of from 40 to 100 volts was applied, the amount necessary varying in the different experiments.

It will be noticed that the method of measurement employed is equivalent to using the hot filament as a bolometer. The change in the resistance of the filament will be proportional to the change in the rate at which energy is supplied to it, provided the change in the energy supplied is small. The details will be clearer after we have considered the magnitude of some of the effects to be observed.

Theory of the Measurements.

Let us first consider the method of calibration. This depends upon the measurement of the steady deflexion D_E of the galvanometer G which occurs when the resistance M is shunted by the resistance N. Let the resistance of M be z and that of N y . If the resistance of the filament when N is not shunted is R and the current flowing through it i , the rate of supply of energy to the filament is

$$E = Ri^2.$$

When M is shunted by N the current i becomes $i + \partial i$, and consequently R is changed to $R + \partial R$. Thus the new steady rate of heat-supply is

$$E + \partial E = (R + \partial R)(i + \partial i)^2.$$

To the first order in the small quantities ∂R and ∂i , which is all that is required, the increment in the rate of energy-supply is

$$\partial E = 2Ri\partial i + i^2\partial R. \quad . \quad . \quad . \quad . \quad (2)$$

To determine ∂i in terms of the quantities measured we proceed as follows. Let V be the electromotive force of the battery B_1 and R_0 the resistance of the whole circuit including the Wheatstone's bridge. Let $V = R_0 i_1$, then i_1 is the current supplied by the battery B_1 . The current i which heats the filament is smaller than i_1 , since a small

fraction π of the latter flows down the high resistance arms FDC. The heating current i is thus

$$i = (1 - \pi)i_1 = (1 - \pi)V/R_0.$$

The resistance of x when shunted by y is $\frac{xy}{x+y}$ and the change in R_0 due to switching on the shunt is

$$\partial R_0 = -x^2/(x+y).$$

The current when the resistance is thus altered is

$$i_1 + \partial i_1 = V/(R_0 + \partial R_0) = V/R_0 \left(1 - \frac{x^2}{R_0(x+y)}\right).$$

Thus to the first order of small quantities

$$\partial i_1 = i_1^2 x^2 / V(x+y). \quad . \quad . \quad . \quad . \quad (3)$$

Since $i = (1 - \pi)i_1$, $\partial i = (1 - \pi)\partial i_1 = (1 - \pi) \frac{i_1^2 x^2}{V(x+y)}$,

and ∂E may be written

$$\partial E = (1 - \pi)^2 i_1^2 \left\{ 2R \frac{i_1 x^2}{V(x+y)} + \partial R \right\}.$$

To find ∂R from the deflexions D_E of the galvanometer it is necessary to consider the theory of the Wheatstone's bridge circuit. If the resistances of CD, DF, FE, and EC are b , a , β , and α respectively and z is the current through the galvanometer G, then

$$i_1 = \left\{ G(a+b+\alpha+\beta) + (b+\alpha)(a+\beta) \right\} \frac{V}{\Delta},$$

where Δ is the usual determinant*, and

$$z = (a\alpha - b\beta) \frac{V}{\Delta} = \frac{i_1}{1+\pi} \frac{1}{1+\pi + \frac{G}{b} + \frac{G}{a}} \left(\frac{\alpha}{b} - \frac{\beta}{a} \right)$$

to the first order in π . Thus if the Wheatstone's bridge is in adjustment when $\beta = R$, the increments ∂z and $\partial \beta (= \partial R)$ due to a change of i_1 from i_1 to $i_1 + \partial i_1$ will be related by the equation

$$\partial z = - \frac{i_1}{1+\pi} \left(1 + \frac{\partial i_1}{i_1} \right) \frac{1}{G+a \left(1 + \pi + \frac{G}{b} \right)} \partial R = -k D_E,$$

where k is the insensibility of the galvanometer. In our

* J. J. Thomson's 'Elements of Electricity and Magnetism,' p. 306.

experiments k was 1.29×10^{-8} , *i. e.* 1.29×10^{-8} amp. gave 1 scale-division. Since $\partial i_1/i_1$ was at most about 0.0005, it may be neglected in this equation. Thus

$$\partial R = 1.29 \times 10^{-8} \frac{1+\pi}{i_1} \left(G + a \left[1 + \pi + \frac{G}{b} \right] \right) D_E \quad (4)$$

and

$$\begin{aligned} \partial E = (1-\pi)^2 i_1^2 \left\{ 2R \frac{i_1 x^2}{V(x+y)} \right. \\ \left. + 1.29 \times 10^{-8} \frac{1+\pi}{i_1} \left(G + a \left[1 + \pi + \frac{G}{b} \right] \right) D_E \right\}. \quad (5) \end{aligned}$$

We shall now consider the change in the rate of supply of energy which occurs when the thermionic current is turned on and off. Were it not for disturbing effects this would be a simple matter. From equation (1) we see that when a thermionic current of strength T flows from the filament, the sum of the work done and the energy carried away by it is $T \left\{ \phi + 2 \frac{R}{e} \theta \right\}$. The whole of this energy cannot be regarded as lost by the filament, since the electrons do not flow into it at the absolute zero of temperature but at the temperature θ_0 of the rest of the electrical system. We shall therefore write the increment $\partial E'$ in the energy supply due to the thermionic current as

$$\partial E' = -T \left\{ \phi + 2 \frac{R}{e} [\theta - \theta_0] \right\}. \quad (6)$$

The terms involving θ and θ_0 are not exact. They are calculated on the supposition that Maxwell's law of distribution of velocities can be applied to the electrons. This is only approximately true when a current is flowing, the deviation depending on the nature of the collisions which the electrons undergo. However, $2 \frac{R}{e} \theta$ only amounts to about 5 per cent.

of ϕ at 2000°K , so that the error involved here cannot be very great. It is of the same order as the work done by the thermionic current against the Thomson effect in the filament and the Peltier effect at the junctions. This we are also disregarding, as its magnitude is unknown although it must be much smaller than ϕ .

The important disturbing effects which have to be considered are the Joule heating effect due to the flow of the thermionic current inside the filament before it escapes, and the direct effect it produces on the galvanometer G due to incomplete compensation. Consider the former first. The

flow of electrons, which constitutes the thermionic current when it is outside the filament, will distribute itself about the Wheatstone's bridge circuit in a manner which depends on the value of the various resistances and the position of the return wire PQ. The actual current flowing at any point of the filament will be due to the superposition of this current upon that supplied by the battery B_1 . However the additional current may distribute itself, there will be one point in the filament where it contributes nothing to the current i which flows along the latter. Let the value of i at this point be i_0 . Since the relation between currents and potentials in a network is a linear one, i_0 would be equal to the value C_0 of i when the thermionic current is prevented from flowing, were it not for the change ∂R_1 in the resistance R of the filament which is produced by the thermionic current. The potential of the battery B_1 being V ,

we have $C_0 = V/R_0$ and $i_0 = V/(R_0 + \partial R_1) = C_0 \left(1 - \frac{\partial R_1}{R_0}\right)$

to the first order in $\partial R_1/R_0$. If ρ_0 is the resistance per unit length of the filament when the thermionic current is not flowing, $R = \int \rho_0 dx$. If ρ_0' is the value of ρ_0 when the thermionic current is escaping, $R + \partial R_1 = \int \rho_0' dx$. As the change in the resistance may be supposed, without serious error, to be distributed uniformly along the filament, we may put $\rho_0' = \rho_0 \left(1 + \frac{\partial R_1}{R}\right)$. Taking the point where the

current along the filament, when the thermionic current is allowed to escape, is i_0 as origin let the coordinates of the ends of the filament be $+x_1$ and $-x_0$. The current which

is heating the filament at any point x is then $i_0 + \int_0^x j dx$, j being

the thermionic current flowing into unit length of the filament at any point. Thus the total rate of supply of energy due to the Joule heating effect of the various currents when the thermionic current is escaping is

$$\begin{aligned} \int_{-x_0}^{x_1} \rho_0' (i_0 + \int_0^x j dx)^2 dx &= \int_{-x_0}^{x_1} \rho_0 C_0^2 \left(1 + \frac{\partial R_1}{R}\right) \left(1 - 2 \frac{\partial R_1}{R_0}\right) dx \\ &+ 2 \int_{-x_0}^{x_1} \rho_0 C_0 \left(1 + \frac{\partial R_1}{R}\right) \left(1 - \frac{\partial R_1}{R_0}\right) \left[\int_0^x j dx\right] dx \\ &+ \int_{-x_0}^{x_1} \rho_0 \left(1 + \frac{\partial R_1}{R}\right) \left[\int_0^x j dx\right]^2 dx. \end{aligned}$$

When there is no thermionic current the Joule heating effect is $\int_{-x_0}^{x_1} \rho_0 C_0^2 dx$, so that the extra effect due to turning on the thermionic current is

$$\begin{aligned} & \int_{-x_0}^{x_1} \rho_0 (i_0 + \int_0^x j dx)^2 dx - \int_{-x_0}^{x_1} \rho_0 C_0^2 dx \\ &= RC_0^2 \left[\frac{\partial R_1}{R} - \frac{2\partial R_1}{R_0} \right] + 2 \int_{-x_0}^{x_1} \rho_0 C_0 \left(1 + \frac{\partial R_1}{R} \right) \left(1 - \frac{\partial R_1}{R_0} \right) \left[\int_0^x j dx \right] dx \\ & \quad + \int_{-x_0}^{x_1} \rho_0 \left(1 + \frac{\partial R_1}{R} \right) \left[\int_0^x j dx \right]^2 dx. \quad . \quad . \quad (7) \end{aligned}$$

The middle term in (7) reverses when the direction of the heating current C_0 is reversed. The other two terms do not. We shall see in a moment that the effect of the second term can readily be eliminated. The magnitude of the third term was negligible in all our experiments, being equal to only 1/500 of the first term in the most unfavourable case.

In the above expressions ∂R_1 is a negative quantity. If we consider ∂R_1 to be positive when it represents a diminution in R , the diminution in the Joule heating effect due to turning on the thermionic current is

$$RC_0^2 \left[\frac{\partial R_1}{R} - 2 \frac{\partial R_1}{R_0} \right] - 2 \int_{-x_0}^{x_1} \rho_0 C_0 \left(1 - \frac{\partial R_1}{R} \right) \left(1 + \frac{\partial R_1}{R_0} \right) \left[\int_0^x j dx \right] dx$$

if we disregard the third term. The total diminution in the rate of supply of energy is made up of this together with the loss due to the escape of the thermionic current. To the required accuracy it is therefore :—

$$\begin{aligned} \partial H = & T \left(\phi + 2 \frac{R^*}{e} (\theta - \theta_0) \right) + RC_0^2 \left[\frac{\partial R_1}{R} - 2 \frac{\partial R_1}{R_0} \right] \\ & - 2 \int_{-x_0}^{x_1} \rho_0 C_0 \left(1 - \frac{\partial R_1}{R} \right) \left(1 + \frac{\partial R_1}{R_0} \right) \left[\int_0^x j dx \right] dx. \\ & . \quad . \quad . \quad (8) \end{aligned}$$

The first R is starred to indicate that it is the gas constant and not a resistance. The first two terms of (8) have the same direction independently of the direction of C_0 . Since the deflexions of the Wheatstone's bridge galvanometer, for a given change in the resistances, reverse when C_0 is reversed, it follows that the deflexions due to the first two terms of (8) reverse with C_0 . The third term gives rise to

a galvanometer deflexion whose direction is independent of that of C_0 .

If the distribution of the thermionic current is quite symmetrical about the centre of resistance of the filament the bridge galvanometer will be exactly compensated, both in the "filament shunted" and the "standard shunted" arrangements. The compensation here referred to is that which is necessitated by the direct disturbing action of the thermionic current on the Wheatstone's bridge circuit. The theory of the compensation has been fully discussed in our previous papers* on the converse heating effect. The present method of experimenting affords no means of testing whether the compensation is precise or not; so that it is necessary to be sure that the method used eliminates any effect arising from lack of balance. In all except the first three experiments below the thermionic current was saturated, so that its distribution about the filament must have been determined solely by the distribution of temperature about the latter. With a given distribution of thermionic current from the surface of the filament the distribution of the equivalent current in the filament and in the Wheatstone's bridge circuit is entirely determined by the distribution of the various resistances. Thus the magnitude and direction of the galvanometer deflexion due to lack of compensation will be independent of the direction of C_0 , except in so far as the direction of C_0 may affect the distribution of temperature and resulting thermionic emission about the filament. Assuming that the thermionic current doubles in every 30° rise of temperature, and that the absolute temperature of the filament varies as the square root of the energy supplied locally, an effect might arise in this way which would make the observed effects about 2 per cent. too big with the largest thermionic currents used. With the smaller thermionic currents this effect would be quite inappreciable. The data available for this estimation are not very precise, but they have been selected in doubtful cases so as to lead to an upper limit, *i. e.* so as to over-estimate rather than under-estimate the effect. Neglecting this effect for the present, the deflexion due to incomplete compensation will be determined by the thermionic current T and the distribution of the resistances in the circuit, and will be independent of the direction of C_0 . Let the part of the galvanometer deflexion which is due to this cause be $D = p\psi$, where p is the galvanometer deflexion due to unit change of the resistance R . ψ is thus the value of the galvanometer deflexion due to

* *Loc. cit.*

lack of balance expressed in terms of the change in R which would produce the same effect. It is clear from what has been said, that the observed deflexion D_T of the galvanometer G when the thermionic current is turned on, is not due entirely to the change ∂R_t of the resistance arising from the change in the rate of supply of heat. Instead of being equal to $p\partial R_t$ it is equal to $p(\partial R_t + \psi)$, where $p\psi$ is the deflexion arising from the lack of compensation.

Since the alteration in the rate of supply of energy to the filament due to either turning on the thermionic current or shunting the resistance x_1 is small, it will be proportional to the corresponding change in temperature or resistance of the filament. If D_E is the galvanometer deflexion and ∂R_e the corresponding change in the resistance of the filament caused by shunting x , we have

$$\frac{\partial H}{\partial E} = \frac{T\left(\phi + 2\frac{R^*}{e}(\theta - \theta_0)\right) + RC_0^2\left(\frac{\partial R_t}{R} - 2\frac{\partial R_t}{R_0}\right) - 2\int_{-x_0}^{x_1} \rho_0 C_0\left(1 - \frac{\partial R_t}{R} + \frac{\partial R_t}{R_0}\right)\left[\int_0^x j dx\right] dx}{(1 - 2\pi)i_1^2\left(2R\frac{i_1 x^2}{V(x+y)} + \partial R_e\right)} \\ = \frac{\partial R_t}{\partial R_e} = \frac{D_T - p\psi}{D_E} \dots \dots \dots (9)$$

If the corresponding values of T , ∂R_t , and D_T when C_0 is reversed are denoted by dashes, we have, adopting the convention that the positive direction of the deflexions reverses with C_0 ,

$$\frac{T'\left(\phi + 2\frac{R^*}{e}(\theta - \theta_0)\right) + RC_0^2\left(\frac{1}{R} - \frac{2}{R_0}\right)\partial R_t' + 2\int_{-x_0}^{x_1} \rho_0 C_0\left(1 - \frac{\partial R_t'}{R} + \frac{\partial R_t'}{R_0}\right)\left[\int_0^x j dx\right] dx}{(1 - 2\pi)i_1^2\left(2R\frac{i_1 x^2}{V(x+y)} + \partial R_e\right)} \\ = \frac{\partial R_t'}{\partial R_e} = \frac{D_T' + p\psi}{D_E} \dots \dots \dots (10)$$

By addition of (9) and (10), remembering that $V = R_0 i_1$ and $C_0 = (1 - \pi)i_1$, where π is a small fraction whose square may be neglected, we have, after transposing,

$$\phi + 2\frac{R^*}{e}(\theta - \theta_0) = \frac{(1 - 2\pi)i_1^2}{T + T'} \frac{\partial R_t + \partial R_t'}{\partial R_e} \frac{2R i_1 x^2}{V(x+y)} \left(1 + \frac{(x+y)\partial R_e}{x^2}\right). \dots \dots \dots (11)$$

We see also from (9) and (10) that

$$\frac{\partial R_t + \partial R_t'}{\partial R_e} = \frac{D_T + D_T'}{D_E}.$$

Thus

$$\phi = \frac{(1-2\pi)i_1^2}{T+T'} \frac{D_T + D_T'}{D_E} \frac{2Ri_1x^2}{V(x+y)} \left(1 + \frac{(x+y)\partial R_e}{x^2}\right) - 2\frac{R^*}{e}(\theta - \theta_0). \quad (12)$$

Of the quantities on the right-hand side R^*/e is a known constant, i_1 , T , T' , D_T , D_T' , D_E , R , and θ_0 were measured during the experiments, and π , x , and y were known. Their values were $\pi = .01$, $x = 1$ ohm, $y = 100$ ohms. θ was only estimated, but its value does not matter much as the term

$2\frac{R^*}{e}(\theta - \theta_0)$ amounts only to about 5 per cent. of ϕ . The term $\frac{(x+y)\partial R_e}{x^2}$ varies from about 5 per cent. to about

10 per cent. in the different experiments. The value of ∂R_e is readily obtained from the corresponding deflexion D_E of the galvanometer G by using the theory of the Wheatstone's bridge circuit. With the resistances and galvanometer used the appropriate relation is

$$\partial R_e = 1.30 \times 10^{-8} \times (G + 100R(1.01 + 0.001G)) \times D_E. \quad (13)$$

It will be observed that the bolometric measurement of the cooling effect due to the thermionic current and the measurement of the Joule heating effect due to a small increase of the main current, are not made under quite the same conditions. The thermionic cooling all occurs at the surface of the filament, whereas the Joule heat is produced uniformly throughout the volume. The mean difference of temperature developed by a given supply of energy will, therefore, be smaller in the latter case, on account of the temperature gradient which is required to drive the energy to the surface of the filament. By considering an analogous case, in which there is no radiation but the loss by radiation is represented by conduction through a surrounding conductor of much lower thermal conductivity than the filament, it becomes clear that the error thus introduced is a negligible fraction of the change of temperature which is measured.

Results of the Experiments.

The Table which follows contains the results of all the measurements we have made. The data are set forth in detail in order to show that formula (12) has been tested under a great variety of conditions. This seems especially important in view of the quite different results obtained by Wehnelt and his pupils in their experiments on lime-coated wires. In the table, column I. gives the number of the experiment. Column II. gives the mean deflexion D_T of the galvanometer G , in scale-divisions, caused by turning the thermionic current on and off for 30-second intervals. Column III. gives the mean galvanometer deflexion caused by opening and closing the key K_3 for intervals of 30 seconds. Column IV. gives the value of T , the thermionic current, in microamperes. Column V. gives the value of i_1 , the current in the main circuit in amperes. Column VI. gives the resistance R of the filament in ohms. Column VII. gives the electromotive force of the battery B_1 in volts. Columns VIII.-XI. give the values of the fraction $\frac{i_1^2 D_T}{T D_E} \frac{2Ri_1^2 x}{V(x+y)}$ under different conditions. The value in column VIII. is that obtained with the "filament shunted" and the main current flowing in the direction from the filament to the standard ($F \rightarrow S$); column IX. exhibits the corresponding quantity under like conditions, except that the main current is reversed and flows from the standard to the filament ($S \rightarrow F$). Columns X. and XI. are respectively the same as VIII. and IX., except that the "filament shunted" arrangement is replaced by the "standard shunted" arrangement. If it were not for the effects which reverse when the current i_1 is reversed the values in columns VIII.-XI. in any one experiment should be identical and approximately equal to ϕ . The differences in these numbers thus measure the magnitude of these reversible effects, which are eliminated in the final formula. It will be noticed that the divergence of the numbers is much greater for the "standard shunted" than for the "filament shunted" arrangement. This is in accordance with the theory of the measurements as developed above, since the point at which $i=i_0$ is nearer the centre of the filament with the filament shunted arrangement. Column XII. contains the value of $\phi + 2 \frac{R^*}{e} (\theta - \theta_0)$ calculated from (12). It will be noticed that both the "standard shunted" and "filament shunted" arrangements give essentially concordant values for this quantity.

A glance at the Table will show that the experiments involve the following range of variation of the variables entering into the formula :—the thermionic current T from about 20 to 800 microamperes, the heating current i_1 from 0.430 to 0.687 ampere, the resistance R of the filament from 4.216 to 5.533 ohms, the potential V from 12.10 to 24.4 volts, D_T from 2.4 to 198 divisions and D_E from 20.4 to 107.5 divisions. The results thus afford a very thorough test of the constancy of ϕ under widely varying conditions.

Naturally the accuracy which may be expected in the final result differs very considerably in different cases. It is obvious that a determination which involves a deflexion of only 2.4 divisions as a factor cannot be comparable in accuracy, as regards errors of measurement, with one in which the corresponding deflexion is 200 divisions. There is of necessity a slight steady drift of the galvanometer spot due to uncontrollable causes in experiments of this character. The absolute effect of this is just the same for both large and small values of D_T , so that its importance in the final result is much greater for small than for large deflexions. Under the circumstances it is almost surprising that the measured values of ϕ exhibit so much constancy and consistency over so wide a range.

We might have picked out some of the experiments as being more reliable than others, but we have not done so, as our aim has been to examine the question of the constancy and definiteness of ϕ over a wide range of variation of the thermionic emission and other conditions. In this connexion it is worth repeating that the values deduced from experiments with large values of T (and consequently of D_T) are subject to an error due to effects which do not reverse with i_1 and which are only roughly calculable. These effects are unlikely to amount to more than 2 per cent. of ϕ with $T=8 \times 10^{-4}$ amp., the largest value of T used, but they would be serious if T were appreciably larger. Conversely it is probable that they may be neglected with the small values of T used in most of the experiments.

Taking $R^*/e = \frac{1.346}{4.69} \times 10^{-6}$ erg/°C. \times E.S.U., $\theta = 2000^\circ$ K, $\theta_0 = 290^\circ$ K, the term $2 \frac{R^*}{e} (\theta - \theta_0) = 0.3$ volt with sufficient accuracy. This estimate cannot be wrong by more than 0.05 volt for the average temperature, but it may be 0.05 volt higher at the highest than at the lowest temperatures.

Cooling Effect.

Value of ϕ .

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
No.	D _T .	D _E .	T.	i_1 .	R.	V.	Fil. Sh. F→S.	Fil. Sh. S→F.	Stan. Sh. F→S.	Stan. Sh. S→F.	$\phi + 2 \frac{R}{e} (\theta - \theta_0)$.
1.	7.10	20.6	16.15	.430	4.216	24.4	5.080	5.840	4.714	7.363	5.57
	6.50	21.3	16.43	.430	4.218	24.4					6.16
	16.60	20.8	33.00	.430	4.260	24.4					
	2.40	20.4	5.90	.430	4.262	24.4					
2.	7.25	21.2	23.3	.430	4.273	24.3	4.525	4.900	3.991	5.929	5.06
	33.00	21.1	72.6	.430	4.275	24.3					4.81
	15.50	21.0	43.0	.430	4.238	24.3					
	16.00	21.2	42.7	.430	4.241	24.3		4.570			
3.	25.1	21.0	72.9	.430	4.264	24.3	5.105				4.94
	26.0	19.5	73.75	.430	4.264	24.3					
4.	5.25	48.8	34.2	.485	4.712	12.10	5.277		4.389	5.084	4.84
	12.6	49.1	34.14	.485	4.702	12.10					4.44
	9.3	49.4	30.95	.485	4.655	12.10		3.410			
	6.00	49.16	31.00	.485	4.651	12.10					
5.	3.60	59.33	26.00	.520	4.725	12.23			4.995	5.492	4.16
	10.75	58.80	25.27	.520	4.723	12.23					

6.	16.00 26.00 24.09 17.83	74.25 72.91 72.41 72.58	110.2 110.3 100.0 98.6	.588 .588 .588 .588	5.059 5.052 4.997 4.995	12.20 12.20 12.20 12.20	5.550	4.150	2.470	6.290	4.59 5.08
7.	9.5 11.5 12.8 8.83	72.42 74.58 72.00 79.00	53.0 52.8 56.0 56.5	.588 .588 .588 .593	4.892 4.890 4.938 4.946	12.20 12.20 12.20 12.20	4.770	4.030	2.320	6.285	4.62 4.50
8.	14.7 14.0	78.30 78.30	75.8 76.5	.617 .617	4.970 4.972	12.18 12.18	4.745	4.478			4.86
9.	14.00 13.09 17.00 11.00	78.92 78.58 79.66 77.75	71.7 71.0 77.0 74.0	.615 .615 .615 .615	4.954 4.952 5.002 5.004	12.18 12.18 12.18 12.18	4.395	4.680	2.220	6.736	4.78 4.725
10.	12.00 17.17 13.00 13.41	81.00 83.00 81.66 79.66	74.00 75.70 69.20 70.10	.625 .625 .625 .625	4.995 4.994 4.943 4.945	12.11 12.11 12.11 12.11	4.735	4.950	2.510	7.370	5.17 5.12

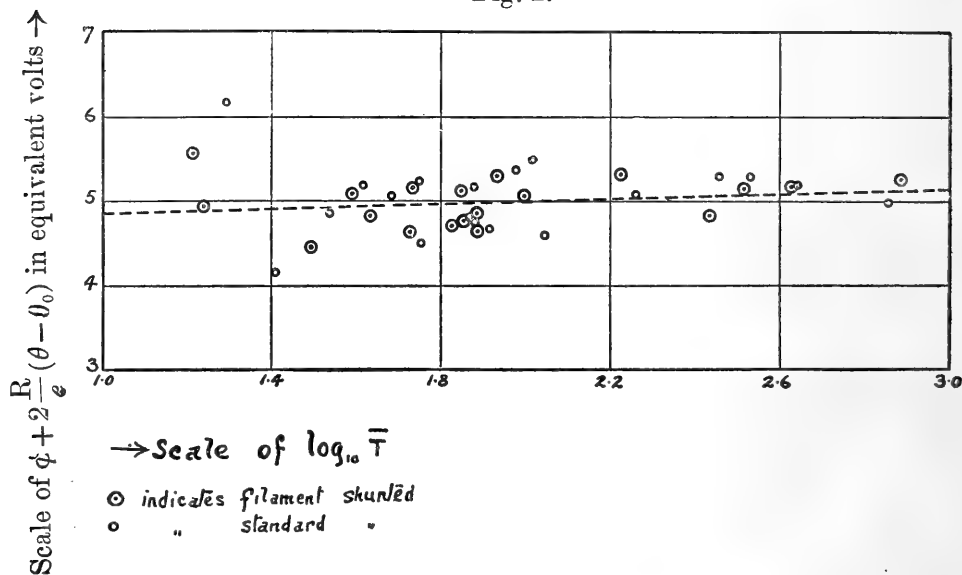
16.	40.6 39.5 58.75 23.2	57.8 56.25 57.5 58.4	168.4 166.6 181.2 178.0	.663 .664 .664 .664	5.162 5.158 5.208 5.209	24.6 24.6 24.6 24.6	5.170	5.100	3.510	6.220	5.31 5.04
17.	37.0 92.55 59.75 62.0	59.0 59.1 58.1 59.5	284.5 292.0 270.5 272.5	.677 .677 .677 .677	5.335 5.335 5.280 5.281	24.5 24.5 24.5 24.5	4.230	5.106	3.630	6.580	5.29 4.84
18.	75.0 69.66 107.66 43.9	59.5 59.1 58.8 58.75	327.0 321.0 343.0 336.0	.676 .676 .676 .676	5.320 5.318 5.369 5.369	24.6 24.6 24.6 24.6	4.820	5.160	3.580	6.640	5.17 5.29
19.	53.75 134.5 86.25 93.7	60.2 60.9 60.75 59.75	426.0 449.0 422.0 425.0	.687 .687 .687 .687	5.431 5.428 5.376 5.377	24.6 24.6 24.6 24.6	5.195	5.685	2.945	6.985	5.18 5.18
20.	198.0 127.7 219.3 84.9	59.5 58.6 61.9 58.8	814.0 708.0 869.0 564.0	.686 .686 .686 .686	5.472 5.471 5.525 5.533	24.6 24.6 24.6 24.6	4.315	5.875	2.123	7.520	5.27 4.99

The mean of the 18 values of $\phi + 2\frac{R}{e}(\theta - \theta_0)$ in column XII. given by measurements with the standard shunted arrangement is 5.01 volts; the mean of the 19 values with the filament shunted arrangement is 4.99 volts. Thus there is no certain difference between the results given by the standard shunted and filament shunted arrangements. The mean of all the 37 experiments gives $\phi + 2\frac{R}{e}(\theta - \theta_0) = 5.00$ volts, or $\phi = 4.7$ volts. We see no reason at present why this value should not be correct to 0.1 volt.

The question whether or no ϕ varies with θ is important. To see if our results give any information about this we have plotted in fig. 2 the experimental values of

$$\phi + 2\frac{R}{e}(\theta - \theta_0)$$

Fig. 2.



against the logarithm of the mean value of the corresponding thermionic currents (\bar{T}). Since the thermionic currents are nearly proportional to $e^{-\text{const.}/\theta}$ the differences of $\log \bar{T}$ will be nearly proportional to the differences of θ if the range of θ is not too large. It will be seen that there is a distinct indication of a slight increase in $\phi + 2\frac{R}{e}(\theta - \theta_0)$ as $\log \bar{T}$ increases. Too much attention ought not to be paid to the

points to the left of the diagram, which are a long way from the line. They correspond to the measurements with small thermionic currents, and are necessarily subject to a large error. In some cases also these currents were not saturated, which may introduce systematic errors. The increase referred to is larger than the $R\theta$ term would cause. Moreover, the small systematic error which occurs with large values of T , and which at present we are not able to calculate accurately, tends to make the measured value of ϕ too small when T is large. It will therefore tend to off-set the effect of the $R\theta$ term. Thus there seems to be a small but definite increase of ϕ with θ .

The discussion of this question will not be pursued further at present. In fact there are a number of points connected with the theory of these effects which we shall be able to deal with more satisfactorily when data relating to the thermionic emission from osmium at different temperatures are available. We expect to have these data at our disposal very soon. We wish to point out, however, that the above experiments afford a strong confirmation of the views about the nature of the emission of electrons from hot bodies which have been put forward by one of the authors. In particular, since osmium is closely related to platinum both chemically and physically, one would expect it to have a very similar value of ϕ . The above value is very close to the value of the corresponding quantity which we obtained from the converse heating effect when electrons were absorbed by platinum, and is not very different from the values of the latent heat, expressed in equivalent volts, which one of the writers and others have deduced from the temperature variation of the emission of electrons by platinum.

We are glad to be able to take this opportunity of thanking Mr. A. A. Barnes, who assisted us with the preliminary experiments and made several valuable suggestions, and Mr. Cornelis Bol, who took most of the observations.

Palmer Laboratory,
Princeton, N. J.

LXIII. *The Age of Pleochroic Haloes.*
 By J. JOLY, F.R.S., and E. RUTHERFORD, F.R.S.

[Plate IX.]

IT is now well established that the minute circular marks seen in sections of certain coloured rock minerals—notably the coloured micas—are due to the effects produced by the alpha radiation of a central radioactive particle. The circular mark, in fact, represents the section or projection of a sphere defined by the range in the particular containing mineral of the most penetrating alpha ray emitted. If the parent radioactive substance is uranium, the fully developed halo is defined by a sphere having the radius of the furthest reaching ray, RaC. If the parent substance is thorium, the extreme radius of the sphere will be defined by the range of ThC.

Haloes are found in which the effects of other and less penetrating alpha rays of the uranium and thorium families may be clearly shown, and in some the quantity of radioactive material is so small that the halo may be described as “under-exposed”; so that the maximum effects of RaC or ThC being distributed over a relatively large spherical surface or shell, may be faint or absent, and the containing mineral only notably darkened by those inner rays whose actions are more concentrated owing to the lesser spherical shells to which their maximum ionization effects are confined. Thus, in the case of the uranium derivatives, the halo may be limited by the range of RaA, by Ra emanation, by Ra, or even by ionium or uranium.

The halo is in every case the result of the integral actions of rays emitted since a very remote period. Haloes in the younger rocks are unknown. The quantity of radioactive material involved is very small. More especially haloes of true spherical form are necessarily formed around very minute nuclei, so that even if these were entirely composed of a parent radioactive element, it is only by the integration of effects over a very prolonged period that any results are brought about.

It is of interest to seek some estimate of the time which may have been required to generate these haloes. This can be done if the following data are available:—

(a) The number of alpha rays which will produce a certain intensity of staining in a particular mineral.

(b) The mass of the nucleus of a halo of similar or comparable intensity of staining in this same mineral, and from

* Communicated by the Authors.

this an estimate of the quantity of radioactive substances which may be concerned in generating the halo.

It is evident that while we can obtain the numerical values involved in (a) with a considerable degree of accuracy, certain assumptions enter into the numerical values required in (b), which render them uncertain within particular limits. Thus, while the dimensions of the nucleus may be determined with fair accuracy, and its mineral nature inferred with considerable confidence, we have no means, at present, of ascertaining the amount of radioactive material it contains. This amount can only be stated on the basis of analyses made on specimens of the mineral large enough to be subjected to examination. Evidently, however, a probable minor limit to the age is obtained by making our assumptions exceed by a safe margin any of the ascertained results.

The following experiments and observations have been confined to the brown mica, Haughtonite, of Co. Carlow. In this mica, haloes due to the uranium family of elements are very beautifully defined, and are found in every stage of development; from the smallest, due to uranium or ionium, to fully darkened haloes completed to the range of RaC. The mica is of a rich clear brown colour, with high lustre and perfect cleavage. Particulars with reference to this mica and of its contained haloes have been given elsewhere*.

The age of the containing granite is probably late Silurian or early Devonian. The evidence for this is found in its relations with the surrounding rocks. It has upheaved and metamorphosed slates of Silurian age, and fragments of it are contained in Old Red Sandstone sediments which rest unconformably on the upturned edges of the Silurian slates, and overlap directly on to the granite. Its upheaval is generally referred to the Caledonian earth-movements†.

Some of the haloes may have been formed somewhat subsequent to the crystallization of the containing mica. This is suggested (a) by the fact that some of the crystallized nuclei giving rise to the haloes are oriented in the plane of cleavage; their greatest dimensions coinciding with that plane as if they had been developed *in situ*; and (b) by the existence of veins traversing the biotite which evidently contain radioactive substances, seeing that they are bordered by the characteristic staining, and faithfully reproduce the

* Phil. Mag. April 1910; Proc. Royal Dublin Soc. xiii. p. 73; 'Bed-rock,' Jan. 1913.

† Mineralogical and geological particulars respecting the granite are given by Sollas (Trans. Royal Irish Academy, xxix., Jan 1891). The Geological Survey of Ireland Reports on Co. Dublin and Co. Carlow &c., may also be consulted.

appearance of a tubular halo *. A photograph of these veins is given in 'Bedrock' for January 1913. Such conduits of radioactive substances often diverge from heavily-stained areas located on the outer margins of the crystal. Haloes are sometimes found linearly arranged along the veins, showing that they partook of the radioactive substances contained in them. It is known that towards the close of the period of consolidation of a granitic mass, mother liquors, rich in the rarer elements concentrated from the magma, make their appearance and penetrate the granite, and often the adjacent rocks. The genesis of radioactive ore deposits seems in many cases traceable to this phenomenon. It is not impossible that the venation of the mica is referable to similar developments on a minute scale. This, however, cannot have been long subsequent to the period of consolidation. The haloes may most safely be regarded as of early Devonian age.

The experiments on the number of alpha rays required to produce notable staining of the Carlow mica were carried out in the Physical Laboratory of the University of Manchester. The mica was placed beneath and in contact with a lead plate which was perforated with a circular aperture 0.42 cm. in diameter. At a distance of 1.5 cm. vertically over the centre of the aperture a capillary alpha-ray tube, containing 25 millicuries of radium emanation to start with, was fixed. The whole was placed under a bell-glass in which a partial vacuum could be made. The thickness of the walls of the alpha-ray tube was equivalent to 1.4 cm. of air at normal density. The average range of the three sets of alpha rays falling on the mica was deduced as 3.5 cm. of air. This would ensure a penetration of about 0.016 mm. in the mica. The quantity of emanation used and the duration of the exposure enable direct determination of the number of alpha rays required to produce a particular effect.

Two cleavage flakes of the mica were dealt with. To one of these flakes three exposures on adjacent areas were given. On the second flake two exposures on adjoining areas were given. Calling the first three exposures A, B, C, and the second D, E, the number of alpha rays in each case was :—

Spot A	received	3.7	10^{13}	alpha rays	per square cm.
„ B	„	1.6	„	„	„
„ C	„	1.5	„	„	„
„ D	„	3.7	„	„	„
„ E	„	1.5	„	„	„

* Rutherford, Phil. Mag. Jan. 1910.

The amount of darkening of the mica produced by these exposures was sensibly the same for A and D and for C and E. B was slightly darker than C or E. The depth of staining was, therefore, very consistently dependent on the exposure. In some places the areas overlapped a little, and this part of the mica faithfully produced an effect due to the added densities of the overlapping spots.

A subsequent measurement of the thickness of these flakes of mica, by focussing with a high power on the upper and lower faces of the flakes as they rested on the stage of the microscope, showed that the flake containing A, B, and C was where thinnest 0.022 mm. thick, and the second flake, containing D and E, was where thinnest 0.014 mm. thick. The close agreement in the effects of the staining on the two flakes shows that the whole of the alpha rays must have been absorbed in the second flake as well as in the first.

The intensity of the darkening of the mica in these experiments is such as to best admit of comparison with the less developed haloes: those darkened uniformly out to the range of Ra (0.0156 mm.), or RaF (0.0177 mm.), or Ra Emanation (0.0196 mm.). The darkening is too faint to be measured against the more exposed haloes which extend to RaA or RaC. These are, indeed, generally almost opaque centrally. Observations involving comparison of the halo with the experimentally produced staining are, then, necessarily restricted to the less exposed haloes, whose radial dimensions may be assumed to be 0.016, 0.018, and 0.020 mm.

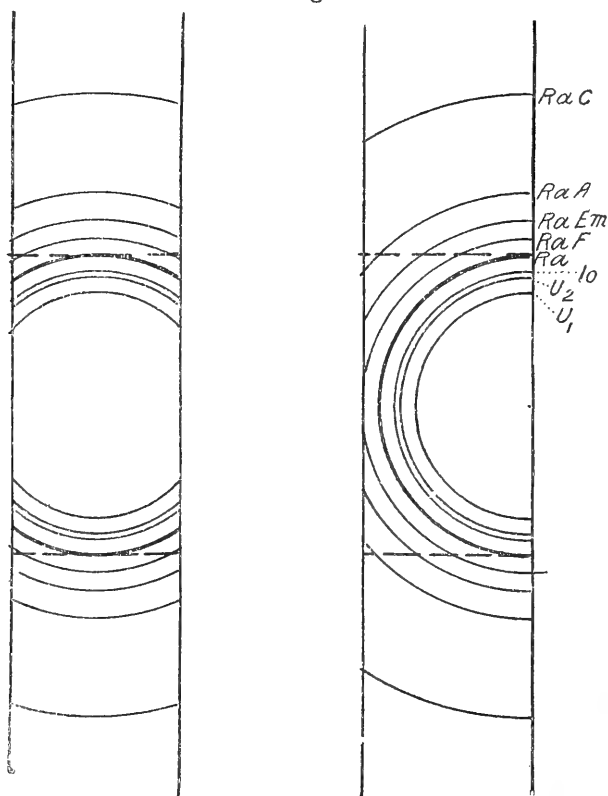
From the experiments it may be deduced that the numbers of rays falling upon circular areas of these radial dimensions which will give the depth of staining of spots A, B, C, will be:—

Radius of halo.....	0.016	0.017	0.018	0.020
Intensity of A	296×10^6	337×10^6	370×10^6	466×10^6
„ „ B	128 „	146 „	160 „	202 „
„ „ C	120 „	136 „	150 „	189 „

The observations on the haloes, designed to afford an estimate of their age, must be directed, as already intimated, to estimating the rate at which alpha rays are being emitted by the nucleus. We have to consider also how the staining effects produced by such radially emitted rays may be brought into comparison with the parallel rays used in the experiment. The cleavage flakes of mica used in the

observations to be presently recorded average from 0.016 to 0.018 mm. in thickness, thicker flakes being too dark for convenient observation. The accompanying diagram of a

Fig. 1.



flake 0.017 mm. in thickness, containing a nucleus placed centrally in the flake and again near its surface, shows that in the case of haloes extending radially 0.016 mm., the total ionization is by no means included within the flake. Only four out of the eight rays complete their ranges within the semi-halo. The maxima of RaC and RaA are wholly excluded. In the case of the centrally placed nucleus the maxima of RaEm and RaF exert but little effect. These excluded rays, however, affect the central area, where their velocities are greatest and ionization effects least. It is also seen that in cleavage flakes of this thickness as much as one-half the entire effects of the rays may be removed with the adjacent cleavage flakes. When the nucleus is at the surface the hemisphere only is contained in the flake. Any accurate allowance for these deficiencies is impossible, as they vary with the position of the nucleus in the flake. There is a small set off against them in the fact that the rays which in the experiment darken the mica are not wholly included

within it. It would seem that a general allowance of 50 per cent. would not be too much to make; that is, we may consider that only half the rays actually emitted by the nucleus are effective in generating that part of the small haloes which enters into the observations.

The measurements on the dimensions of the nuclei of the haloes were made in the Iveagh Geological Laboratory of Trinity College, Dublin. As it is obviously very necessary to secure accuracy in these measurements, care was taken by attention to the best conditions of illumination and magnification and by repetition of the readings to guard against error. Professor H. H. Dixon, F.R.S., independently checked many of the observations. It was found that the best definition was obtained with an oil-immersion of Zeiss (apochromatic 3 mm. N.A. 1.4), and with a No. 7 of Leitz; but the oil-immersion gave the best definition. With careful attention to the lighting the definition could be got very perfect, and there was no uncertainty whatever as to the reliable nature of the measurements, which could be repeated again and again with always the same results. The readings were effected by two distinct methods: (1) by a micrometer eyepiece with travelling line; (2) by the camera lucida combined with the following method of measuring the diameter of the referred image. Two *fine* lines are drawn with a drawing-pen in indian-ink on smooth white paper. The lines meet at a point and very slowly diverge. The separation of the lines was about 3 millimetres at a distance of 15 cm. from the point of intersection. The camera lucida being in position the image is referred in the usual manner to the sheet of paper. The latter is now shifted till the image of the nucleus appears to fit accurately between the lines. While still looking at the object a mark is made with a pencil across the lines just where the nucleus is referred. This is, say, at a distance d_1 from the intersection. An engraved scale divided to 0.01 mm. is now substituted for the mica, and one of the subdivisions brought to fit, as before, between the lines, at a distance d_2 from the intersection. This point is marked. The diameter, x , of the nucleus is then obviously found from the ratio $x : 0.01 :: d_1 : d_2$. This method gave very consistent results in successive measurements*.

In some few cases the diameter of the nucleus is the mean of two not very different diameters, the development of the nucleus not being such as would permit of the assumption that it was of approximately spherical form. In some cases

* Proc. R. D. S. xiii. p. 441.

the nucleus possesses a definite crystalline form, apparently dimetric. Two dimensions are then read : the axial length of the prism and its width transversely.

In comparing the density of the staining of the halo with that of the artificially darkened areas, the following procedure was found most satisfactory :—Two microscopes are placed side by side. The halo is observed in one of them, the spot in the other. The magnification is alike and the light is from the same source. Daylight only could be used. The spot covered but half its field, and the adjoining unacted on mica was, when necessary, brought to the exact same colour and luminosity as the mica around the halo by interposition of a tinted solution and manipulation of the substage fittings. In the case when the mica containing the halo is the lighter in colour these adjustments are applied to it. The depth of tint of spot and halo are now compared. These comparisons were always repeated without adjustment of the colour and luminosity of the field. The former were more consistent and more easy to be sure of. Professor H. H. Dixon quite independently checked many of these comparisons. In the majority of cases the comparison was restricted to determining whether the halo should be judged lighter or darker than, or the same as, the spots A or C. Generally there could be no doubt as to the conclusion arrived at. It will be seen presently that the interest of the results principally turns on that conclusion. However, an effort was made to evaluate the difference in staining of the halo and the spot in a few cases. For this purpose a transparent screen for producing different graded amounts of light absorption was prepared as follows :—A “Process” plate was exposed in the dark room in such a manner that successive strips of it received quantities of light in the proportions 1 : 2 : 3 : 4, &c. This was done by uncovering successive strips of it at intervals of one second. When developed and fixed, and a slip cut from the plate with a diamond, an absorption screen was available having successive areas darkened approximately in the proportions of the exposures. It was found that spot A was almost exactly of the darkness of the 3 second exposure; this area bringing the field of the spot into agreement with it. From this we may assume that the area receiving 6 seconds exposure is of double the density of spot A.

The mode of using this screen is evident from what has been already said. Colour and luminosity having been adjusted as before so that the fields of both spot and halo are alike, the screen is slipped in above the spot (or halo) till the darkening of these objects is brought into equality.

The nuclei are in most cases possessed of all the optical appearances of zircon ; they are transparent, colourless, and of high refractive index. An attempt to determine the index by use of refracting liquids failed. In the cases tried the nuclei were probably buried in the mica. There is no doubt that the index is considerably higher than that of the mica. Some may be orthite ; some, possibly, brookite. Many of the nuclei in certain parts of the granite show no definite crystalline shape, but are granular in appearance. In other places they are all in the form of well-developed dimetric crystals placed with their long axis parallel with the cleavage of the mica. These definite crystals are beyond doubt zircons. They seem somewhat less radioactive than the irregular nuclei. Again, some nuclei are plate-like crystals, rectangular in shape and developed in the plane of cleavage. It is not practicable to ascertain the volume of these as their thickness cannot be measured. Probably their mass is often comparable with that of the smallest nuclei.

It would be very desirable to ascertain directly the radium content of these nuclei. An attempt was made by reducing a considerable quantity of the mica to a very fine powder, and then effecting separations according to density by use of heavy liquids, to isolate the zircons. But nothing of a minuteness comparable with the nuclei was extracted. It is probable that their removal from the mica is difficult. It is not safe to use solvents, for there is evidence that zircons may carry their radioactive constituents as a surface accretion and always as a purely foreign admixture. We could not then be sure that a solvent which acted on the mica did not also remove the radioactive constituents of the zircon, thus falsifying the result in the very direction which is most to be avoided.

It would appear that, for the present, we can only estimate the uranium content by analogy with known results obtained on large zircons. Strutt * has given results on 14 zircons of very different geological ages. The quantity of U_3O_8 in grams per gram of zircon varies from 1.4×10^{-4} to 75.3×10^{-4} . The highest result is very exceptional, the next highest being 38×10^{-4} , and this is from the exceptionally radioactive lavas of Vesuvius. After this 13.3×10^{-4} is the highest. The mean of all is 14×10^{-4} . In other experiments Strutt found 865×10^{-12} gram of radium per gram in zircons †. This involves less than 40×10^{-4} gram per gram of U_3O_8 .

* Proc. R. S., A, lxxxiii. p. 298.

† Proc. R. S., A, lxxviii. p. 150.

He also found * 0.34 millionths of one per cent. of radium in zircon ; and in another specimen 0.52 millionths of one per cent. The latter quantity involves about 1.5 per cent. of uranium. The closely allied, and probably derived, mineral cyrtolite was found by Strutt † to contain 3.67 per cent. of U_3O_8 and 5.05 per cent. of ThO_2 . Two analyses of cyrtolite are cited by Dana ; one showing 1.59, the other 1.4 per cent of U_3O_8 .

J. W. Waters showed that in gneiss of the Inner Hebrides and granite of Mourne the radioactivity was concentrated mainly in the zircons ; in Cornish granite chiefly in anatase or rutile ; and in Dalbeattie granite chiefly in orthite. Quantitative results are not given ‡.

It will be seen that the highest of the above results is that for cyrtolite, which rises to 3.67 per cent. of U_3O_8 . This figure does not, presumably, limit the quantity of uranium which might be present. But there is no reason to believe that radioactive constituents ever constitute a large part of zircon. On the contrary, it has been shown by Mügge § and by Gockel || that the radioactive matter constitutes an impurity or foreign substance in zircon.

Uranium is not recorded by Dana as a constituent of orthite or brookite. Strutt ¶ found in one specimen of orthite 0.073 per cent. of U_3O_8 , and in another radium equivalent to 3 per cent. of uranium.

From the foregoing results it would seem safe to assume 10 per cent. of uranium as an upper limit to the amount now contained in the nuclei of the haloes in this mica.

The periods of time which emerge from the measurements to be presently cited are such that the wasting of the uranium should be taken into account. We must, accordingly, calculate back, deriving the mass of transformed uranium from the number of alpha rays required to form the halo according to the observations and the experimental data. The estimated existing mass of uranium in the nucleus thus becomes the amount remaining after the time t ; so that if M is the mass transformed and W the existing mass, $W/(M + W)$ is the fraction remaining, or $e^{-\frac{t}{L}}$. Exponential tables give the value of t/L corresponding to $e^{-\frac{t}{L}}$, where L is the average

* Proc. R. S., A, lxxvi. p. 312.

† Proc. R. S., A, lxxvi. p. 88.

‡ Phil. Mag. 1909 and 1910.

§ *Centralbl. f. Min. &c.*, 1909, p. 148.

| *Chemiker Zeitung*, 1909, No. 126.

¶ Proc. R. S., A, lxxvi. p. 312.

life of uranium. From this t is found. As an example of the mode in which the figures in the ensuing table are derived :—halo No. 4 has a nuclear mass of 418×10^{-14} gram, and the uranium present is taken as 418×10^{-15} gram. The radius of the halo is 0.016 mm., and as it is darker than spot A we calculate that the number of alpha rays required to produce this halo is not less than 2.95×10^8 rays, or 5.9×10^8 for the whole halo. Now 8 rays are produced for every atom of uranium transformed. Thus the number of uranium atoms transformed has been 0.74×10^8 . Taking the mass of one atom of hydrogen as 1.6×10^{-24} *, the mass of an atom of uranium is 381×10^{-24} . The mass transformed is, hence, 28×10^{-15} gram. The quantity present being assumed as 418×10^{-15} , this becomes 0.9373 of the original mass. The exponential tables now give the corresponding value of t/L as 0.065, and as L is 7.2×10^9 , the value of t is found to be 0.47×10^9 years. The age is greater than this as the darkening of the halo exceeds that of spot A, but in this case no attempt was made to evaluate this excess.

The following table contains the results of 30 measurements of nuclei. There would have been no difficulty in adding to this number almost indefinitely, but it is thought that the number given is sufficient. Moreover, considerable time and labour are required to complete the careful measurement of each halo. In Nos. 24, 25, and 26 the nuclei are well developed, apparently dimetric, crystals with prismatic and terminal faces. The mass is probably somewhat exaggerated, as outside dimensions are given. No allowance is made for a slight elongation of the derived halo. Both these facts will tend to lower the age.

The nuclei of Nos. 29 and 30 have been photographed, and are reproduced in Plate IX. No. 29 (fig. 1) is magnified 1450 diameters; No. 30 (fig. 2) is magnified 1400 diameters. It is very difficult in such photographs to show at once the nucleus and the halo, for the intense conditions of exposure and development requisite to bring out the former are quite unsuited to reproduce the latter. The nucleus of No. 29 is characteristic of the granular type. Near it is a relatively large nucleus of well crystallized zircon. It has given rise to a less intense halo. The halo, No. 29 (which is developed round the small nucleus), is of a rich brown colour and certainly darker than spot A. Centrally it is so dark that the exposure required to take it has resulted in complete over-exposure of the surrounding halo. In calculating the volume of this nucleus it is assumed to be ellipsoidal in

* Rutherford and Geiger, Proc. R. S., A, lxxxi. p. 162.

shape, and the mean diameter is taken as that of the equivalent sphere. In No. 30 the nucleus is rectangular in outline and is some distance down in the mica. It is apparently a flat, rectangular crystal; but its volume has been calculated on the assumption that it is cubical. It was easier to photograph this halo owing to the fact that the cleavage flake in which it is contained is so thin as only to be of a pale straw-yellow. Notwithstanding its thinness the halo is not less than twice as dark as spot A.

No.	Diam. of nucleus. cm. $\times 10^5$.	Mass of Zircon. gm. $\times 10^{14}$.	Radius of Halo. cm. $\times 10^4$.	Comparison of Halo with intensity of spots A, B, or C.	No. of α -rays for whole halo. $\times 10^{-8}$.	Mass of trans-formed U. gm. $\times 10^{15}$.	Age, years.
1	10	243	18	Dark as C.	3.0	14	400×10^6
2	38	13481	20	Nearly opaque.	9.3	43	> 20 "
3	16	990	16	Darker than A.	5.9	28	> 200 "
4	12	418	16	" "	5.9	28	> 470 "
5	33	8800	16.5	" "	6.4	30	> 30 "
6	37	12320	16.5	" "	6.4	30	> 20 "
7	20	1980	16	Between A and B.	4.2	20	80 "
8	23	3080	16	Very much darker than A.	5.9	28	≥ 60 "
9	12	418	16	Dark as B.	2.6	12	200 "
10	14	660	16	Darker than A.	5.9	28	> 270 "
11	21	2420	16	Much darker than A.	5.9	28	≥ 90 "
12	22	2640	16	Darker than A.	5.9	28	> 80 "
13	26	4400	16	Very much darker than A.	5.9	28	≥ 50 "
14	13	506	16	Dark as A.	5.9	28	390 "
15	30	6600	16	Very much darker than A.	5.9	28	≥ 30 "
16	17	1210	16	Darker than A.	5.9	28	> 160 "
17	25	3740	16	Very much darker than A.	5.9	28	≥ 50 "
18	15	792	16	Dark as A.	5.9	28	250 "
19	27	4840	18	" "	7.4	35	50 "
20	27	4840	17	" "	6.8	32	50 "
21	24	3388	17	Darkness = $A \times 2$.	13.6	64	140 "
22	26	4400	17	Darkness = $A \times 7/3$.	15.8	75	120 "
23	23	3080	17	" "	15.8	75	170 "
24	$57 \times 18 \times 18$	8580	17	Dark as A.	6.8	32	30 "
25	$48 \times 32 \times 32$	22000	17	Darkness = $A \times 2$.	13.6	64	20 "
26	$40 \times 22 \times 22$	9020	17	Dark as A.	6.8	32	30 "
27	12.5	462	17	Dark as C.	2.7	13	200 "
28	21	2420	18	Dark as A.	7.4	35	100 "
29	29	5984	16	Darker than A.	5.9	28	> 40 "
30	$21 \times 21 \times 21$	5720	19	Darkness about $A \times 2$.	16.5	78	100 "

It must be borne in mind that the higher values of the age are those of most significance. Low values of course are deduced whenever the mass of the nucleus is large and the surrounding halo faint. Although the darkness of the halo generally varies with the size of the nucleus, there is no definite proportion of uranium in the zircon or other minerals forming nuclei, and cases of apparent low age are plentiful. They are explained if we suppose that in these cases our

assumption as to their uranium content is excessive. What is significant is the fact that in many cases we can find nuclei so small surrounded by well darkened haloes.

In many examples given in the table the age must exceed that which is given in the last column. This is so because only in some of the last observations, and in those in which the halo happened to match closely the staining of one of the spots, is there any numerical evaluation of the relative darkness of spot and halo. The results are numbered in the order in which they were obtained. The highest of the measurements point to an age not less than four hundred millions of years as the time required to generate these haloes : in other words, as the age of the early Devonian. The treatment of the subject throughout this paper has been such as to render this a minor limit.

Sources of error must now be inquired into :—

(a) The nuclei are the *complete* nuclei. The possibility that the nuclei measured were detached fragments of larger nuclei, the greater part being cleaved off in opening the mica, was investigated by comparing the contiguous faces of cleaved flakes and making sure that the part of the halo-sphere removed contained nothing that could be regarded as part of the nucleus, or that could suggest the loss of any part of it. Not a single case of a divided nucleus was met with. The fact is the cleavage of zircon is very imperfect, and even if it lay just at the surface of cleavage it would almost certainly remain bodily in the one flake or the other ; or, possibly, drop out. Again, many of the observed nuclei were demonstrably beneath the surface of the flake. This was rendered quite certain by observations on thick cleavage flakes, using a very strong light.

(b) The crystallographic direction in which a part of the rays traverses the mica in the case of the halo, is not the same as that in which the rays move in the mica when generating the experimental darkening. The fact, however, that in sections of haloes there is uniform darkening in all crystallographic directions, negatives the idea that error can arise from this source.

(c) Nothing is known of any mode by which the mere passage of time can intensify a halo or increase the effects of the original ionization. In the case of light-sensitive salts the ionization set up by exposure appears to weaken by the passage of time. No intensification of the latent image is known. A recombination of the products of dissociation and weakening of the halo with time would rather be expected. The halo is probably very stable.

(d) The rate of formation of the experimental staining is very fast compared with the rate of formation of the halo. It does not seem likely that any significance is to be ascribed to this fact. For the distribution of the alpha rays projected into the mica in the experiment is actually a very sparse one. Molecularly speaking they are finally separated by very great distances ; so that the molecular groups, in which the entering rays expend their energy, remain generally isolated and undisturbed by succeeding rays. The interval of time between succeeding rays would not, therefore, appear to matter, and the resulting staining would be the same for each ray.

(e) Exposure to light does not appear to affect, one way or the other, the staining produced in this mica by the alpha ray. An experiment in which spots D and E were half covered by lead foil and then exposed in bright sunlight, concentrated by a lens, for several hours, revealed no effect whatever. Strong heating obliterates haloes. In the experiment strong heating was avoided.

(f) Thorium is absent from these nuclei. No thorium haloes have been found in this mica.

Comparing the value indicated for the age of the Devonian by the foregoing results with estimates arising from the measurement of accumulated radioactive *débris*, it will be seen that the halo indicates a somewhat excessive age. The helium ratio gave Rutherford * 241 millions of years for a specimen of fergusonite, probably from ancient rocks. Strutt, by the same method, arrived at 150 millions of years as the age of the Carboniferous Limestone and 710 millions as the age of the Archæan †. Boltwood's results with the lead ratio ranged from 246 to 1640 millions of years ; the higher being referable, probably, to Archæan rocks ‡. Becker, dealing with Pre-Cambrian minerals of the Llano Group, found, by the lead ratio, from 1671 to 11,470 millions of years ; regarding his figures as a " *reductio ad absurdum* " §. Boltwood criticised these results, questioning the reliability of the material dealt with. Becker urged in reply that there was no evidence of any effect on the lead ratio arising from incipient alteration of the material. A. Holmes || investigated the age of a Devonian syenite by the lead ratio, and found this to be 370 millions of years ; he rejects, however, results showing a greater age, on the ground that original lead was probably present in sufficient quantity to falsify the result.

* Phil. Mag., Oct. 1906, p. 368.

† Proc. R. S., 1908-1910.

‡ Am. J. of Sc., 1907.

§ Bull. Geol. Soc. Am., 1908.

|| Proc. R. S., June 1911.

The results founded on the accumulation of radio-active *débris* are open to the objection that addition or subtraction of the measured substances may have occurred over the long period of time involved. The results obtained from the halo are less likely to be affected by this source of error. It is of interest to find, therefore, that the results obtained from it are not very discordant with some of the higher results obtained by the lead ratio. There may be significance in this rough agreement, or errors of a nature as yet unknown may affect both determinations. We are not in a position to say. But it is certain that if the higher values of Geological Time so found are reliable, the discrepancy with estimates of the age of the ocean, based on the now well-ascertained facts of solvent denudation, raises difficulties which at present seem inexplicable. Discussion of hypotheses whereby the reliability of the one method or the other may be called in question is not within the scope of this paper.

LXIV. *On the Production of Fluorescent Röntgen Radiation.*

To the Editors of the 'Philosophical Magazine.'

GENTLEMEN,—

IN the current number of this magazine Mr. J. Crosby Chapman attacks an hypothesis of mine that an intermediary cathode ray conveys the energy from the primary X-ray to the homogeneous secondary ray.

Mr. Chapman finds by experiment that the cathode rays which emerge from a gold foil under the influence of Sn X-rays lose 52 per cent. of their energy in passing through a second gold leaf, the energy being measured by their power of ionizing air. With this I agree; in fact I have done the experiment myself. He thence concludes that the cathode rays excited in a gold foil by hard primary X-rays ought to emerge from the foil—or a certain fraction of them should emerge—carrying a large percentage of the original power possessed by those cathode rays of exciting homogeneous secondary rays in gold. Clearly the conclusion does not immediately follow. It seems to me that arguments of this kind are always liable to one defect at least, viz., that the absorption coefficient is taken as a definition of the quality of the radiation. Perhaps homogeneous X-rays are sufficiently defined by an absorption coefficient, but certainly the same cannot be said of primary X-rays or of cathode rays.

When, therefore, Mr. Chapman concludes finally that homogeneous or fluorescent radiation cannot be to the

Phil. Mag. S. 6. Vol. 25. No. 148. April 1913. 2 Y

smallest extent an effect of β -ray activity, his argument is—so it seems to me—inconclusive. It is to be remembered, also, that Beatty has shown that homogeneous radiations *are* produced by cathode rays of sufficient individual energy.

Mr. Porter and I have been trying for some time to solve this problem, using homogeneous, not heterogeneous, X-rays. The method is more difficult because the radiation employed is much weaker, but I believe it is by no means impossible to follow it to the end. At any rate, we have made some progress. We had not intended to publish any of our results until they were more fully advanced; yet, in view of Mr. Chapman's letter, it seems better to do so, with the reservation that we do not ourselves consider them as final.

If cathode rays do intervene between the exciting X-rays and the homogeneous excited rays, the effect should be more obvious in cases where it is known that the energy of the excited rays forms a reasonable fraction of the energy of the exciting X-rays. These occur when the exciting rays are homogeneous X-rays emitted by atoms of somewhat greater weight than those in which the rays are to be excited. For that reason Mr. Porter and I have been investigating the action of Mo X-rays on ethyl bromide, sulphur dioxide, and air, comparing these results with the action of Se X-rays on the same gases. It will be observed that Mo and Se lie on either side of Br as regards atomic weight. Mo X-rays can excite Br X-rays, but Se X-rays cannot. If there is truth in the hypothesis of the intermediary cathode ray, three results may be expected and looked for:—

- (1) The cathode ray produced by the Mo X-ray should show some deficiency in penetrating power in ethyl bromide, since it is spending energy in a special fashion.
- (2) The same cathode ray should be deficient in ionizing power in ethyl bromide, since it is spending energy in other ways. In the same way there is a sharp contrast between the action of Mo X-rays and Se X-rays on ethyl bromide and SO_2 . The former rays produce even a little less ionization in ethyl bromide than in sulphur dioxide, while Se rays produce far more. It is apparently easier to ionize ethyl bromide than sulphur dioxide, and the defective action of the Mo X-rays is to be ascribed to their being spent somewhat in producing Br X-rays.
- (3) The most direct result, but the most difficult to measure, should, of course, be the production of secondary Br X-rays by Mo cathode rays.

So far we have verified the first two of these results, as far as we are at present able to interpret our work. We found the absorption coefficients of the cathode rays produced in gold by Se X-rays to be in air at atmospheric pressure 26.2 cm.^{-1} , and in ethyl bromide of equal density 24.5 . The absorption coefficients of the Mo X-rays were 16.3 in air and 29.2 in the ethyl bromide. It may seem paradoxical that the faster Mo cathode rays should actually have a higher absorption coefficient in ethyl bromide than the slower Se cathode rays; but, again, it is to be remembered that absorption coefficients represent an average of conditions.

We have also found a deficiency in the ionizing power of the Mo X-rays acting on ethyl bromide. But we are not satisfied with measurements which depend on cathode-ray streams of somewhat doubtful composition, and are about to use cathode rays of known speed. I may add that we are also substituting another metal for the gold leaves, because it seems very probable from Mr. Chapman's proof of the identity of the homogeneous radiations from Au and Br that we have been prejudicing our own case.

These results indicate that Lenard's rule, viz., that the penetration of cathode rays depends only on the density of the matter penetrated is not universal, which, after all, might be expected. When Mr. Chapman says that there is no experimental evidence whatever of its violation in any case, he cannot have noticed a reference to these results in an address which I gave at Dundee last September.

As I have said above, we hope to carry out all three of the tests I have mentioned.

W. H. BRAGG.

LXV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 200.]

November 20th, 1912.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On the Hafslo Lake and the Solvorn Valley (Norway).'
By Horace Woollaston Monckton, Treas.L.S., F.G.S.

The district dealt with lies north of the main Sogne Fjord and west of the Lyster Fjord. Attention is drawn to a series of valleys running from the area of the Jostedal snowfield and cutting the belt of Silurian rocks which crosses the district in a north-easterly and south-westerly direction, and to a second series of valleys which run parallel to the snowfield and to the Silurian belt. The author

traces the valley of the Vejtestrands Lake, which belongs to the first of the above series, until it reaches the Hafslo Lake, which lies at a point where the valleys of the two series intersect. The present line of drainage follows a valley of the second series from the lake to the fjord, but a disused outlet from the lake to the fjord is described belonging to the first series. The author, while thinking that the disused outlet is probably the older of the two, gives reasons for believing that both outlets were in use perhaps simultaneously during the latter part of the Glacial Period, when a glacier filled and overflowed the basin of the Hafslo Lake.

The author describes some giants' kettles and other examples of erosion by water, which for various reasons he believes to date from a time when the glacier extended to the places where they are now found, and it is suggested that they were the work of a river flowing under the ice or between the ice and the rock.

2. 'On the Genus *Aulophyllum*.' By Stanley Smith, B.A., M.Sc., F.G.S., Clare College, Cambridge.

LXVI. *Intelligence and Miscellaneous Articles.*

ON THE CURRENT POTENTIAL CURVES OF THE OSCILLATING SPARK.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

M. ROSCHANSKY has kindly drawn my attention to a numerical error which I have made on p. 719 in the above paper (Phil. Mag., Nov. 1912) in estimating the maximum current density which completely ionized air is capable of carrying with the field which exists in the spark. The field in the spark is there wrongly quoted as 10·5 volts per cm., whereas it should be 10·5 volts per mm. (Roschansky, *Ann.d.Phys.* xxxvi. p. 290, 1911). The corrected estimate for the maximum current density is

$$C=600,000 \text{ amp./sq. cm.,}$$

instead of the 63,000 there stated. I may add that the argument of the paragraph is not affected, as it is concerned with the order of magnitude only of the quantity, the calculation being of necessity only a rough one.

I also find that the conclusion of M. Roschansky, that at high frequencies the spark tends to behave like a pure resistance, which was referred to on p. 713 as being in disagreement with my observations, has been to some extent withdrawn in his later paper (*l. c.* p. 305).

Yours faithfully,

S. R. MILNER.

The University of Sheffield,
17th Feb., 1913.

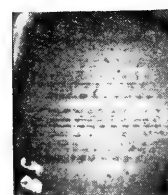
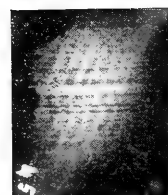


FIG. 10.

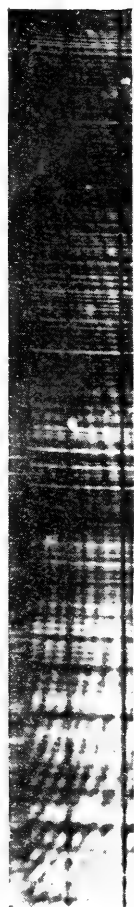
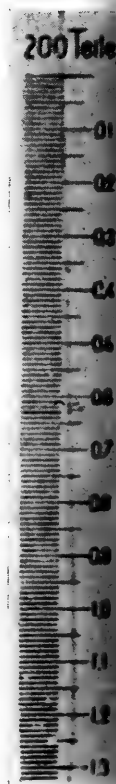
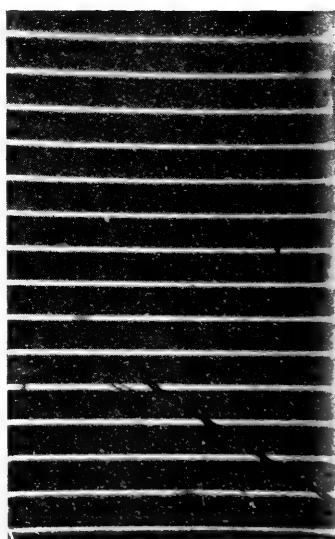


FIG. 9.

FIG. 7.



FIG. 8.



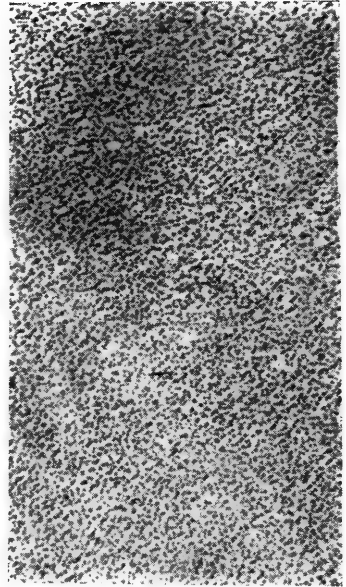


FIG. 1.

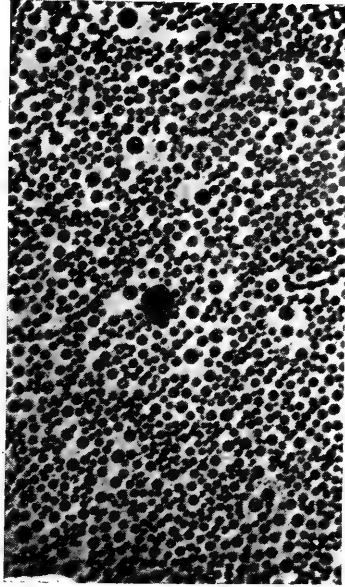


FIG. 3.

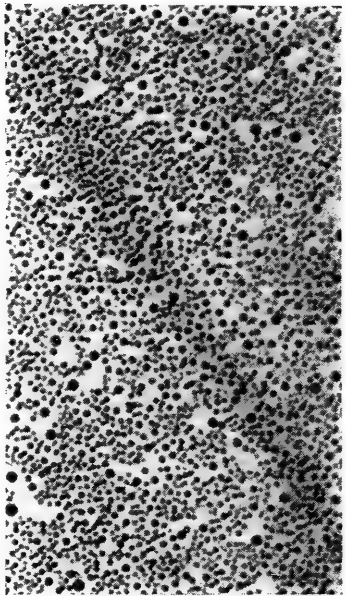


FIG. 2.

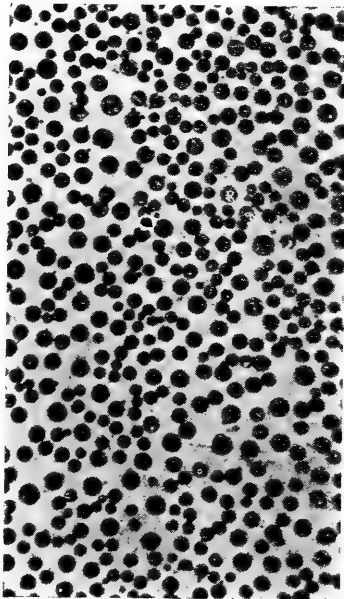
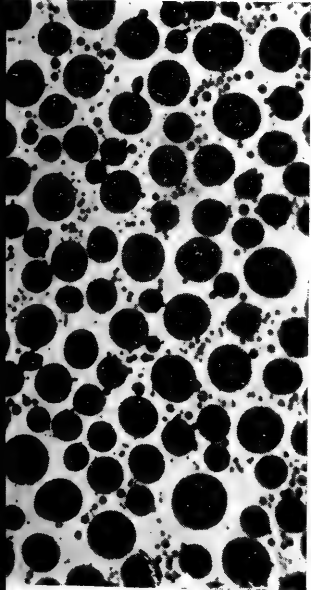
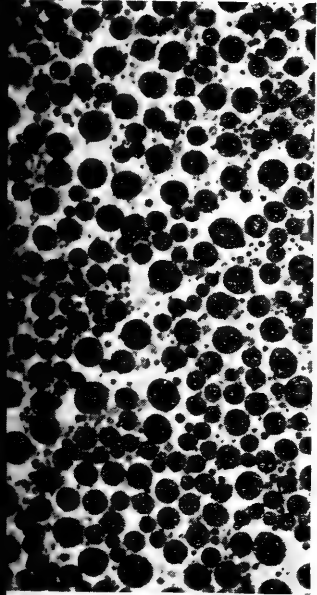


FIG. 4.



SATELLITES OF MERCURY LINES.

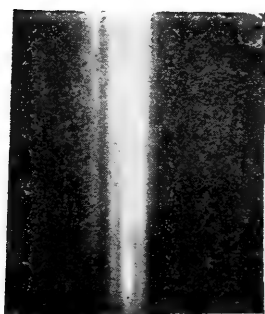


FIG. 1. $\lambda = 5769$.

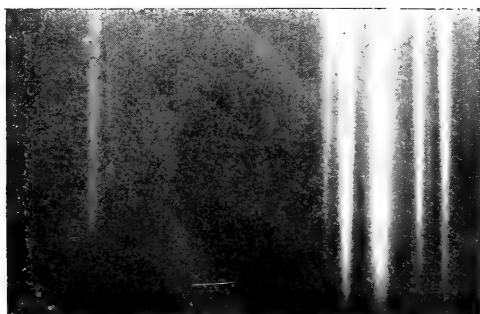


FIG. 2. $\lambda = 5790$.

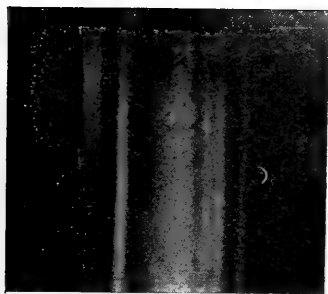
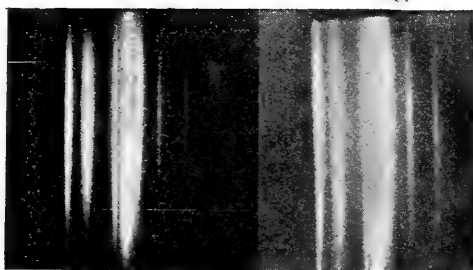


FIG. 3. $\lambda = 5461$.



a FIG. 4. $\lambda = 4359$. b

SATELLITES OF MERCURY LINES.



FIG. 1. $\lambda = 5769$.

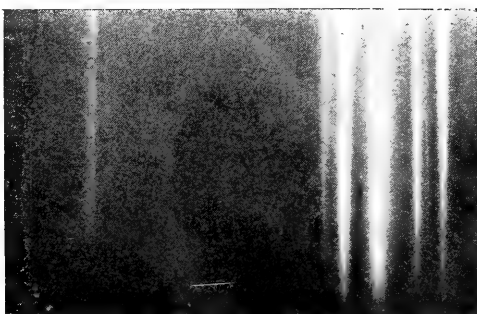


FIG. 2. $\lambda = 5790$.

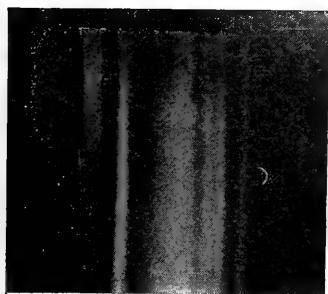
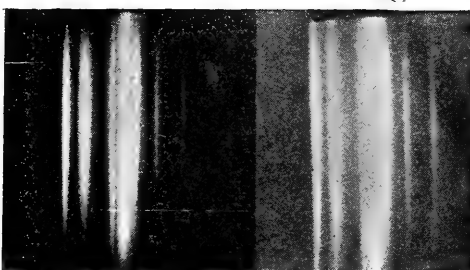


FIG. 3. $\lambda = 5461$.



a b
FIG. 4. $\lambda = 4359$.



Note.—In FIG. 1—FIG. 5 α is the spectrum of the uncondensed brush
 b is the spectrum of the condensed brush
 c, d, e is the spectrum of the condensed brush

FIG. 1.
Lithium Carbonate
·005 per cent.
Point = ·5 mm. diam.

Time of Exposure in minutes.	Current in amperes.	Potential Dif- ference in volts.	No. of Discharges per $\frac{1}{2}$ Alternation of Current.
120	·014	1120	...
120	·016	940	20
115	·034	715	7 or 8
30	·053	555	8
60	·012	394	...
120	·019	464	7-15
60	·046	267	7 or 8
60	·066	1100	4
15	·163	212	1
120	·013	675	...
120	·015	620	20
75	·042	600	5

FIG. 3.
Lithium Carbonate
·1 per cent.
Point = ·5 mm. diam.

FIG. 5.
Lithium Carbonate
·01 per cent.
Point = ·1 mm. diam.

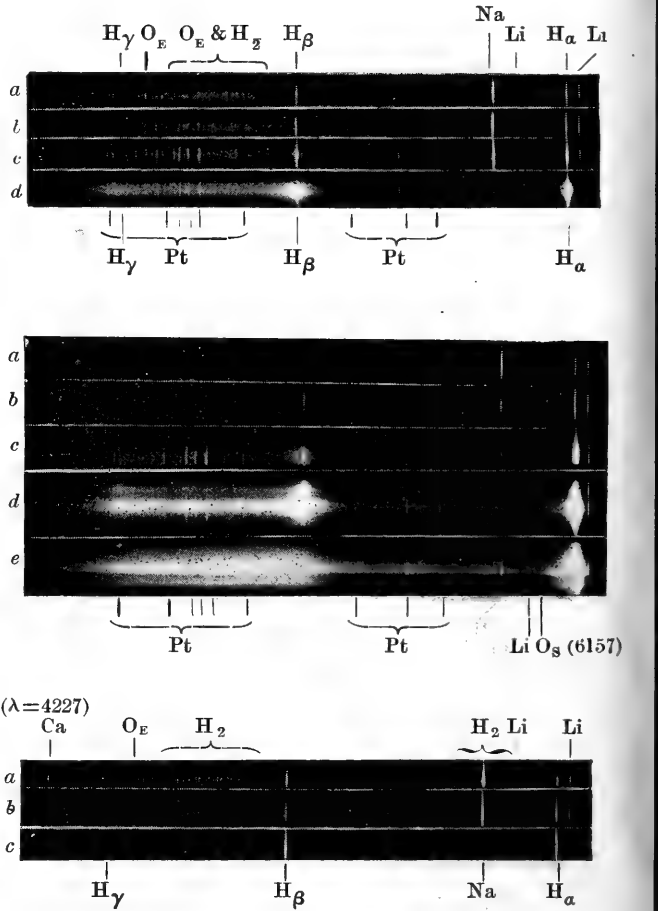
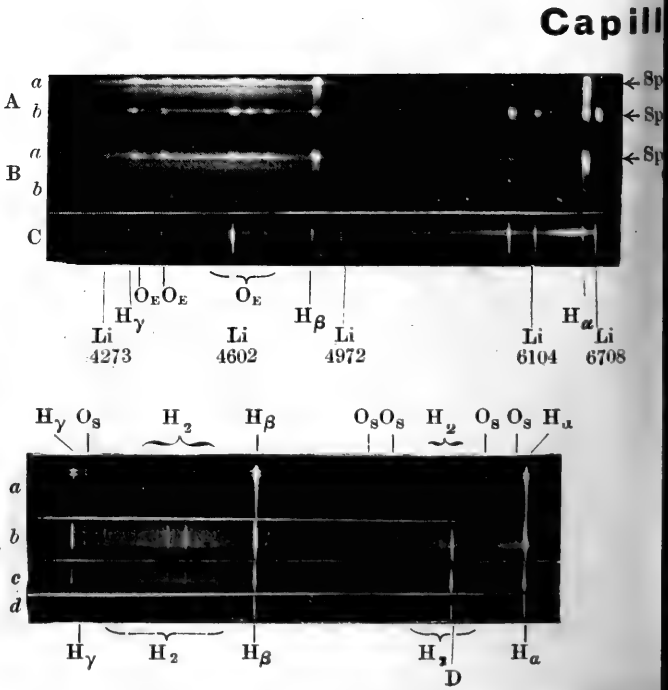


FIG. 7.
Lithium Sulphate.

Note.—All spectra
are without con-
denser or spark-
gap.

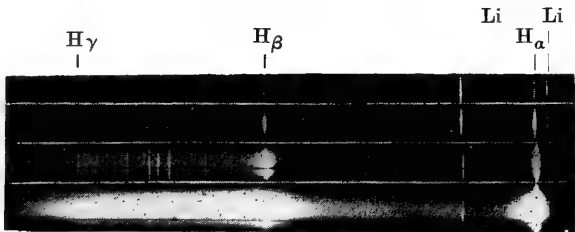
FIG. 9.
Distilled Water.

Time of Exposure in minutes.	Current in amperes.	Potential Dif- ference in volts.	Diameter of Capillary in mm.
15	·025 ?
60	·021	3100	·05 +
60	·026	1530	"
60	·023	1260	"



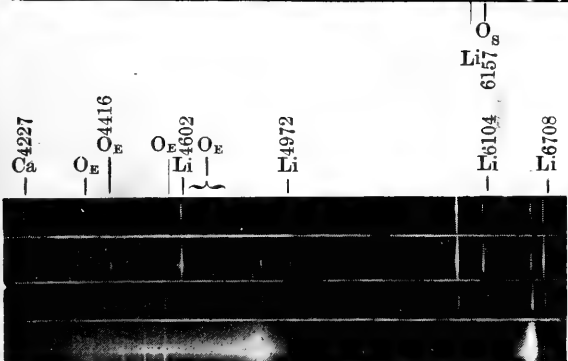
H₂=Secondary Spectrum of Hydrogen.
O_s=Series Spectrum of Oxygen.
O_E=Elementary line of Oxygen.
Li=Spectrum of Lithium.

charge.



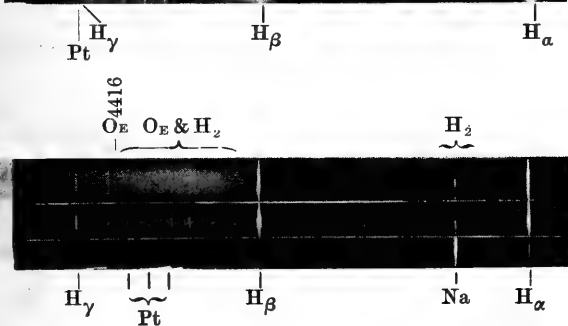
Time of Exposure in minutes.	Current through Brush in amperes.	Potential Dif- ference in volts.	No. of Discharges per 1/2 Alternation of Current.
80	·014	650	20
80	·029	550	7 or 8
80	·064	610	2 or 3
40	·084	410	1

FIG. 2.
Lithium Carbonate
·01 per cent.
Point =·5 mm. diam.



Time of Exposure in minutes.	Current through Brush in amperes.	Potential Dif- ference in volts.	No. of Discharges per 1/2 Alternation of Current.
60	·053	500	20
60	·057	520	4
60	·084	565	2
15	·17	425	2

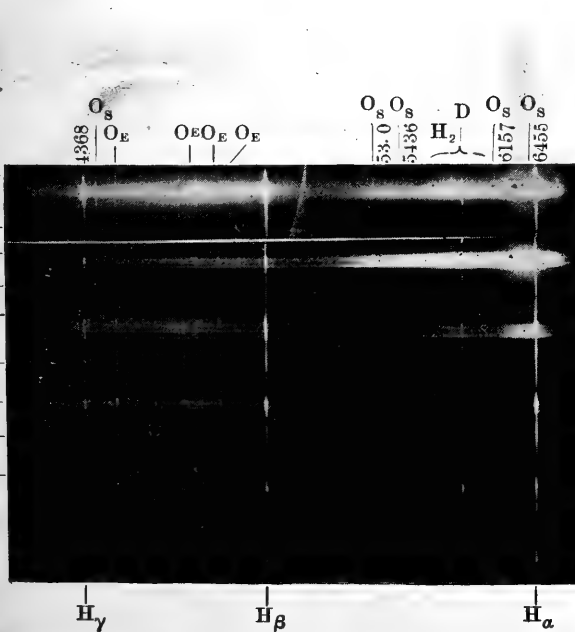
FIG. 4.
Lithium Sulphate
·1 per cent.
Point =·5 mm. diam.



Time of Exposure in minutes.	Current through Brush in amperes.	Potential Dif- ference in volts.	No. of Discharges per 1/2 Alternation of Current.
42	·043	3600	20
60	·0·4	950	4
60	·027	950	2

FIG. 6.
Distilled Water.
Point =·5 mm. diam.

charge.



Time of Exposure in minutes.	Current in amperes.	Potential Dif- ference in volts.	Diameter of Capillary in mm.
60	·045	785	·05 +
60	·032	725	„
60	·029	840	„
60	·021	880	„
60	·013	760	„
60	·009	760	„

FIG. 8.
*Dilute Sulphuric
Acid*
·1 per cent.

Note.—In FIG. 1—FIG. 5 *a* is the spectrum of the uncondensed brush.
b is the spectrum of the condensed brush without spark-gap.
c, d, e is the spectrum of the condensed brush with spark-gap.

H_2 = Secondary Spectrum of Hydrogen.
 O_s = Series Spectrum of Oxygen.
 O_E = Elementary line of Oxygen.
 Li = Spectrum of Lithium.

Brush Discharge.

FIG. 1.
 Lithium Carbonate
 .005 per cent.
 Point = .5 mm. diam.

Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	No. of Discharges per 1/2 Alternation of Current.
120	.014	1120	...
120	.016	940	20
115	.034	715	7 or 8
30	.053	555	8
60	.012	394	...
120	.019	464	7-15
60	.046	267	7 or 8
60	.066	1100	4
15	.163	212	1
120	.013	675	...
120	.015	620	20
75	.042	600	5

FIG. 3.
 Lithium Carbonate
 .1 per cent.
 Point = .5 mm. diam.

FIG. 5.
 Lithium Carbonate
 .01 per cent.
 Point = .1 mm. diam.

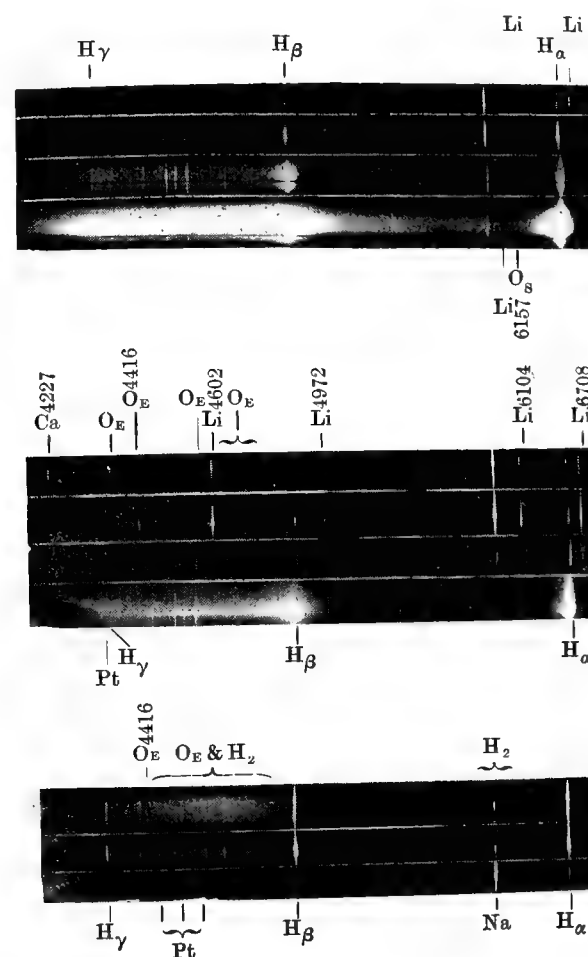
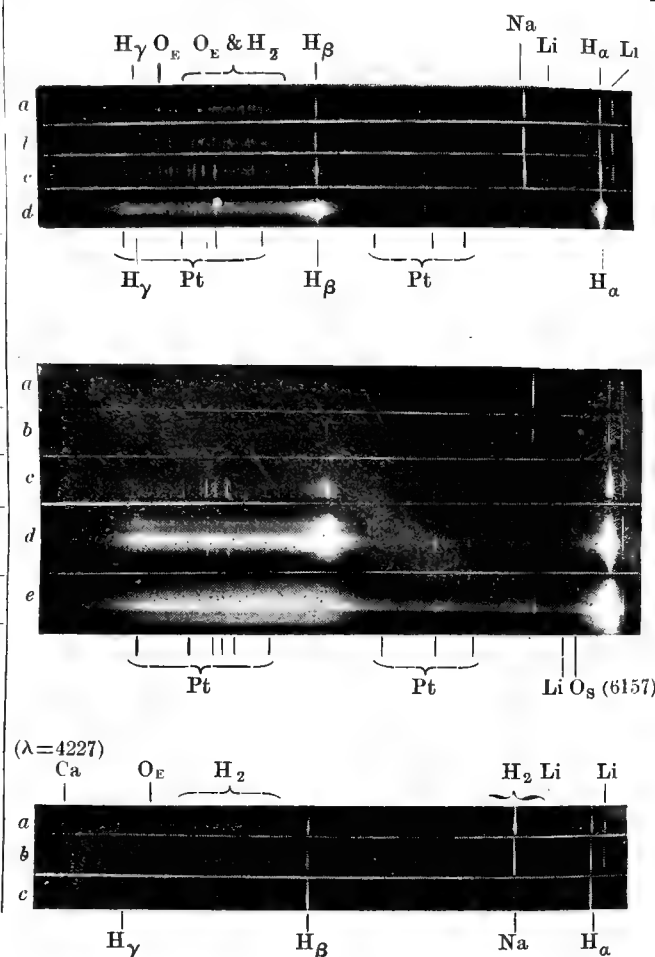


FIG. 2.
 Lithium Carbonate
 .01 per cent.
 Point = .5 mm. diam.

FIG. 4.
 Lithium Sulphate
 .1 per cent.
 Point = .5 mm. diam.

FIG. 6.
 Distilled Water.
 Point = .5 mm. diam.

Capillary Discharge.

Note.—All spectra are without condenser or spark-gap.

FIG. 7.
 Lithium Sulphate.

Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Diameter of Capillary in mm.
15025 ?
60	.021	3100	.05 +
60	.026	1530	"
60	.023	1280	"

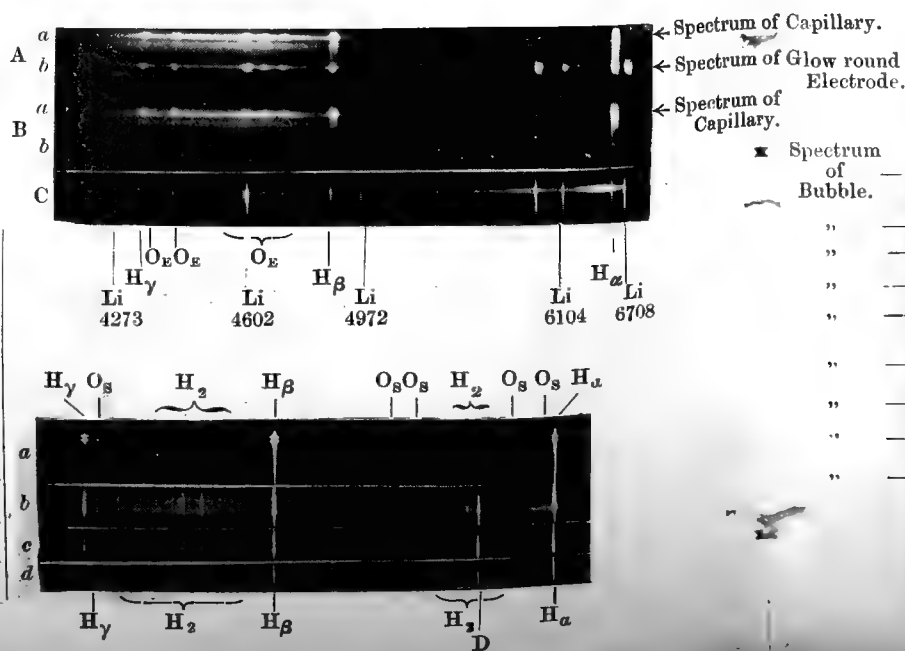
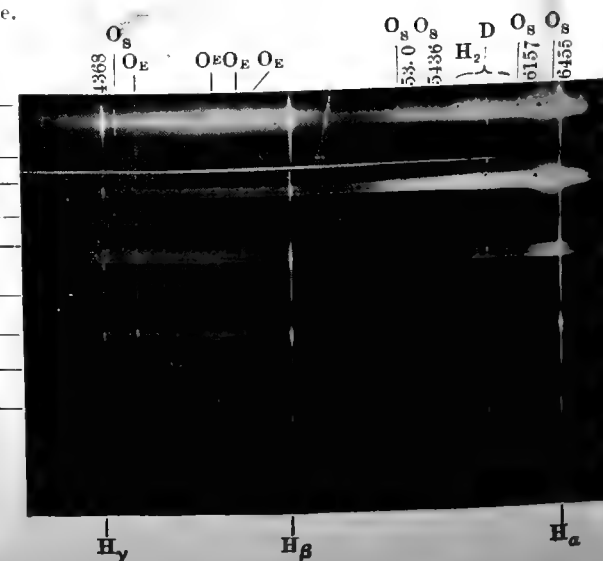


FIG. 9.
 Distilled Water.



Time of Exposure in minutes.	Current in amperes.	Potential Difference in volts.	Diameter of Capillary in mm.
60	.045	785	.05 +
60	.032	725	"
60	.029	840	"
60	.021	880	"
60	.013	760	"
60	.009	760	"

FIG. 8.
 Dilute Sulphuric
 Acid
 .1 per cent.

FIG. 3.

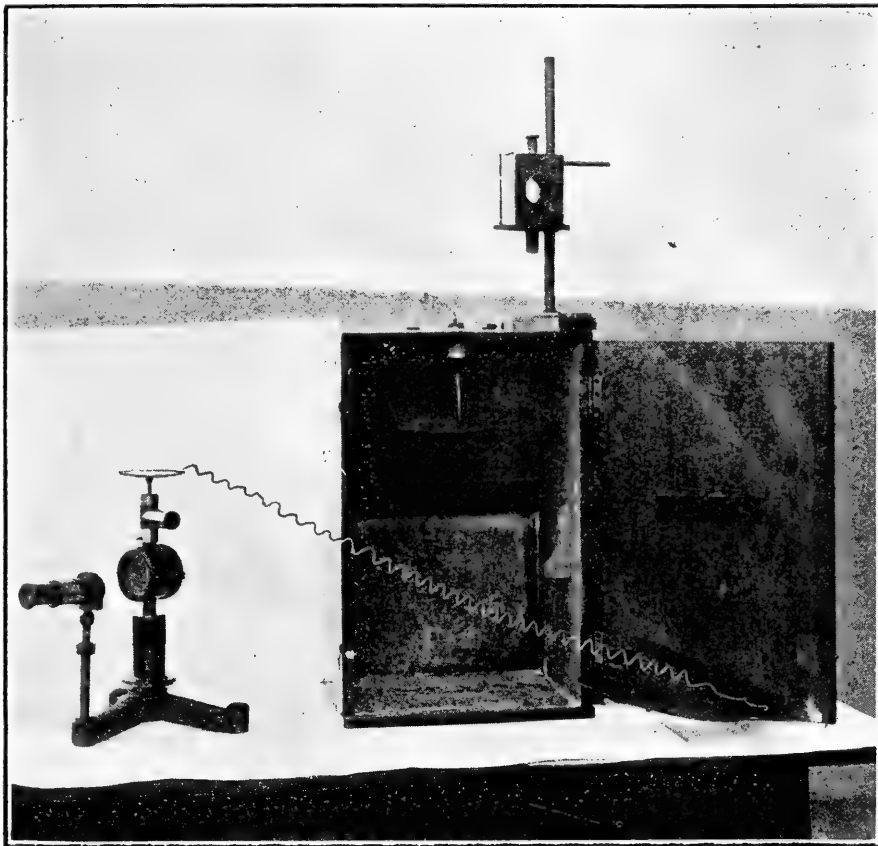
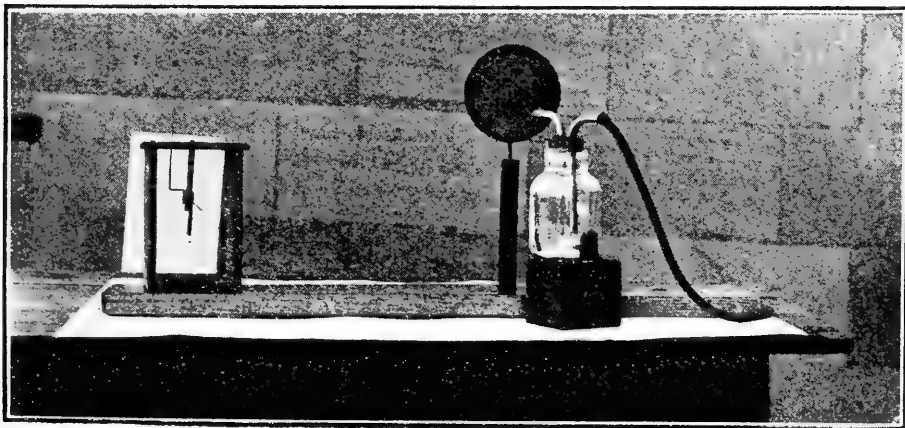


FIG. 4 A.



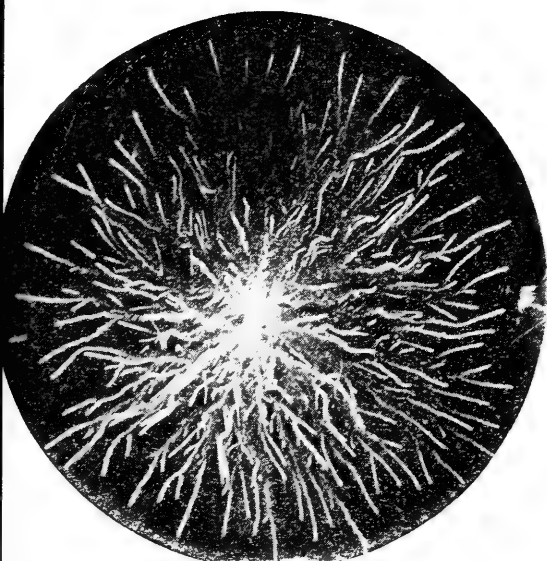


FIG. 5.—Starch.

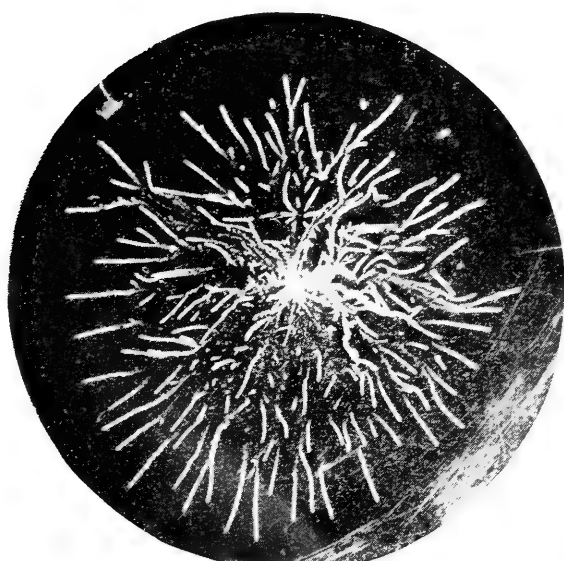


FIG. 6.—Sulphur.

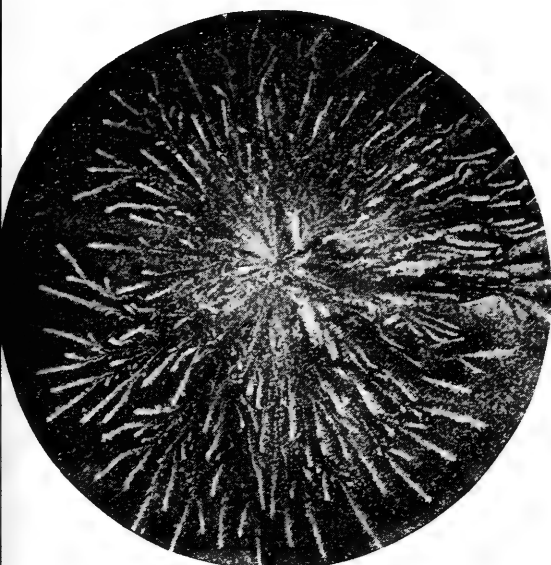


FIG. 7.—Boracic Acid.

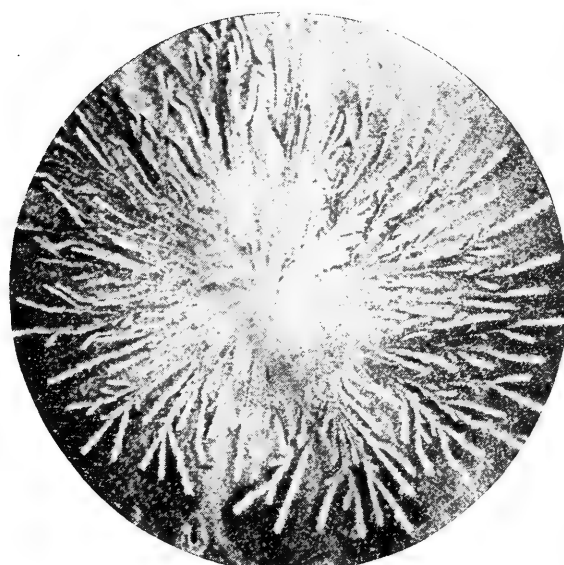


FIG. 8.—Aluminium.



FIG. 9.—Sifted Sulphur upon a charged surface.

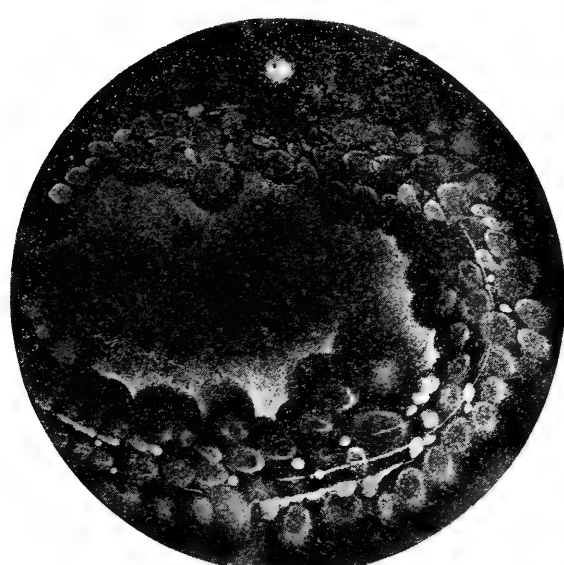


FIG. 10.—Sulphur on a positively charged surface.

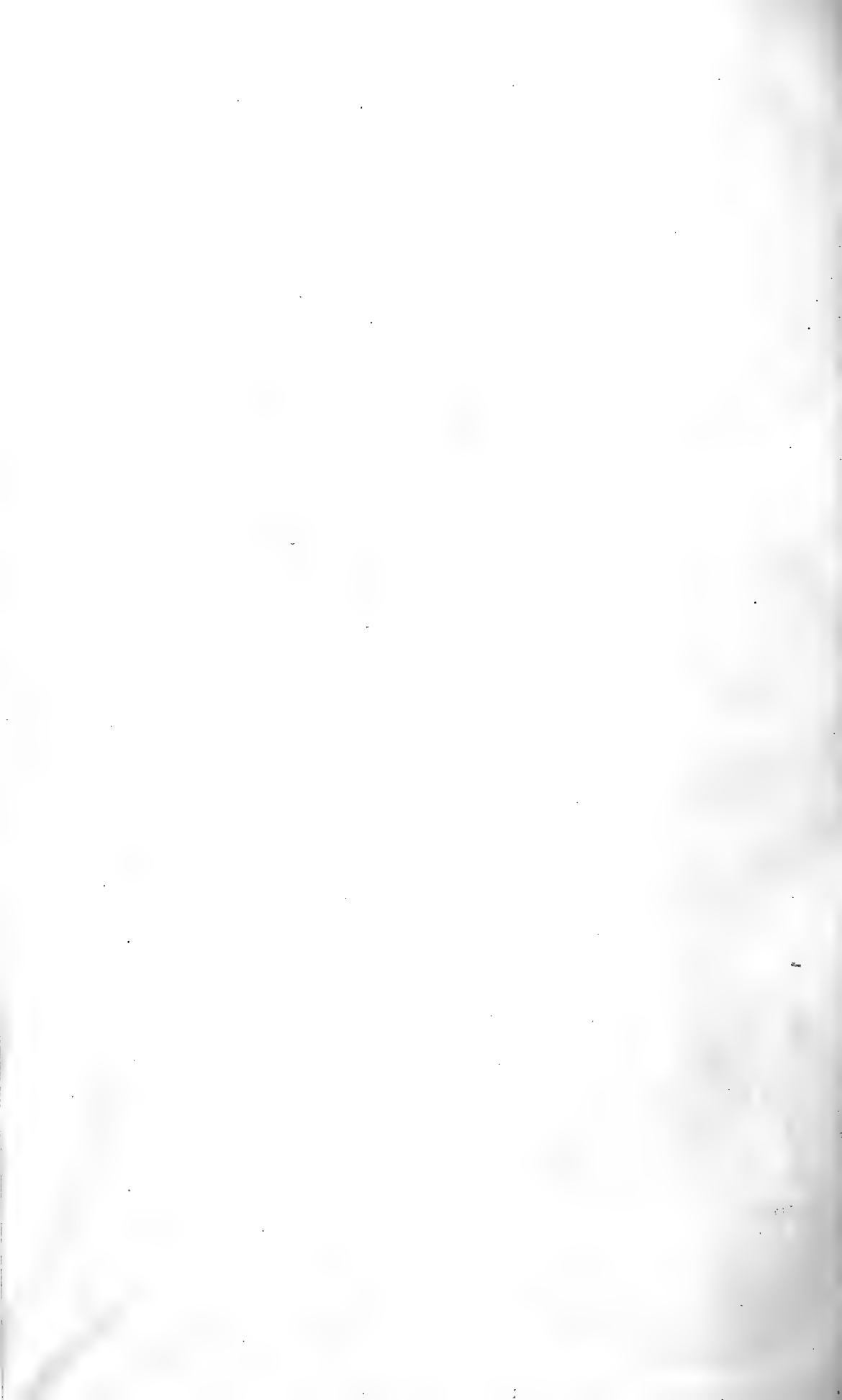
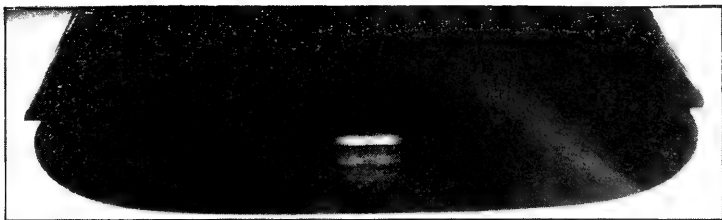


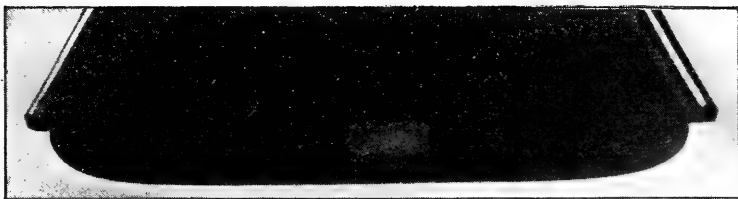
FIG. 3.



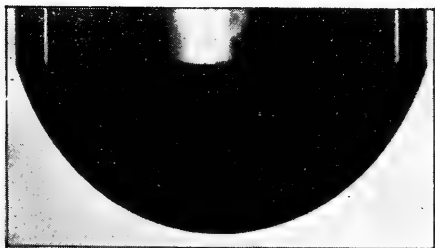
A.



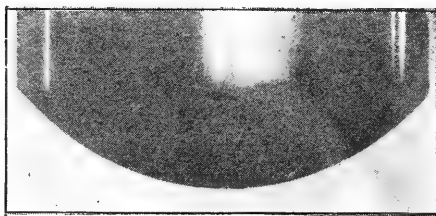
B.



C.



D.



E.

FIG. 1.

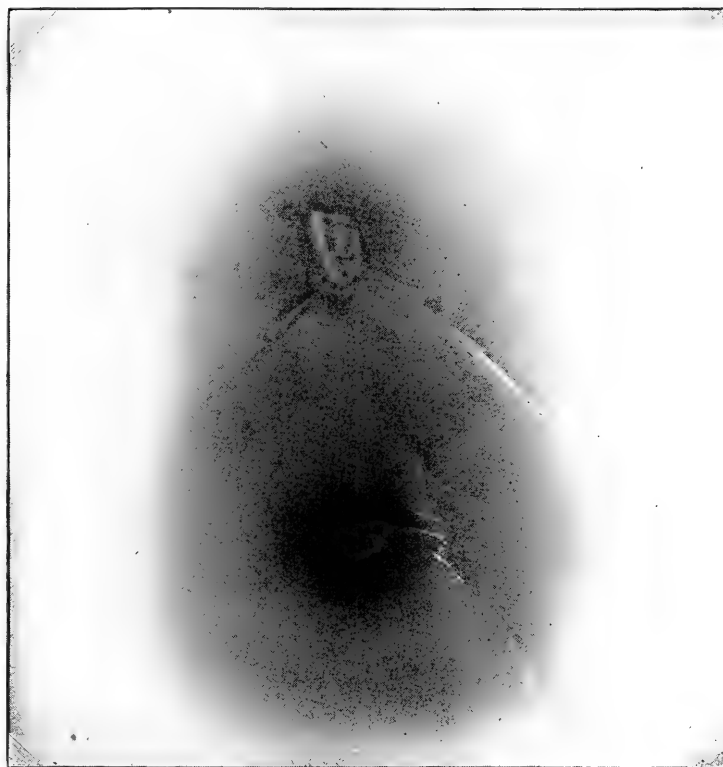
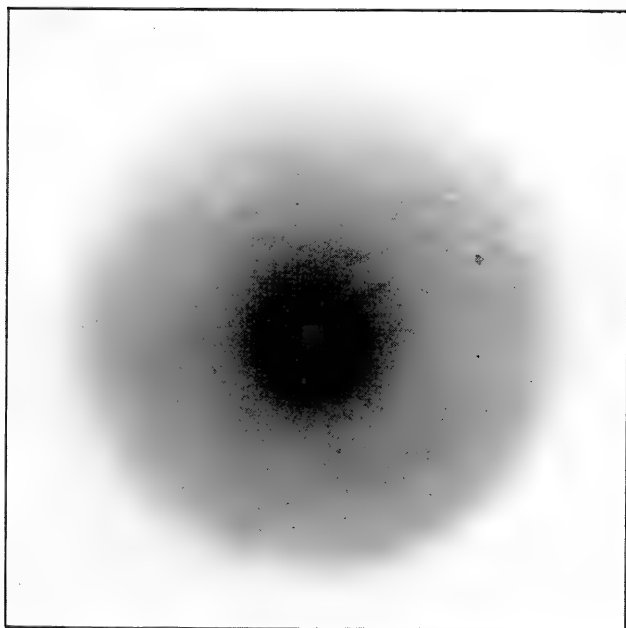
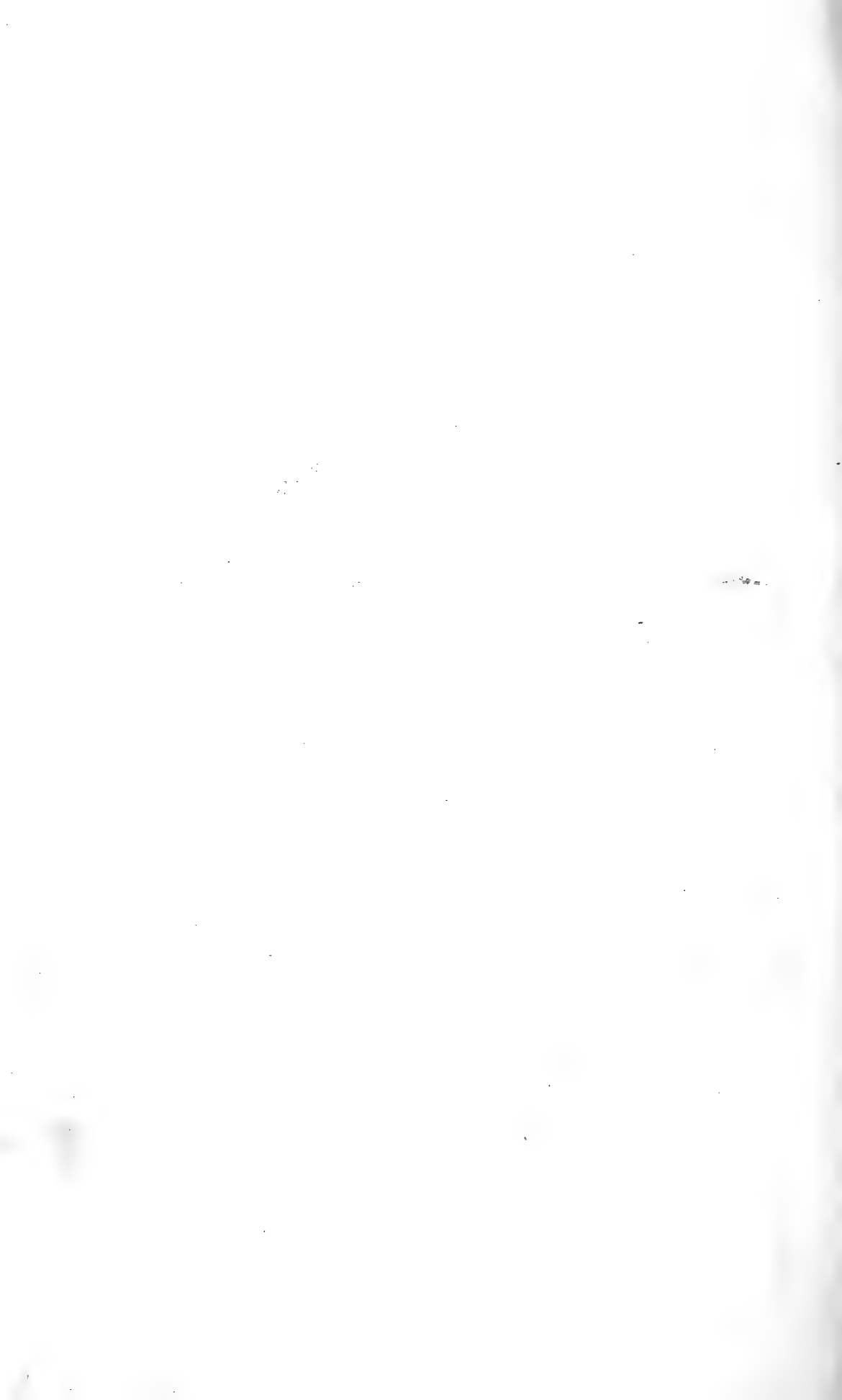


FIG. 2.





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LXVII. *The Dispersion of Metals.* By LYNDE P. WHEELER,
*Assist. Prof. of Physics, Sheffield Scientific School of Yale
University* *.

THE increase in our experimental knowledge of the dispersion of metals which has occurred in the past ten years, invites a more complete discussion than it thus far seems to have called forth of those relations between the optical and other physical constants of metals which theory demands. The most detailed investigation of these relations which has been made up to the present time appears to be that of Nicholson †. In his paper he uses the equations of the theory to calculate (in the manner first pointed out by Schuster) the ratio of the number of free electrons to the number of molecules in unit volume, and also to the calculation of the value of the so-called dielectric constants of the metals. He discusses, however, only the classical measurements of Drude, and hence the consideration of dispersion was practically excluded. In fact, nowhere, to the author's knowledge, has there appeared an adequate discussion of the more modern measurements of Minor ‡, Bernoulli §, Tool ||, Ingersoll ¶, and Tate **, in the light of the demands of the electron theory.

* Communicated by the Author.

† Nicholson, *Phil. Mag.* [6] xxi. p. 245 (1911).

‡ Minor, *Ann. d. Phys.* x. p. 581 (1903).

§ Bernoulli, *Ann. d. Phys.* xxix. p. 585 (1909).

|| Tool, *Phys. Rev.* xxxi. p. 1 (1910).

¶ Ingersoll, *Astroph. Journ.* xxxii. p. 265 (1910).

** Tate, *Phys. Rev.* xxxiii. p. 321 (1912).

As a result of the work of these investigators, we possess measures of the optical constants at wave-lengths extending in the cases of silver, copper, cobalt, and steel from about 0.23μ to 2.25μ ; in the case of nickel from 0.42μ to 2.25μ ; and for gold from 0.4μ to 0.7μ . The values of the indices of refraction (n) and of the coefficients of absorption ($n\kappa$) obtained by these observers for the metals named (with the exception of steel), are brought together in the second and third columns of Tables I.-V., and are shown graphically in the two lower curves of the corresponding figs. 1-5. The observations at all of the wave-lengths at which measurements were made are not included, but none are omitted except where the trend of the curves is so uniform that many points are unnecessary. The data for steel are omitted because the chemical and physical complexity of this material is such as to render all the physical constants required for a comparison with theory so uncertain as to make such a study fruitless.

A study of these tables or curves reveals two salient facts with regard to the precision of the measurements. First, that the results of different observers at the same wave-lengths differ in general by an amount considerably in excess of the errors inherent in the methods of measurement employed; and, second, that in an equally general manner the different observers are in very close agreement as to the amount and trend of the dispersion. Thus it will be observed that for those regions of the spectrum where the results of the different observers overlap, the curves for both n and $n\kappa$ are in general parallel though not coincident; and also that the departures from parallelism are in the main much less than the discrepancies in the absolute values. In copper alone is there any real disagreement as to the trend of the dispersion. Here the measures of Tool and Tate would locate the minimum in the curve for n further up in the spectrum than do those of Ingersoll*.

The discrepancies in the values obtained at any given wave-length are to be attributed to differences in the state of the reflecting surface. These arise from small differences in the method or duration of polishing, or possibly (as is suggested by the work of Lummer and Sorge† on glass) they may arise from different states of strain existing in the

* Bernoulli's values for nickel also form an exception to the general parallelism of the dispersion curves. Too much stress cannot be laid on his measures, however, as his experimental method seems open to objection. See Voigt, *Ann. d. Phys.* xxix. p. 956 (1909).

† Lummer and Sorge, *Ann. d. Phys.* xxxi. p. 325 (1910).

surface of different samples of the same material. There seems to be, at least tacitly, a general opinion that since Drude's specification of the "normal" condition for a reflecting surface, it only requires sufficient care in the preparation of a metallic mirror in order to get consistent results; and that, consequently, our knowledge of the optical constants is nearly as precise as that of the methods of measurement used. It is safe to say, however, that no one who has had much experience in this line of work has held such an opinion for long. In fact, experience teaches that it is well nigh impossible to exactly reproduce (even by the same observer) the same condition of the reflecting surface in different samples of the identical material, or even in the same sample at different times. Thus we cannot regard the experimental values of the optical constants of metals as anything but rather rough approximations to the specific values characteristic of the substances. Hence any theoretical relation dependent for its numerical evaluation on the absolute values of the optical constants is incapable of yielding dependable results.

On the other hand, since, as has been pointed out above, the data at our command as to the *relative* values of the optical constants at different wave-lengths are in general of a higher order of precision, it would seem that a comparison of these results with the dispersion formulæ yielded by the electron theory should yield results of some value. To make such a comparison is the object of this paper,

It may be mentioned in passing, that it would seem to be possible to obtain accurate absolute values really representing specific properties of the substance in the case of mercury; for the author has shown that in the case of this metal it is possible to reproduce exactly* surface conditions entirely free from all films of impurity. The possibility of different states of surface strain at different times would also of course be eliminated. Work on the dispersion of mercury is now under way in order to obtain with this more promising material, data which will enable us to make a more satisfactory comparison with theory than is possible with other substances.

With regard to the properties of the metals revealed by the data under discussion, it will be observed that all five of the substances show in general a decrease of the absorption coefficient (increase in transparency) with increasing frequency of the incident light. In the cases of silver and gold

* Wheeler, Phil. Mag. xxi. p. 229; also Am. Jour. Sci. xxxii. p. 85 (1911).

and, with less certainty, copper, there is a minimum in the curve followed by a feeble maximum further up in the spectrum. Thus, for silver there is a distinct "transmission" band in the ultra-violet with its centre at about 0.316μ ; for gold, a less distinct one in the visible spectrum central at about 0.480μ ; while for copper there are apparently two minima of absorption, one in the ultra-violet at about 0.3μ , and the other in the visible spectrum at about 0.55μ . In the cases of nickel and cobalt, the minima in the absorption curves (if they exist) have not been reached within the limits of the spectrum over which these observations extend; both of these metals show a more or less steady decrease in $n\kappa$ throughout the whole range, though in the case of cobalt a minimum seems to be indicated not far beyond the range of the observations in the ultra-violet. It is to be noted, further, that the reflexion coefficient (not shown in tables or figures) shows a minimum value at the same points in the spectrum as does $n\kappa$.

The indices of refraction also show marked minima in the cases of the three better conductors. That for silver occurs at 0.395μ ; that for copper at about 0.62μ (Ingersoll's results would place it beyond 0.7μ); and that for gold is apparently located just beyond the longest wave-length for which we have measurements (0.7μ). For nickel and cobalt there are no such marked minima; the curves show an index decreasing tolerably uniformly with increasing frequency throughout the range over which the experiments extend. A minimum in the case of cobalt seems imminent, however, just beyond that range. For a large range of the spectrum the numerical value of the index is, in the case of the three better conductors, less than unity; while for the other two it is approaching such a value in the ultra-violet. The fact that the index of refraction is less than unity for silver and gold and copper in the visible spectrum has been verified, it may be remarked, by the direct measurement of the deviation produced by prisms of very acute angle.

The theoretical relations which it is proposed to discuss are those yielded by the well-known equation of condition for the propagation of waves in a medium possessing both conductivity and a dielectric constant,

$$\nabla \cdot \nabla E = \frac{K}{C^2} \ddot{E} + 4\pi\sigma \dot{E},$$

where E is the electric force, σ the conductivity, K the dielectric constant, C the velocity of light (which enters owing to the use of electromagnetic units), and $\nabla \cdot \nabla$ is

the Laplacian operator. A wave-train advancing in the x direction with a velocity V may be specified by

$$E_y = E_0 e^{ip\left(\frac{x}{V} - t\right)},$$

where p is the frequency and $i = \sqrt{-1}$. With the aid of this, the equation of condition becomes

$$\frac{C^2}{V^2} = K + i \frac{4\pi C^2 \sigma}{p}.$$

Since the real part of the ratio C/V is by definition the index of refraction (n), we set $C/V = n(1 + i\kappa)^*$, and hence we have

$$n^2(1 - \kappa^2 + 2i\kappa) = K + i \frac{4\pi C^2 \sigma}{p}. \quad (1)$$

The significance of $n\kappa$ becomes evident on substituting the value of V in the equation of the wave-train, which then becomes

$$E_y = E_0 e^{-\frac{pn\kappa}{C}x} e^{ip\left(\frac{n}{C}x - t\right)}.$$

Hence $n\kappa$ is seen to be of the nature of an extinction or absorption coefficient.

Now in equation (1) it is to be observed that the values of K and σ contemplated are those operative for currents of the frequency of those set up by the incident wave-train. If we use the (constant) values for them given by experiments with steady currents, the equation yields, on equating the imaginary and real terms of each side,

$$n^2\kappa = \frac{2\pi C^2 \sigma}{p} \quad \text{and} \quad n^2(1 - \kappa^2) = K,$$

relations, which as has been many times pointed out, are far from being experimentally confirmed. And in view of the enormous frequency of the currents which accompany light-waves, it is not surprising that such discrepancies should present themselves. If, however, K and σ can be expressed as functions of the frequency, then equation (1) will yield dispersion formulæ with which the results of experiment can be compared. Such expressions for K and σ have been obtained by several investigators, proceeding from the general hypotheses of the electron theory. The formulæ thus obtained for K involve, however, too many undetermined constants to allow of a satisfactory evaluation with the experimental data at our command. Hence it seems best for

* Drude's notation.

the present purpose to leave K indeterminate in the equations. The expressions which have been obtained for σ , on the other hand, contain but one undetermined constant, and consequently can be profitably used.

The development of σ in terms of the frequency of the current is best accomplished by the method due to Lorentz, Jeans, and H. A. Wilson. It seems preferable to that of Drude, in that the frictional term in the equation of motion of the free electrons in the latter's method receives a more probable physical interpretation in the more recent method. In this method the equation of motion of the electrons is obtained from a consideration of the loss of momentum (in the direction of the acting electric force) sustained by a group of electrons having velocities lying between v and $v + dv$. If we assume that the electric force is given by $E = E_0 e^{-ipt}$, and that the law of the distribution of the velocities among the groups is that of Maxwell, we obtain from a consideration of the rate of production of heat per unit volume,

$$\sigma = 2q\sigma_0 \int_0^\infty \frac{\left(v + i\sqrt{\frac{\alpha}{q}}\right) e^{-qv^2} dv}{\left(1 + \frac{\alpha}{qv^2}\right)}, \quad \dots (2)^*$$

where q is three-halves of the square of the average electronic velocity, σ_0 is the electrical conductivity for steady currents, and

$$\alpha = \frac{\pi p^2 m^2 \sigma_0^2}{4N^2 e^4}, \quad \dots \dots \dots (3)$$

with e the charge, m the mass, and N the number of electrons per unit volume.

If we now expand $(\alpha/qv^2 + 1)^{-1}$ in series and integrate term by term, we get

$$\sigma = \sigma_0 \left[\frac{1}{\alpha} \left(1 - \frac{2!}{\alpha} + \frac{3!}{\alpha^2} - \dots \right) + \frac{i}{2} \sqrt{\frac{\pi}{\alpha}} \left(1 - \frac{1.3}{2\alpha} + \frac{1.3.5}{(2\alpha)^2} - \dots \right) \right]$$

or,

$$\sigma = \sigma_0 \left[\frac{1}{\alpha} \sum_0^\infty \frac{n!}{\alpha^{n-1}} + \frac{i}{2} \sqrt{\frac{\pi}{\alpha}} \sum_0^\infty \frac{(2n-1)(2n-3)\dots 1}{(2\alpha)^{n-1}} \right]. \quad (4)$$

These integrations were first performed by Nicholson†. I am

* H. A. Wilson, *Phil. Mag.* [6] xx. p. 835 (1910). Wilson there assumes the electric force to be given by $E = E_0 \cos pt$, and hence his value for σ lacks the imaginary term of the above.

† Nicholson, *loc. cit.*

unable, however, to confirm his values for the numerical coefficients in the expansions, but find them as given above.

If we had made use of the average velocity of the electrons instead of assuming the Maxwellian distribution, we should have been led to the expression

$$\sigma = \sigma_0 \left[\frac{1 + i \frac{pm\sigma_0}{Ne^2}}{1 + \frac{p^2 m^2 \sigma_0^2}{N^2 e^4}} \right],$$

the real part of which is the formula given by Schuster and Jeans. It is included here for the sake of a comparison of the results of the two hypotheses as to the electronic velocities.

If now we write S_1 and S_2 for the two series in equation (4) and substitute the value of σ in equation (1), we obtain, on separating the real and imaginary parts,

$$n^2 \kappa = \frac{8C^2 N^2 e^4}{p^3 m^2 \sigma_0} S_1, \quad . \quad . \quad . \quad . \quad (5)$$

and

$$n^2(1 - \kappa^2) = K - \frac{4nC^2 N e^2}{p^2 m} S_2, \quad . \quad . \quad . \quad . \quad (6)$$

in which, in the first terms of each series the value of α is quoted from equation (3). Equation (6) differs from that given by Nicholson (*loc. cit.*) in that the second term on the right-hand side is π times as great*. I am unable, however, to find any error in the formula as given above.

The hypothesis of equal velocities for the electrons yields on similar treatment,

$$n^2 \kappa = \frac{2\pi C^2 N^2 e^4}{p^3 m^2 \sigma_0} \left(1 + \frac{\pi}{4\alpha}\right)^{-1}$$

and

$$n^2(1 - \kappa^2) = K - \frac{4\pi C^2 N e^2}{p^2 m} \left(1 + \frac{\pi}{4\kappa}\right)^{-1}.$$

Thus, neglecting the correction terms, the values of $n^2 \kappa$ are, on this hypothesis, $\pi/4$ times as great as those given by the assumption of the Maxwellian distribution, while to the same approximation the values of $n^2(1 - \kappa^2)$ are the same on both hypotheses. Now Nicholson, owing to the absence of the factor π in equation (6), of course finds that the value of $K + n^2(\kappa^2 - 1)$ on the equal velocity hypothesis is π times as

* In addition there are minor differences in the values of the numerical coefficients in S_1 and S_2 .

great as on the other. He then uses the values of K yielded by the two formulæ to discriminate between the two hypotheses. This argument, if the formulæ as given above are correct, is illusory. Further, since the value of N is not independently known, it is impossible to discriminate between the two hypotheses by means of the difference between the two results for $n^2\kappa$. The equations resulting from the assumption of the Maxwellian distribution have been adopted for the computations of this paper, because that assumption seems on the whole to the present author to have more inherent probability.

In using equations (3), (5), and (6) for numerical evaluations it is convenient to use, following Schuster, the ratio of the number of free electrons to the number of molecules per unit volume in place of N . Calling this ratio r , we have $N=r/M\tau$, where M is the mass of the hydrogen atom and τ the relative atomic volume. If, to simplify further, we gather together those constants which are the same for all metals, writing $a=e^4/\pi^3m^2M^2C^2$, and use the wave-length *in vacuo* (λ), in place of p , then equations (3), (5), and (6) become

$$\alpha = \frac{\sigma_0^2 \tau^2}{ar^2 \lambda^2} \quad . \quad . \quad (7) \qquad n^2 \kappa = \frac{aCr^2 \lambda^3}{\sigma_0 \tau^2} S_1, \quad . \quad . \quad (8)$$

$$K + n^2(\kappa^2 - 1) = \frac{C\sqrt{\pi ar} \lambda^2}{\tau} S_2, \quad . \quad . \quad . \quad (9)$$

in which form the equations have been used in this paper for purposes of calculation. It is to be remarked that the series S_1 and S_2 are semiconvergent. That the use of only three terms in either series yields, however, a more than ample accuracy for the purposes in hand, is easily seen. For the ratio of the absolute values of the $(n+1)$ st to the n th terms is in S_1 , $(n+1)/\alpha$, and in S_2 $(2n+1)/2\alpha$. Hence S_1 does not begin to diverge until the number of terms is equal to $(\alpha-1)$ and S_2 until the number of terms is $(2\alpha-1)/2$. Thus the best approximation attainable in the use of the series will be, in the case of S_1 when $(\alpha-2)$ terms, and in the case of S_2 when $(2\alpha-3)/2$ terms are employed: the approximation being better the larger the value of α . Now the values of α^* for the five metals and the range of the

* These are calculated as follows:—a first approximation for r is obtained from equation (8) with $S_1=1$; then with this value of r the first approximation for a is calculated by equation (7); then with this value of a , S_1 and a second approximation for r are computed, and thence the second approximation for α . The process is then repeated as often as may be necessary; three approximations being the greatest number required for any of the metals discussed in this paper.

spectrum considered, vary between 12 and 2020. Taking the smallest value of α which occurs, we find by using ten terms that $S_1=0.865$ and $S_2=0.895$; while by using three terms, $S_1=0.875$ and $S_2=0.901$. Thus the error committed in using only three terms is, in this the most unfavourable case, but 1.2 per cent. in the case of S_1 , and 0.6 per cent. in the case of S_2 .

We proceed now to the discussion of these equations in the light of the experimental data which we have reviewed. In the first place, we observe that equation (8) gives directly the theoretical dispersion of the *product* of the two optical constants. If we assume that r is constant (as seems to be at least tacitly the general impression), the equation expresses a law of great simplicity, namely, that the product of the index of refraction and the coefficient of absorption is proportional to the cube of the wave-length of the incident radiation. On account of the variation of α and therefore of S_1 with the wave-length, this statement is only an approximate one; but that it very nearly expresses the facts for the five metals under discussion is evident from the circumstance that the maximum variation in S_1 found is only about 10 per cent. Now that this law is not even remotely fulfilled by the data at hand will appear on inspection of the fifth column in the tables, where the values of $n^2\kappa/\lambda^3$ as computed from the data of the second, third, and fourth columns are given. Hence we are forced to conclude that r is not a constant, but is a function of the frequency. That is, the number of electrons taking part in the conduction current depends on the frequency of the radiation which sets up that current.

If, then, we regard equation (8) as determining r , we have that r varies as $\sqrt{n^2\kappa/\lambda^3}$, the constant of proportionality differing for each substance. The numerical values of r , calculated in this way, are given in the sixth column of the tables, and are shown in the figures by the full lines in the upper halves. Owing to the fact already pointed out, that the only result of such calculations on which much quantitative dependence can be placed is with respect to *relative* values, the absolute values of r have been computed for only one observer's results in the regions of overlapping, except where there is marked discrepancy in the dispersion.

An inspection of these curves shows in the first place that the numerical values of r are, at the longest observed wave-length, of the order of magnitude unity or rapidly approaching such a value. What the value of the ratio would become at infinite wave-length cannot be deduced from the equation,

because S_1 becomes absolutely divergent at very long wave-lengths, and because the value of $n^2\kappa$ for zero frequency is unknown. In the second place, it is to be observed that for each metal r increases in value uniformly and in a practically linear manner throughout that portion of the spectrum in which the absorption coefficient has a value in excess of about 4. The point where this approximately linear relation ceases to hold lies in each case either in the red end of the visible spectrum, or else not far back in the infra-red. And in the third place, it is to be noted that the rate of increase of r becomes much greater in the regions of greater transparency (smaller $n\kappa$); and that the value of r does not fall off again after passing through a transmission band, though at the shortest wave-lengths observed there is an apparent decrease in its rate of growth*. The magnitude of the ratio at its maximum is, for silver about 16, for copper about 12, for gold 7 to 8, for nickel 2 to 3, and for cobalt 4 to 5.

The fact that this equation of the electron theory leads to the conclusion that the number of free electrons in a metal varies with the frequency of the current, does not seem to have been noticed before. The circumstance indicated, that r increases with decreasing absorption, becoming in general largest when the absorption is least, does not seem to carry with it any immediately obvious suggestion for an elucidation of the mechanism of the phenomenon. A possible physical explanation may lie in the dual nature generally ascribed to the absorption of light by metals, the first cause being the taking up of the incident energy by the free electrons, and the second the expenditure of the incident energy in forcing vibrations in the relatively fixed ions. The absorption due to the second cause must be supposed to vary with the wave-length in such a way as to be relatively much greater in the neighbourhood of those wave-lengths corresponding to the natural free periods of the ions. In other words, the ions should produce a "band" type of absorption, the breadth of the bands being proportioned to the range of frequencies to which they are capable of responding. On the other hand, the electrons being free and of small mass should take up energy (if at all) from a much wider range of frequencies, and hence cause a more

* In the case of cobalt, after an increase of r with decreasing $n\kappa$ similar to that taking place with the other metals, there is a subsequent falling off in r , while $n\kappa$ is also rapidly decreasing. Too much emphasis should not be placed on such an anomaly, however, in view of the uncertainties of the data.

continuous absorption throughout the spectrum. That the character of the absorption of metals is, for the longer wavelengths at least, of this second type is obvious from an inspection of the curves shown in the several figures. Moreover, as the presence of free electrons is theoretically the distinguishing characteristic of metals in this connexion, it is a natural inference that the major part of the absorption of light by metals is due in general to the electrons.

If this is so, then it would be possible to imagine the total absorption due to the two causes to decrease, while that due to the second was increasing; and even that there should be a minimum of the total absorption coincident with or nearly coincident with a maximum of the ionic absorption. Then, if in such a resonance region the disturbance within the ions is great enough to set free some electrons, the increase in r would be accounted for. Further, these same considerations would indicate that as the part due to the electrons becomes less, the resultant absorption should change its type, and that it should take on more of the character of the absorption in transparent bodies. That such a change really does occur, the absorption band at the upper end of the spectrum plainly discernible for silver, and indicated for copper and gold, would seem to make certain. Further evidence in confirmation of such a change in the type of absorption, is offered by the great relative increase in the values of n in the cases of silver, copper, and gold at or after the minimum point of the absorption curve.

The above hypothesis offers no explanation of why the electrons should absorb less of the incident energy at higher frequencies. If it were possible to form a sound dynamical notion as to why the electron, with its minute dimensions and mass and simple structure, should take up *any* energy from waves which at the shortest used in these measurements are still more than ten million times the electronic diameter, then perhaps the mechanism of the indicated decrease in absorption with increasing frequency would be capable of elucidation. At present, however, and certainly as far as the experiments under discussion go, there seems to be no light on this question. If the fact of decreasing electronic absorption with increasing frequency be granted, nevertheless, then the above hypothesis appears to be sufficient to reconcile the experimental data*.

* It may be possible that the increase in r is to be attributed to a transition layer or region of interpenetration of air and metal. This might naturally be supposed to be relatively poorer in free electrons than the main body of the metal. Then, if at the longer wave-lengths the radiation did not penetrate this layer, while at the shorter it did,

It remains to discuss equation (9) in the light of the experiments. Since the values of r can now be regarded as known (from equation (8)), it is obvious that this equation gives us the means of ascertaining the values of K throughout the spectrum. Further, it will be seen that the value of K consists of two parts: that due to the term involving r , and that due to $n^2(\kappa^2 - 1)$. The latter is the value of K to be expected if no free electrons were present; hence, we may speak of the "dielectric" and the "conductor" parts of K . In order to trace separately the influence of these two parts, the values of each are given in the tables; in column 7 the values of $n^2(\kappa^2 - 1)$ as computed from columns 3 and 4, and in column 8 (headed A) the values of the conductor term as calculated from the right-hand side of equation (9). In column 9 is given the algebraic sum of the two terms, or K ; which latter is also shown in the broken line curves in the upper halves of the figures.

It is obvious from these results, in the first place, that the values of K are not zero—the value demanded by a perfect conductor. In the second place, we observe that the presence of free electrons (the conductor term) plays the preponderating role in the so-called dielectric constant, particularly at the shorter wave-lengths. The dielectric term, however, increases relatively to the conductor term with increasing wave-length in all of the metals except cobalt. Thus in silver the dielectric term increases tolerably uniformly throughout the region covered by the measurements from about 1 per cent. to about 60 per cent. of the conductor term; in copper from about 0.1 per cent. to 33 per cent.; in gold from 1 per cent. to 27 per cent.; in nickel from 13 per cent. to 29 per cent.; while in cobalt the proportion varies from 5 per cent. through a maximum of about 17.5 per cent. (at the red end of the visible spectrum) to about 6.5 per cent. at the extreme infra-red wave-length measured. As in the case of equation (8), it is impossible to predict from equation (9) the relative magnitudes of the two parts for infinite wave-length, both because of the divergence of S_2 at large values of λ , and because of lack of knowledge

the increase in r would be explicable. This hypothesis, however, even more than the former, fails to elucidate the mechanism of absorption. If it is adopted it would seem to be necessary to attribute the major part of the absorption to the relatively fixed ions. Hence, further assumptions as to the nature and connexions of these ions would be necessary in order to explain the existence of the type of absorption which experiment reveals. However, this is hardly the place in which to follow further such speculations; the experimental basis is not sufficient either in extent or precision.

of the values of $n^2(\kappa^2 - 1)$ under the same circumstances. It is worthy of note also, that the dielectric term is of relatively greater importance at the shorter wave-lengths, in the poorer conductors.

Finally, we must compare the form of the curves for K as shown in the figures with that demanded by theory. The expressions which have been deduced for K are of the form

$$K = 1 + \sum \frac{k}{\omega^2 - p^2},$$

where k involves the charge, the mass, and the number in unit volume of the relatively fixed ions; ω is their natural "free" frequency; and the summation is to extend to as many terms as there are such free periods. Now, both from the forms of the curves actually found as well as from considerations of inherent probability, it is evident that we have here to deal, not with sharply defined isolated natural periods, but with resonance extending over considerable finite ranges of wave-lengths. If we therefore transform the formula in the manner of Schuster* so that it becomes applicable to the cases under consideration, we obtain a quite complicated equation involving the values of the frequencies at the edges of the absorption bands, as well as the constants k .

Now the data at present available for a satisfactory determination of all the constants thus demanded are sufficient neither in extent nor precision, as was remarked earlier in this paper. Nevertheless, it can be stated that the theoretical equation with suitable values of the constants can be made to yield a curve approximating to that found, *e. g.*, for silver. It is scarcely worth while to give details of such calculations here, however, as owing to the limitations of the data which have been mentioned, the determination of these constants is largely guess work.

It is to be noted that if we had data available sufficient in extent and precision to permit a satisfactory evaluation of the other constants in such a dispersion formula for K , then that equation would allow us to determine the value of k . This in turn would yield information as to the number of vibrating ions in unit volume, just as equation (8) gives us the number of free electrons. With this added information we should get some light on the magnitude of the part played in the absorption by metals, by the relatively fixed ions; information which could not fail to be of use in unravelling the mechanism of that process.

* Schuster, 'Theory of Optics,' p. 152.

TABLE I.

Silver.

Observer.	λ .	n .	$n\kappa$.	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$.	r .	$n^2(\kappa^2-1)$.	A.	K.
Minor.....	0.231 μ	1.43	1.11	129.	15.7	-0.80	46.3	47.1
"250	1.49	1.32	125.	15.4	-0.47	51.8	52.3
"298	1.56	0.91	53.6	10.1	-1.61	49.5	51.1
"346	0.219	1.10	5.80	3.41	+1.16	40.9	39.7
"395	0.155	1.91	4.81	3.01	3.64	25.6	22.0
"450	0.164	2.39	4.29	2.91	5.67	32.8	27.1
Tate460	0.270	3.25					
Minor.....	.500	0.169	2.94	3.97	2.74	8.63	38.1	29.5
Tate500	0.273	3.56					
Minor.....	.550	0.176	3.31	3.50	2.57	10.9	43.4	32.5
Tate580	0.234	4.20					
Drude589	0.181	3.67					
Minor.....	.589	0.177	3.64	3.15	2.44	13.2	47.0	33.8
Tate620	0.291	4.52					
Drude630	0.203	3.96					
Ingersoll65	0.154	4.34	2.43	2.14	18.8	50.1	31.3
Tate660	0.299	4.87					
"700	0.308	5.20					
Ingersoll87	0.203	6.07	1.88	1.89	36.8	79.1	42.3
"	1.25	0.37	8.88	1.69	1.77	78.6	152.	73.4
"	1.75	0.55	12.3	1.27	1.55	151.	260.	109.
"	2.25	0.77	15.4	1.04	1.41	230.	394.	164.

Fig. 1.—Silver.

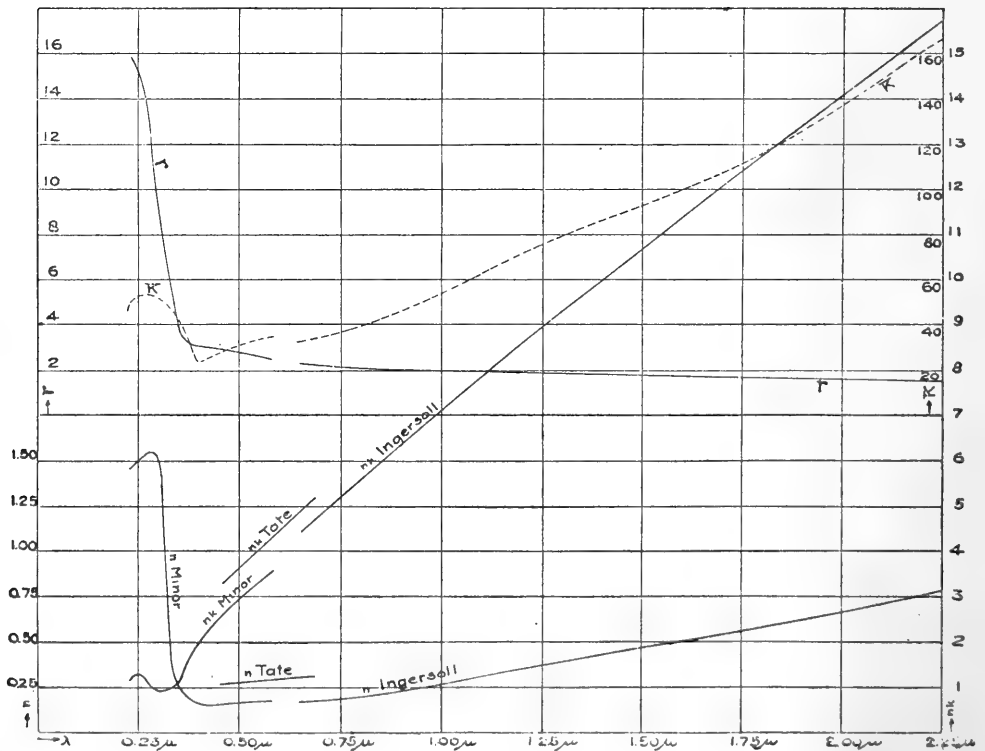


TABLE II.—Copper.

Observer.	λ .	n .	n_K .	$\frac{n^2 K}{\lambda^3} (10)^{-12}$	r .	$n^2(K^3-1)$.	A.	K.
Minor.....	0.231 μ	1.39	1.46	163.	11.8	0.19	50.0	49.8
"257	1.40	1.42	117.	9.96	0.06	52.1	52.0
"298	1.26	1.32	62.7	7.31	0.16	51.5	51.3
"347	1.19	1.47	41.8	5.97	0.73	56.7	56.0
"395	1.17	1.76	33.4	5.34	1.73	66.1	64.4
"450	1.13	2.15	26.6	4.77	3.34	76.6	73.3
Tate460	1.57	2.26					
Tool460	1.19	2.29	27.9	4.89	3.72	82.4	78.7
"500	1.17	2.38	22.2	4.37	4.30	86.9	82.6
Tate500	1.50	2.37					
Minor.....	.500	1.10	2.34	20.6	4.19	4.24	83.2	79.0
Tate540	1.38	2.46					
Tool540	1.07	2.41	16.4	3.13	4.66	84.1	79.4
Minor.....	.550	0.892	2.23	12.0	3.20	4.18	77.0	72.8
Tool560	0.855	2.42					
Tate580	1.07	2.84					
Tool580	0.600	2.79	8.60	2.71	7.44	72.4	65.0
Drude589	0.641	2.62					
Minor.....	.589	0.617	2.63	7.90	2.60	6.52	71.6	65.1
Tate600	0.980	3.19					
Tool620	0.580	3.32	8.10	2.63	10.9	80.4	69.5
Drude630	0.580	3.04					
Tool640	0.615	3.58	8.40	2.68	12.4	87.5	75.1
Tate640	0.958	3.53					
Ingersoll65	0.44	3.26	5.21	2.10	10.4	70.5	60.1
Tool660	0.655	3.78	8.64	2.72	13.9	94.1	80.2
Tate660	0.996	3.70					
"700	1.035	3.82					
Ingersoll87	0.35	3.85	2.05	1.32	14.7	79.4	64.7
"	1.25	0.56	7.28	2.09	1.33	52.7	165.	113.
"	1.75	0.83	9.46	1.47	1.12	90.7	273.	182.
"	2.25	1.03	11.7	1.06	1.02	136.	420.	284.

Fig. 2.—Copper.

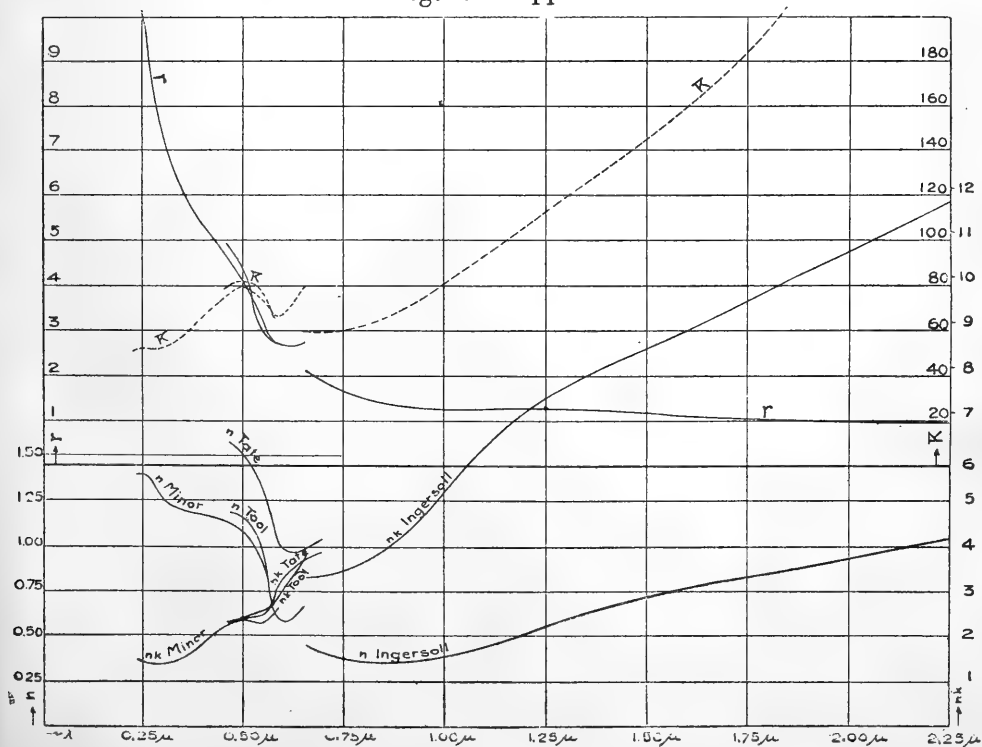


TABLE III.

Gold.

Observer.	λ .	n .	$n\kappa$.	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$.	r .	$n^2(x^2-1)$.	A.	K.
Tool	0.400 μ	1.58	1.79	44.2	7.49	0.71	66.5	65.8
„420	1.57	1.80	38.2	6.97	0.78	67.9	67.1
„440	1.55	1.79	32.4	6.40	0.83	68.6	67.8
„460	1.45	1.74	25.7	5.70	0.93	67.0	66.1
Tate460	1.66	1.83					
Tool480	1.28	1.69	19.6	4.96	1.21	63.3	62.1
Tate480	1.53	1.87					
Tool500	0.935	1.75	13.1	4.07	2.19	58.3	56.1
Tate500	1.33	2.01					
Tool520	0.670	2.01	9.55	3.47	3.60	51.7	47.9
Tate520	1.10	2.19					
Tool540	0.535	2.31	7.83	3.15	5.02	51.3	46.3
Tate540	0.937	2.55					
Tool580	0.415	2.75	5.85	2.72	7.40	50.9	43.5
Tate580	0.729	3.02					
Drude.....	.589	0.366	2.82					
Tate600	0.666	3.24					
Tool620	0.350	3.16	4.64	2.42	9.88	51.8	41.9
Tate620	0.645	3.41					
Drude.....	.630	0.306	3.12					
Tool660	0.320	3.54	3.94	2.23	12.4	54.1	41.7
Tate660	0.636	3.73					
„680	0.617	3.86					
Tool700	0.280	3.80	3.10	1.97	14.3	53.8	39.5

Fig. 3.—Gold.

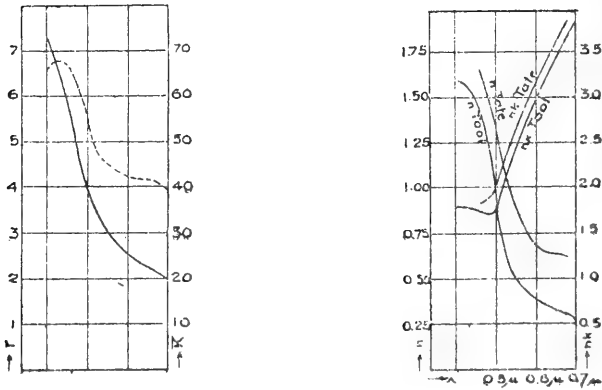


TABLE IV.

Nickel.

Observer.	λ .	n .	$n\kappa$.	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$.	r .	$n^2(\kappa^2-1)$.	A.	K.
Tool	0.420 μ	1.42	2.53	48.3	2.38	4.40	34.0	29.6
Bernoulli436	1.74	3.28					
Tool460	1.46	2.75	41.3	2.21	5.44	34.9	29.4
Bernoulli492	1.74	3.37					
Tool500	1.54	2.98	36.6	2.11	6.47	42.8	36.3
"540	1.63	3.20	33.0	1.98	7.50	46.7	39.2
Bernoulli546	1.76	3.44					
"578	1.75	3.48					
Tool580	1.73	3.41	30.2	1.90	8.62	51.3	42.7
Drude589	1.79	3.32					
Bernoulli615	1.85	3.72					
Tool620	1.82	3.61	27.6	1.82	9.74	56.0	46.3
Drude630	1.89	3.56					
Ingersoll65	1.91	3.93	27.4	1.81	11.8	61.2	49.4
Tool660	1.95	3.84	26.0	1.77	11.0	61.8	50.8
"700	2.03	3.98	23.5	1.68	11.7	66.2	54.5
Ingersoll87	2.45	4.80	17.9	1.48	17.0	88.0	71.0
"	1.25	2.92	6.15	9.22	1.07	29.3	132.	103.
"	1.75	3.45	7.76	5.00	0.79	48.3	188.	140.
"	2.25	3.95	9.20	3.19	0.60	69.2	237.	168.

Fig. 4.—Nickel.

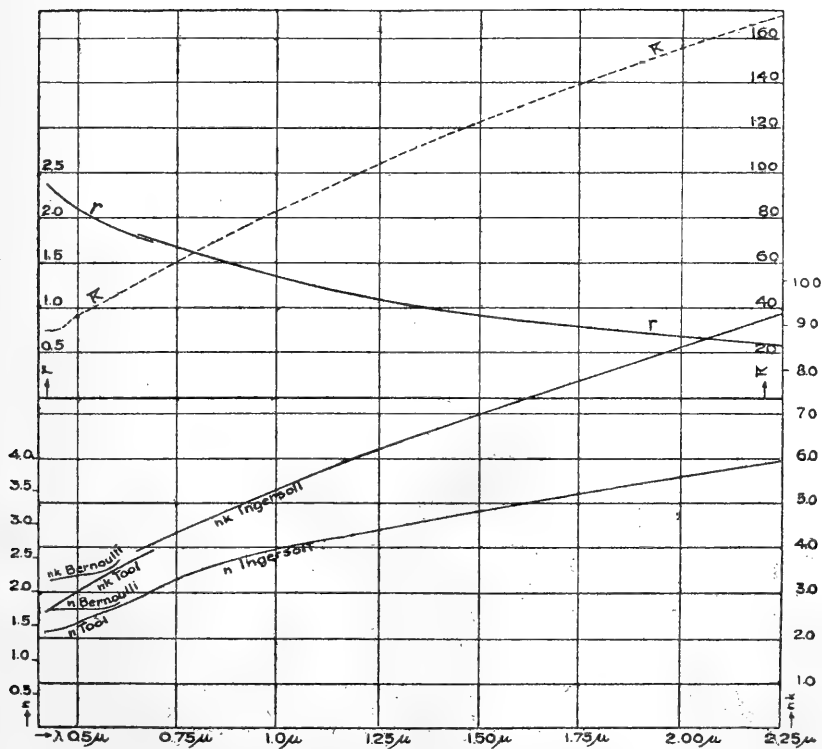
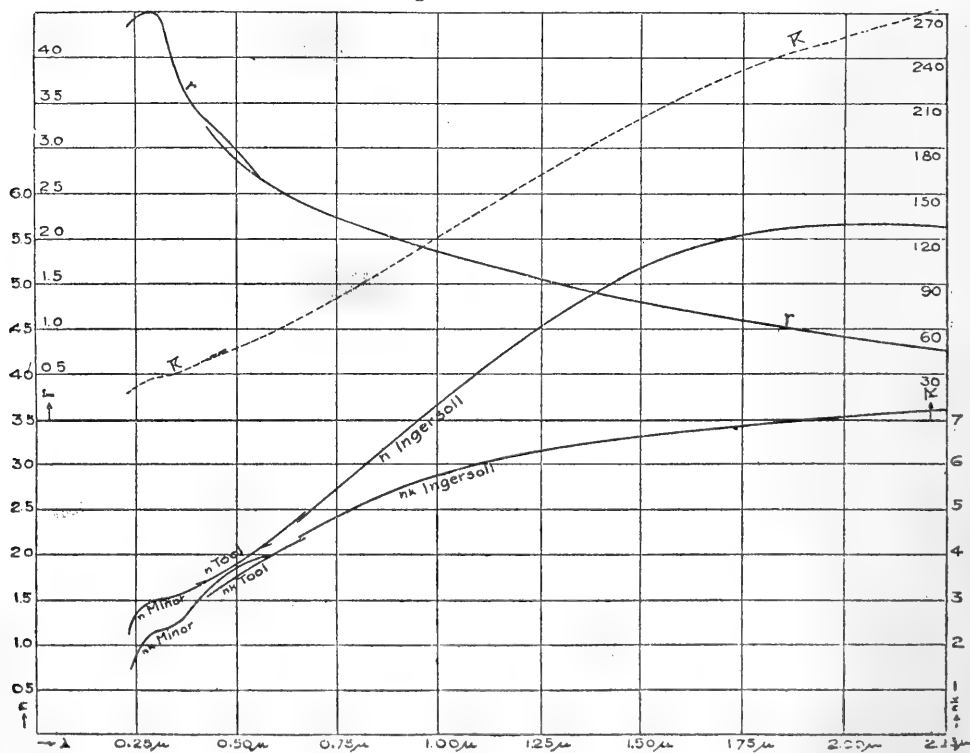


TABLE V.
Cobalt.

Observer.	λ .	n .	$n\kappa$.	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$.	r .	$n^2(\kappa^2-1)$.	A.	K.
Minor	0.231 μ	1.10	1.43	127.	4.33	0.83	18.6	17.7
"298	1.50	2.33	132.	4.48	3.17	32.0	28.9
"347	1.54	2.47	92.0	3.74	3.74	35.2	31.5
"395	1.63	2.91	77.1	3.44	5.83	42.0	36.2
Tool420	1.68	3.07	69.6	3.26	6.60	44.9	38.3
Minor450	1.79	3.42	67.2	3.22	8.49	50.8	42.3
Tool480	1.86	3.41	57.2	2.97	8.16	53.3	45.1
Minor500	1.93	3.71	57.4	2.98	10.0	57.8	47.8
"550	2.05	3.90	48.2	2.74	11.0	64.1	53.1
Tool560	2.09	3.81	45.4	2.65	10.1	64.5	54.4
Minor589	2.12	4.04	41.8	2.55	11.8	68.4	56.6
Drude600	2.21	4.03	41.3	2.53	11.4	70.4	59.0
Minor630	2.22	4.19	37.2	2.41	12.7	73.8	61.1
Drude630	2.22	4.19					
Tool640	2.34	4.26	37.8	2.43	12.6	76.6	64.0
Ingersoll65	2.35	4.40	37.6	2.42	13.8	78.3	64.5
Tool680	2.50	4.44	35.3	2.35	13.5	83.1	69.7
Ingersoll87	3.18	5.37	26.0	2.04	18.7	116.	97.6
"	1.25	4.50	6.30	14.6	1.55	19.5	183.	164.
"	1.75	5.53	6.81	7.03	1.08	15.8	247.	231.
"	2.25	5.65	7.18	3.56	0.76	19.5	293.	274.

Fig. 5.—Cobalt.



Summary.

1. From an examination of the available data on the dispersion of silver, copper, gold, nickel, and cobalt, it is concluded that the inaccuracies in the experimentally determined values of the optical constants of these metals are too great to allow of much dependence to be placed on them except for *relative* values. These uncertainties limit seriously the information to be derived from the measurements, and suggest the desirability of obtaining data on the dispersion of mercury, for which metal the causes of the inaccuracies can be eliminated.

2. From a comparison of the data with the dispersion formulæ yielded by the electron theory, it appears

(a) That the number of free electrons is not a constant but increases with the frequency of the currents set up by the incident radiation; slowly and uniformly in the infra-red, and more rapidly in the regions where the metals are more transparent. The explanation of this phenomenon is so involved with that of the mechanism of metallic absorption in general, that a wholly satisfactory elucidation of it seems to be impossible at the present time.

(b) That the dispersion of the so-called dielectric constant for these metals can be determined. It is seen to consist of two parts, of which that which depends on the presence of free electrons is more important than the other or pure dielectric term, especially at the shorter wave-lengths. It also appears that the form of the dispersion curves found is not inconsistent with that demanded by theory, although the inaccuracies of the data do not permit a satisfactory investigation of this point.

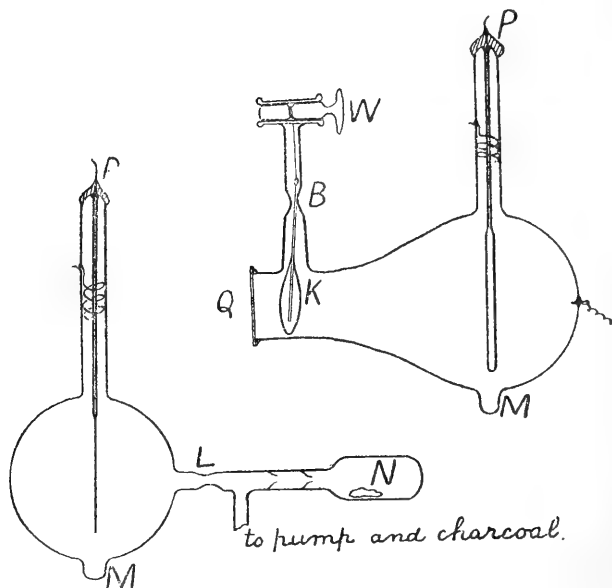
LXVIII. *A Sensitive Photo-Electric Cell.* By A. LL. HUGHES, D.Sc., B.A., Mackinnon Student of the Royal Society; Emmanuel College, Cambridge*.

DURING the course of a research, it was found necessary to measure the transparency of a quartz plate over a considerable region of the spectrum. To effect this, use was made of the well-established law that the photo-electric effect is proportional to the intensity of the light. A photo-electric cell in which some new features were introduced was found to be extraordinarily sensitive. As photo-electric cells are

* Communicated by Professor Sir J. J. Thomson, O.M., F.R.S.

frequently used as radiometers in the visible and in the ultra-violet spectrum, a short account of this form of photo-electric cell seems desirable.

The cell is a pear-shaped flask, which is shown approximately to scale in the figure. A quartz plate *Q*, 4 cm. in diameter, is joined to the flask by sealing-wax. It is impossible to avoid the use of sealing-wax, or some similar cement, when an air-tight joint has to be made between quartz and glass. Communication with the electrodes is made by means of platinum fused into the glass, so that the only waxed joint in the cell is that between the quartz plate



and the flask. The illuminated electrode is a thin layer of sodium which covers the whole of the inside of the flask, and the other electrode is a brass rod projecting into the flask. This is the electrode which is connected to the electrometer, and therefore requires to be well insulated. The glass tube around the platinum wire at *P* is warmed and covered with sealing-wax, which is a good insulator. If the apparatus is properly dried and evacuated, the inside of the glass tube near *P* insulates perfectly. Sodium is introduced into the bulb *N*, and is strongly heated to drive off gases which are removed by a Toepler pump and charcoal in liquid air. Meanwhile the cell is warmed to drive off condensed gases and vapours from the walls. The apparatus is then tilted so as to cause the melted sodium to pass through the traps and constriction *L* into the small bulb *M*. The sodium in *M* is now heated until the inside of the flask becomes covered with a layer of distilled sodium. To prevent any deposition on the quartz window, the following device was employed. A piece of thin lead foil (shown obliquely at *K*) is cut so as

to fill the cross-section of the tube, and this foil is held up by a thin glass rod, which in turn is suspended from the winch W by a silk thread. When sufficient sodium has been distilled, the lead foil is raised by means of the winch and is crumpled up in the side tube out of the path of the light. The blowpipe is then applied to the constriction B, which collapses around the glass rod and is sealed off. Finally the apparatus is sealed off at L.

On looking into the cell, the sodium surface presented a beautiful appearance. It consisted of an immense number of minute solidified drops of sodium which scattered light in all directions.

A very convenient way of measuring the photo-electric current was to balance it against a current flowing through a suitable xylol-alcohol resistance as described by Dr. N. R. Campbell. A Wilson tilted electroscope was used as a null instrument. When conditions were steady, the photo-electric current remained constant to at least 1 part in 1000 over a period of several minutes.

The following test was made on the sensitiveness of the cell. The wave-length λ 4360 was isolated by a monochromator, the aperture-ratio of the lenses being about $f. 5$. The slits were 2 cm. by 2 mm. The energy absorbed by the mercury lamp was 120 watts per second. The photo-electric current obtained with the cell was as large as 580×10^{-11} amp. This appears to be considerably larger than any current which has previously been obtained from a photo-electric cell under similar conditions. The only investigations which furnish sufficient data to effect a comparison are those of Pohl and Pringsheim. They illuminated a smooth surface of sodium by means of a monochromator which transmitted about the same amount of light as that used in these experiments. Their lamp, however, apparently consumed between 360 and 600 watts per second.

The photo-electric current from the surface, when illuminated by λ 4360, was of the order 15 to 20×10^{-11} amp.*

When it is remembered that the lamp used in my experiments probably gave out at the most only one-third as much light as theirs, it appears that this new photo-electric cell is extremely sensitive. The sensitiveness is about 100 to 200 times that of a cell containing the usual smooth surface of sodium which has been solidified from the liquid state. The reason for this is two-fold. First, it has been shown by Elster & Geitel and others, that a surface consisting of a large number of minute solidified drops is more sensitive than a surface prepared in the usual way. Again, the

* Pohl & Pringsheim, *Verh. d. Deutsch. Phys. Ges.* p. 54 (1912).

coefficient of reflexion of sodium is very high, the value given by Drude being 99.7 per cent. Hence less than 1 per cent. is available for producing a photo-electric effect.

In the new cell, however, the light which gets into it is scattered about in all directions, and only a small fraction escapes out of the cell. Thus, by continued reflexion, much more of the light is used up photo-electrically than when only one reflexion takes place. In fact, the cell is analogous to the enclosures used in radiometry to represent a black body.

Photo-electric cells can be used to investigate light-intensities which are far too small to produce any effect with a thermopile and delicate galvanometer. The sensitiveness of photo-electric cells varies in different parts of the spectrum, and so it would be necessary to calibrate them by means of a thermopile and a source of intense light, if it is desired to compare intensities in different parts of the spectrum by means of such cells. This, of course, is unnecessary if the variations of intensity in any one region are to be investigated. Elster & Geitel * have employed photo-electric cells to measure the variations of light-intensity during lunar and solar eclipses. Nichols & Merritt † have applied them to the study of luminescence. Since photo-electric cells can measure quantity of light (intensity \times time), Richtmyer ‡ has indicated how they could be used to measure the speed of photographic shutters. Photo-electric cells can be readily used for investigations in phosphorescence.

If cells of the type described in this paper are required only for wave-lengths longer than λ 3300, the quartz plate can be dispensed with and the whole apparatus made of glass. The winch device would be unnecessary, as the metal could be driven off the part intended to act as window by the application of heat. K, Rb, and Cs are still more sensitive than Na in the visible region, and could be used instead of Na if greater sensitiveness is required. This new form of photo-electric cell has the advantage that only a small quantity of metal is necessary, which, in the case of the more expensive metals Rb and Cs, is worthy of consideration.

I wish to express my best thanks to Professor Sir J. J. Thomson for his interest in this work.

The monochromator used for testing the cell was obtained by means of a Government Grant from the Government Grant Committee of the Royal Society.

* Elster & Geitel, *Phys. Zeits.* p. 1212 (1910); p. 582 (1912).

† Nichols & Merritt, *Phys. Rev.* vol. xxxiv. p. 475 (1912).

‡ Richtmyer, *Phys. Rev.* vol. xxx. p. 394 (1910).

LXIX. *On the Velocities with which Photo-Electrons are emitted from Matter.* By A. LL. HUGHES, D.Sc., B.A.,
Mackinnon Student of the Royal Society; Emmanuel College,
Cambridge*.

INVESTIGATIONS by Professor O. W. Richardson and Mr. Compton† and by the writer‡ have shown that metallic surfaces, when illuminated by ultra-violet light, emit electrons whose maximum energy is a linear function of the frequency. It was shown that the maximum energy, and not the maximum velocity, was proportional to the frequency. Most of the photo-electrons emerge from the surface with velocities appreciably less than the maximum, on account of loss of energy by collisions in their journey from the interior. Those which possess the maximum velocities have, presumably, not lost any energy in this way. If V be the potential required to stop the fastest electrons, and e the charge, then the experimental relation between the maximum energy Ve and the frequency n is

$$Ve = h'n - V_0e, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where h' and V_0 are experimental constants. This is also the type of formula suggested by the quantum theory. If h be Planck's constant, then hn is the unit of energy associated with the frequency n . Since, on several grounds, this unit seems to be the least energy which is involved during emission and absorption of light of this frequency, we may assume, in this particular case, that it is the amount of energy acquired by the photo-electron. V_0e represents the loss of energy in getting away from the parent molecule, or more generally, from the surface. Hence the theoretical relation would be

$$Ve = hn - V_0e \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental values for h' are all less than Planck's h by amounts ranging from 10 to 25 per cent. When one considers the fundamental way in which Planck's constant appears in many branches of physics, combined with the straightforward interpretation of the photo-electric effect on Planck's theory of radiation, one is almost forced to the conclusion that h' is ultimately identical with the universal constant h and that the difference is the result of some secondary effect. Richardson and Compton were inclined to attribute the difference to experimental errors, all of which

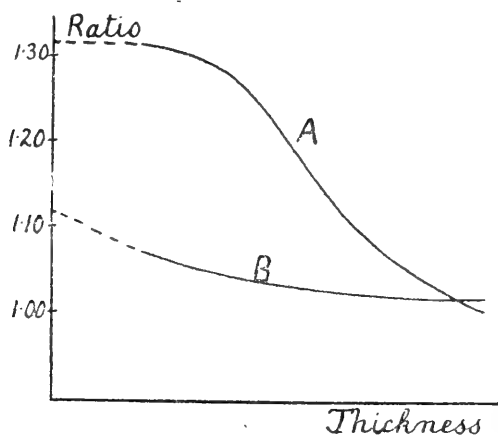
* Communicated by Professor Sir J. J. Thomson, O.M., F.R.S.

† Richardson & Compton, *Phil. Mag.* p. 576 (1912).

‡ Hughes, *Phil. Trans.* vol. ccxii. (A) p. 205 (1912).

tend to make h' too small. I think, however, that the deviations are larger than the possible errors of experiment, and moreover, I found that there was a small but quite regular variation in h' with the position of the metal in the periodic table.

The reconciliation between the experimental and theoretical results is perhaps to be sought in another direction. In the above experiments the maximum velocities of photo-electrons emitted from the *same* side of the plate as the incident light were investigated. Robinson* has lately studied the velocities of photo-electrons from both sides of a thin transparent film of platinum placed perpendicularly to the light. He finds that the velocities are greater on the emergent side than on the incident side. In the figure, curve A gives the ratio



of the *numbers* of photo-electrons emitted on either side, and curve B gives the ratio of the corresponding maximum *velocities* measured in volts. One may surmise that, perhaps, all the electrons are emitted originally from the molecules more or less in the direction of the light, and that subsequent scattering by collisions leads to the emission in all directions. On producing curve B backwards, we find it cuts the ordinate through the origin at 1.12 in such a way as to indicate that this is the limiting ratio of the emergent to the incident energies, for a film of zero thickness. We may regard this as indicating that the energy lost by a photo-electron in swinging round from its original direction of emission is at least 11 per cent. Now Richardson and Compton found h' for platinum to be 5.85×10^{-27} by a direct method and 5.60 by an indirect method, which they considered to give rather more accurate results. Increasing these values by 12 per cent. we get 6.55×10^{-27} and 6.27×10^{-27} , which are in good agreement with Planck's constant, 6.55×10^{-27} erg sec. It

* Robinson, Phil. Mag. xxv. p. 115 (1913).

appears, therefore, that the application of the quantum theory to photo-electricity is quantitatively justified if we keep in mind the electrons which emerge in the direction of the incident light.

No experimental results as to the ratios of the emergent to the incident velocities for other metals are available, and so it is not possible, at present, to test this view further. More precise information would be obtained if the ratios were investigated using monochromatic light.

From equation (1) it is seen that there can be no emission of electrons unless $h\nu$ exceeds V_0e . On putting $V=0$ we get the critical frequency at which the electrons emerge without any velocity. Below this frequency there is no photo-electric effect. Knowing the critical frequency at which the photo-electric effect starts, we may calculate V_0e , the amount of energy required to take an electron from the molecule, and V_0 may be regarded as the ionizing potential.

We shall now make the assumption that the ionization of gases by ultra-violet light is essentially the same as the photo-electric effect in solids, and we may proceed to find the ionizing potential of a gas from the longest wave-length which produces ionization in it. A difficulty arises as to what value to assign to h' for a gas, since h' is only obtained from velocity experiments with solids, and varies slightly from one element to another. The difficulty disappears if we consider that Robinson's experiments, in conjunction with those of Richardson and Compton, justify us in regarding equation (2), and not equation (1), as representing the energy exchanges associated with the emission of photo-electrons from isolated molecules of a gas.

It has been shown by the writer* that the ionization of air by ultra-violet light sets in at about λ 1350. (From a consideration of Lenard's work, Lyman† concludes that the critical wave-length is about λ 1300, which agrees well with my results.) Palmer's work‡ leads us to associate this critical wave-length with the oxygen in the air. If we take h' for oxygen to be 5.72×10^{-27} , which is the mean value for the metals, as an approximation, we get V_0 to be 8.0 volts. This method of calculating V_0 was introduced in a previous paper. But the considerations brought forward earlier in this paper now justify us in using h instead of h' . Taking

* Hughes, Proc. Camb. Phil. Soc. xv. p. 482 (1910). The outside limits given in the paper are λ 1250 and λ 1450. The critical wave-length λ 1350 was obtained from subsidiary experiments in which fluorite plates possessing different transparency limits were used.

† Lyman, *Phys. Zeits.* xiii. p. 583 (1912).

‡ Palmer, *Phys. Rev.* xxxii. p. 1 (1911).

$h=6.55 \times 10^{-27}$ erg sec., $e=4.75 \times 10^{-10}$ E.S.U., and the critical wave-length to be $\lambda 1350$, we get the ionizing potential V_0 ($=hn/e$) to be 9.2 volts. The most recent and accurate work on the ionizing potential is that of Franck and Hertz *, who found that the ionizing potential for oxygen is 9.0 volts, which agrees well with the value calculated from photo-electric experiments.

One point arises in connexion with the ionizing potential. It might be expected that less work is required to remove an electron from a molecule of a substance when solid or liquid than when gaseous. The forces tending to pull the escaping electron back into the parent molecule may be considerably reduced by forces originating in adjacent molecules, and hence the ionizing potential may depend on the physical state of a substance. The spontaneous ionization of a gas can be regarded as the dissociation of uncharged molecules into positive and negative ions. This dissociation should increase rapidly with the temperature in the same way as that of a dissociating vapour. Sir J. J. Thomson has calculated the amount of dissociation—in this case, the spontaneous ionization—in a vapour whose ionizing potential is about 3 volts, and finds that such a vapour should be highly conducting at temperatures of the order of 500° C. According to Dunoyer, the natural conductivity of sodium vapour is of the order of that of ordinary gases, and the inference from this is that the ionizing potential of sodium vapour is considerably higher than that derived from photo-electric experiments on solid sodium (2.2 volts). The author † found that the longest wave-length which produced any photo-electric effect in solid anthracene was about $\lambda 2100$, corresponding to $V_0=5.9$ volts. Now, Stark has obtained intense ionization in anthracene vapour illuminated by the ultra-violet light from a mercury arc in quartz glass. The shortest wave-length emitted by such a lamp is $\lambda 1849$, and the strong ionization observed renders it unlikely that $\lambda 1849$ was the only active line. Hence the ionizing potentials for solid and gaseous anthracene, calculated from photo-electric experiments, can only differ at the most by .7 volt. Experiments which bear on this point are now being made on the photo-electric effect of a substance in different physical states.

I wish to thank Prof. Sir J. J. Thomson for his interest and suggestions in the course of this work.

* Franck & Hertz, *Verh. d. Deutsch. Phys. Ges.* p. 34 (1913).

† Hughes, *Phil. Mag.* xxiv. p. 380 (1912).

LXX. *On the Collapse of Tubes by External Pressure.**By* R. V. SOUTHWELL, B.A.*

IN the issue of this magazine for September 1892† Mr. Basset has given a very clear exposition of the difficulties which we encounter in attempting to construct a theory of flue collapse. The conclusions to which his discussion leads are, that the formula obtained by Prof. Bryan‡ for the collapsing pressure of an infinitely long flue is probably correct as a first approximation, when the inner surface of the tube is free from applied pressures; but that his work, as distinguished from his result, is vitiated by the employment of a faulty expression for the strain energy of bending, and that although the formula may be obtained by other methods, these also must be based upon assumptions which are certainly not exact, and may be so far from the truth as to render the result faulty, even as a first approximation.

I have recently investigated the problem by a method which I believe to be exact, and which does not involve the Theory of Thin Shells§. My results show that Professor Bryan's formula is correct as a first approximation, even when both surfaces of the tube are subjected to pressure, the difference of the pressures being the sole criterion of collapse. In the light of this conclusion, Mr. Basset's remarks seem to require further examination; for the Theory of Thin Shells is apparently more capable than they would suggest of providing a satisfactory formula for flue collapse. I shall attempt in the following pages to indicate the alterations in method which, as I believe, enable us to evade the difficulties remarked by Mr. Basset, and to show how Professor Bryan's formula, thus established, may be extended so as to suggest estimates for the influence of "collapse rings" upon the strength of flues.

For convenience of comparison I shall retain the notation of Mr. Basset's article in dealing with his discussion of the boiler-flue problem, which, in its simplest form, he states as follows:—"Let the flue be regarded as indefinitely long, and be cylindrical; let $a+h$ and $a-h$ be the external and internal radii of its surfaces; and let the outer and inner

* Communicated by Professor B. Hopkinson, F.R.S.

† Phil. Mag. vol. xxxiv. p. 221.

‡ Proc. Camb. Phil. Soc. vi. p. 287 (1888).

§ In a paper read before the Royal Society of London, January 30th, 1913.

surfaces be subjected to pressures Π_1, Π_2 . Then the condition of stability requires that a certain relation should exist between these four quantities, which may be written

$$F(a, h, \Pi_1, \Pi_2) > 0."$$

Mr. Basset suggests two methods by which this problem may be attacked:—"In the first place, let the flue be slightly deformed, and let the period of the small oscillations be found; then the condition of stability requires, that the periods should be real quantities. In the second place, let the potential energy in the deformed state be found; then the condition of stability requires, that the potential energy of the flue when in equilibrium should be a minimum. Either of these methods will determine the mathematical form of the function F ."

I propose to use a third method, practically equivalent to both of the above, and to investigate the conditions which must obtain if a circular tube is in *neutral* equilibrium under the action of external pressure. This is of course the limiting case between stable and unstable equilibrium, and when we have found a value of the pressure for which the equilibrium is neutral, it is easy, by changing the equation into an inequality, to express the condition of stability. When a configuration possesses neutral equilibrium, the period of vibration, for small displacements from that configuration, is infinite: that is to say, configurations of infinitesimal distortion exist which are also in equilibrium, and the condition of neutral stability may be determined from this consideration.

The above remarks lead to no alteration in Mr. Basset's methods, beyond the substitution of equations of equilibrium for his equations (6) of small motion, which become

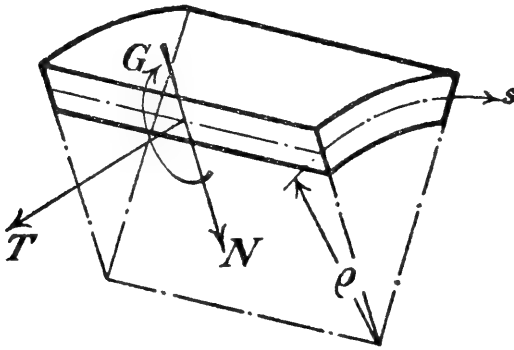
$$\left. \begin{aligned} \frac{dT}{ds} + \frac{N}{\rho} &= 0, \\ \frac{dN}{ds} - \frac{T}{\rho} + \Pi_2 \left(1 - \frac{h}{\rho}\right) - \Pi_1 \left(1 + \frac{h}{\rho}\right) &= 0, \\ \frac{dG}{ds} + N &= 0, \end{aligned} \right\} \quad (1)$$

where ρ is the radius of the deformed middle surface. The proposed alteration refers to the methods by which these equations are to be treated.

In equations (1), T , N and G are the values of the stress-resultants and stress-couples in a position of slight distortion

(see fig. 1). Mr. Basset argues, rightly I think, that there are no perfectly general expressions for these quantities,

Fig. 1.



correct to the third power of the thickness, in terms of the final extensions and curvatures of the middle surface, *when the surfaces of the shell are subjected to pressure* *. But we may proceed by distinguishing two configurations : (1) the position of equilibrium, in which the tube remains circular and merely suffers contraction : this is the configuration of which we are investigating the stability ; and (2) a configuration of infinitesimal displacement from this. If a is the radius of the tube in the former position, we may write

$$\text{and } \left. \begin{aligned} ds &= ad\phi, \\ \frac{1}{\rho} &= \frac{1}{a} - \frac{1}{a^2} \left(w + \frac{d^2 w}{d\phi^2} \right) \end{aligned} \right\} \dots \dots \dots (2)$$

where w is the (infinitesimal) radial displacement at any point, in the outward direction. We may also write T , N and G in the forms

$$\left. \begin{aligned} T &= T_0 + T', \\ N &= N_0 + N', \\ G &= G_0 + G', \end{aligned} \right\} \dots \dots \dots (3)$$

where T_0 , N_0 , G_0 , are values for the first configuration, and T' , N' , G' , are infinitesimal increments due to distortion. It is clear that

$$\text{and } \left. \begin{aligned} N_0 &= 0, \quad \frac{dG_0}{d\phi} = 0 \\ \frac{T_0}{a} &= \Pi_2 \left(1 - \frac{h}{a} \right) - \Pi_1 \left(1 + \frac{h}{a} \right); \end{aligned} \right\} \dots \dots \dots (4)$$

* Cf. also Lord Rayleigh, Proc. Lond. Math. Soc. vol. xx. p. 379.

and the equations (1) thus become, if we neglect infinitesimals of the second order,

$$\left. \begin{aligned} \frac{dT'}{d\phi} + N' &= 0; \\ \frac{dN'}{d\phi} - T' + \left(w + \frac{d^2w}{d\phi^2}\right) (\Pi_2 - \Pi_1) &= 0; \\ \frac{1}{a} \frac{dG'}{d\phi} + N' &= 0. \end{aligned} \right\} \quad . \quad . \quad (5)$$

From equations (5) a condition for stability can be derived, *provided that G' can be connected, accurately to terms in h^3 , with the curvature of the distorted middle surface*; for by eliminating T' and N' we obtain

$$\frac{d}{d\phi} \left(1 + \frac{d^2}{d\phi^2}\right) \left\{ \frac{G'}{a} + (\Pi_1 - \Pi_2)w \right\} = 0. \quad . \quad . \quad (6)$$

I shall now attempt to show that the requisite expression for G' can be derived *without the need for any assumption as to the extension of the middle surface*. We may proceed by Mr. Basset's method, the strain quantities now denoting the infinitesimal increments introduced by distortion. His equation (8) becomes

$$\begin{aligned} R' = (m+n)\sigma_3 + (m-n)\sigma_2 + \left\{ (m+n) \left(\frac{d\sigma_3'}{dr} \right) \right. \\ \left. + (m-n) \left(\frac{d\sigma_2'}{dr} \right) \right\} h' + \dots \quad . \quad . \quad (7) \end{aligned}$$

so that if we write

$$R' = A + A_1 h' + A_2 h'^2 + \dots \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\frac{m-n}{m+n} = E$$

we have

$$\left. \begin{aligned} \sigma_3 &= \frac{A}{m+n} - E\sigma_2, \\ \left(\frac{d\sigma_3'}{dr} \right) &= \frac{A_1}{m+n} - E \left(\frac{d\sigma_2'}{dr} \right). \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Mr. Basset's equation (12) then becomes

$$\left(\frac{d\sigma_2'}{dr} \right) = \frac{1}{a} \left\{ \frac{d\varpi}{d\phi} + \frac{A}{m+n} - E\sigma_2 - \frac{w}{a} - \frac{1}{a} \frac{d^2w}{d\phi^2} \right\} \quad . \quad . \quad (10)$$

and

$$\begin{aligned} Q' &= (m+n)\sigma_2' + (m-n)\sigma_3', \\ &= (m+n)\sigma_2 + (m-n)\sigma_3 + \left\{ (m+n)\left(\frac{d\sigma_2'}{dr}\right) + (m-n)\left(\frac{d\sigma_3'}{dr}\right) \right\} h', \\ &= EA + \frac{4mn}{m+n} \sigma_2 \\ &\quad + h' \left[EA_1 + \frac{4mn}{(m+n)a} \left\{ \frac{d\varpi}{d\phi} + \frac{A}{m+n} - E\sigma_2 - \frac{w}{a} - \frac{1}{a} \frac{d^2 w}{d\phi^2} \right\} \right], \end{aligned}$$

so that

$$\begin{aligned} G' &= - \int_{-h}^h Q' h' dh', \\ &= - \frac{2}{3} h^3 \left[EA_1 + \frac{4mn}{(m+n)a} \left\{ \frac{d\varpi}{d\phi} + \frac{A}{m+n} - E\sigma_2 - \frac{w}{a} - \frac{1}{a} \frac{d^2 w}{d\phi^2} \right\} \right] \end{aligned}$$

correctly to terms in h^3 (11)

Now R' , being the *increment* of stress produced by distortion, vanishes at the surfaces of the tube; and the surfaces are never subjected to tangential stress. Hence the terms Al^3 , $A_1 h^3$, ϖh^3 may legitimately be neglected in the expression for G' *. We have then

$$G' = \frac{8mnh^3}{3(m+n)a} \left[E\sigma_2 + \frac{w}{a} + \frac{1}{a} \frac{d^2 w}{d\phi^2} \right] (12)$$

Now from the first and third of (5) we see that T' must be of the same order as G' ; and

$$\begin{aligned} T' &= \int_{-h}^h Q' dh', \\ &= 2h \left[EA + \frac{4mn}{m+n} \sigma_2 \right] + (\text{terms in } h^3 \dots \text{etc.}). \end{aligned}$$

It follows that the quantity

$$EA + 4 \frac{mn}{m+n} \sigma_2,$$

and therefore also σ_2 , is of order h^2 at least; we shall therefore obtain G' correctly to terms in h^3 if we neglect σ_2 in equation (12).

* See p. 229 of Mr. Basset's article, and references on p. 223, for arguments in favour of this hypothesis.

We thus obtain the familiar expression

$$\frac{8mnh^3}{3(m+n)a^2} \left(w + \frac{d^2w}{d\phi^2} \right); \dots \dots \dots (13)$$

which may be substituted for G' in (6). The solution is of the form

$$w = W \sin k\phi, \dots \dots \dots (14)$$

where

$$\Pi_1 - \Pi_2 = \frac{8mnh^3}{3(m+n)a^3} (k^2 - 1). \dots \dots \dots (15)$$

This is the required condition for neutral equilibrium. If Π_2 is zero, and we give to k the value 2, the condition for stability may be written

$$\Pi_1 < \frac{8mnh^3}{(m+n)a^3}, \dots \dots \dots (16)$$

which is Professor Bryan's result.

The foregoing discussion requires to be read in connexion with Mr. Basset's article, but its purpose may be summarized in general terms. It is intended to show that the accepted formulæ for changes of curvature, in terms of the corresponding changes in the stress-couples, need not be restricted to the case of shells whose surfaces are free from stress,—*provided only that the changes under consideration are not accompanied by any change in the magnitude of the applied surface-tractions*; and in the boiler-flue problem the latter requirement is satisfied.

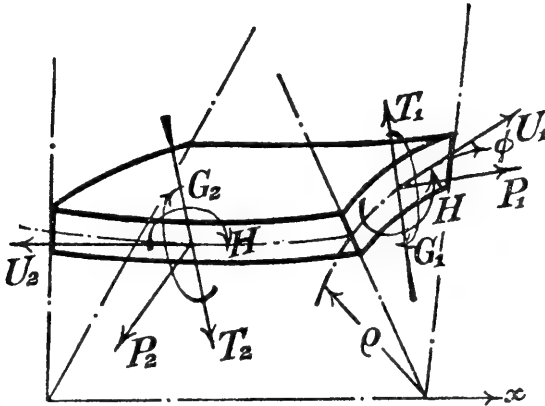
If the problem be approached from considerations of energy, my contention may be expressed as follows:—Although Mr. Basset is right in saying that a complete expression for the potential energy will contain terms depending on Π_1 and Π_2 , yet he has not shown that these pressures, when their intensity remains constant, influence to any sensible extent the *increase of energy* which is involved in a slight displacement from the configuration of equilibrium. The discussion of this paper, and the results which I have obtained independently of the Theory of Thin Shells, seem to show that they will not.

I have now to show that by the methods described above we may obtain an estimate of the effect of "collapse rings." These rings of course tend to prevent distortion of the tube at its ends, and the consequent strengthening effect must be investigated by the consideration of types of displacement in which the departure of the cross-sections from circularity varies in the axial direction. The product of the principal curvatures at a point will now be in general finite

after distortion, and Gauss' theorem* shows that extension of the middle-surface is involved. Hence it may be seen that terms will be introduced into the expression for $(\Pi_1 - \Pi_2)$ which involve the first power of the thickness; and these have now to be determined.

It will be convenient to change our notation for the various stress quantities, and to employ the system which is sufficiently explained by fig. 2.

Fig. 2.



We begin with the consideration of an indefinitely long tube, and take x for the length measured along a generator from a fixed normal section, and $a\phi$ for the length measured along the section from a fixed generator. When the distortion occurs, let u be the displacement along the generator, v the displacement along the tangent to the circular section, and w the displacement along the normal to the cylinder drawn outwards.

The equations of equilibrium may be obtained at once from the figure. They are

$$\left. \begin{aligned} \frac{\partial P_1}{\partial x} + \frac{1}{a} \frac{\partial U_2}{\partial \phi} - \frac{1}{a} \frac{\partial}{\partial x} \left[P_2 \left(\frac{\partial v}{\partial \phi} + w \right) \right] &= 0; \\ \frac{\partial U_1}{\partial x} + \frac{1}{a} \frac{\partial P_2}{\partial \phi} + \frac{T_2}{\rho} &= 0; \\ \frac{\partial T_1}{\partial x} + \frac{1}{a} \frac{\partial T_2}{\partial \phi} - \frac{P_2}{\rho} + \Pi_2 \left(1 - \frac{h}{\rho} \right) - \Pi_1 \left(1 + \frac{h}{\rho} \right) &= 0; \\ \frac{\partial H}{\partial x} + \frac{1}{a} \frac{\partial G_2}{\partial \phi} + T_2 &= 0; \\ \frac{\partial G_1}{\partial x} - \frac{1}{a} \frac{\partial H}{\partial \phi} - T_1 &= 0. \end{aligned} \right\} \quad (17)$$

* *Werke*, Bd. iv. p. 217. Cf. Salmon, 'Geometry of Three Dimensions,' 4th ed. p. 355.

But in order to find the terms in the expression for $(\Pi_1 - \Pi_2)$ which are of order h , we may omit the stress-couples from consideration, since these are of order h^3 ; and the last two of equations (17) then show that T_1 and T_2 may also be neglected.

Thus the first three equations become

$$\left. \begin{aligned} \frac{\partial P_1}{\partial x} + \frac{1}{a} \frac{\partial U_2}{\partial \phi} - \frac{1}{a} \frac{\partial}{\partial x} \left[P_2 \left(\frac{\partial v}{\partial \phi} + w \right) \right] &= 0; \\ \frac{\partial U_1}{\partial x} + \frac{1}{a} \frac{\partial P_2}{\partial \phi} &= 0; \\ \frac{P_2}{\rho} + \Pi_1 \left(1 + \frac{h}{\rho} \right) - \Pi_2 \left(1 - \frac{h}{\rho} \right) &= 0. \end{aligned} \right\} \quad (18)$$

If we now write $P_1 \dots$ in the forms

$$P_1 = [P_1] + P_1' \dots \text{etc.}, \quad (19)$$

where $[P_1] \dots$ are values in the configuration of equilibrium, when the tube is still circular and merely contracted, and $P_1' \dots$ are the increments caused by an infinitesimal displacement, we have at once

$$\left. \begin{aligned} \frac{[P_2]}{a} &= \Pi_2 \left(1 - \frac{h}{a} \right) - \Pi_1 \left(1 + \frac{h}{a} \right); \\ [P_1] &= [U_1] = [U_2] = 0; \end{aligned} \right\} \quad (20)$$

and it is easy to show that, to terms in h ,

$$\left. \begin{aligned} P_1' &= 2 \frac{m^2}{m^2 - 1} E h \left[\frac{\partial u}{\partial x} + \frac{1}{m a} \left(\frac{\partial v}{\partial \phi} + w \right) \right], \\ P_2' &= 2 \frac{m^2}{m^2 - 1} E h \left[\frac{1}{a} \left(\frac{\partial v}{\partial \phi} + w \right) + \frac{1}{m} \frac{\partial u}{\partial x} \right], \\ U_1' &= U_2' = \frac{m}{m + 1} E h \left[\frac{1}{a} \frac{\partial u}{\partial \phi} + \frac{\partial v}{\partial x} \right], \end{aligned} \right\} \quad (21)$$

where E is Young's modulus, and $\frac{1}{m}$ is Poisson's ratio for the material of the tube.

Using these relations to simplify (18), and neglecting second order infinitesimals and higher powers of h than the first, we have

$$\begin{aligned} \frac{\partial^2 u}{\partial x^2} + \frac{m-1}{2m} \frac{1}{a^2} \frac{\partial^2 u}{\partial \phi^2} + \left(\Psi + \frac{m+1}{2m} \right) \frac{1}{a} \frac{\partial^2 v}{\partial x \partial \phi} + \left(\Psi + \frac{1}{m} \right) \frac{1}{a} \frac{\partial w}{\partial x} &= 0, \\ \frac{m+1}{2m} \frac{1}{a} \frac{\partial^2 u}{\partial x \partial \phi} + \frac{m-1}{2m} \frac{\partial^2 v}{\partial x^2} + \frac{1}{a^2} \frac{\partial^2 v}{\partial \phi^2} + \frac{1}{a^2} \frac{\partial w}{\partial \phi} &= 0, \\ \frac{1}{m} \frac{\partial u}{\partial x} + \frac{1}{a} \frac{\partial v}{\partial \phi} + \frac{w}{a} + \frac{\Psi}{a} \left(w + \frac{\partial^2 w}{\partial \phi^2} \right) &= 0, \end{aligned} \quad (22)$$

where Ψ denotes the quantity

$$\frac{(\Pi_1 - \Pi_2)\alpha}{2 \frac{m^2}{m^2 - 1} E h}.$$

A solution of (22) is of the form

$$\left. \begin{aligned} u &= U \sin k\phi \cos \lambda x, \\ v &= V \cos k\phi \sin \lambda x, \\ w &= W \sin k\phi \sin \lambda x, \end{aligned} \right\} \dots \dots \dots (23)$$

where U, V, W, k and λ are constants, k being necessarily integral.

Substituting in (22) from (23), we obtain the following determinantal equation for Ψ :—

$$\begin{vmatrix} \lambda^2 + \frac{m-1}{2m} \frac{k^2}{a^2}, & \left(\Psi + \frac{m+1}{2m}\right)\lambda^2, & \left(\Psi + \frac{1}{m}\right)\lambda^2, \\ \frac{m+1}{2m} \frac{k^2}{a^2}, & \frac{m-1}{2m} \lambda^2 + \frac{k^2}{a^2}, & \frac{k^2}{a^2}, \\ \frac{1}{m}, & 1, & 1 - \Psi(k^2 - 1), \end{vmatrix} = 0. \quad (24)$$

This equation, when expanded and simplified, gives

$$\Psi^2 \frac{m+1}{m-1} \lambda^2 \frac{k^2}{a^2} (k^2 - 1) - \Psi \left[(k^2 - 1) \left(\lambda^2 + \frac{k^2}{a^2} \right) + \frac{\lambda^4}{m} \right] + \frac{m^2 - 1}{m^2} \lambda^4 = 0. \quad (25)$$

But it is easy to see from its expression in (22) that Ψ must be very small in any case of practical importance, so that the term in Ψ^2 may be neglected in equation (25); and from the latter equation that Ψ is of the fourth order in terms of λ , so that λ also must be very small. Hence we may write with sufficient accuracy

$$\Psi = \frac{m^2 - 1}{m^2} \frac{a^4 \lambda^4}{k^4 (k^2 - 1)},$$

or

$$\Pi_1 - \Pi_2 = 2E \frac{h}{a} \frac{a^4 \lambda^4}{k^4 (k^2 - 1)} \dots \dots \dots (26)$$

Considering the problem again in general terms, we see that the resistance offered by the tube to distortion will be due partly to its extension and partly to its bending. The complete expression for $(\Pi_1 - \Pi_2)$ will be of the form

$$\alpha h + \beta h^3 + \gamma h^5 + \dots, \dots \dots (27)$$

where α, β, γ , etc. are functions of the radius and elastic properties of the tube, and of k and λ . In this paper we are

not concerned with terms of higher order than h^3 , and α is given, with sufficient accuracy, by (26).

When λ is zero, the wave-length of the distortion, in the axial direction, is infinite. In this case β must be given by the formula (15) for a flue of infinite length, so that in the notation of equation (26) it is clear that we may write

$$\beta = \frac{2}{3} \frac{m^2}{m^2-1} E \frac{(k^2-1)}{a^3} + (\text{terms involving powers of } \lambda).$$

Now we have already seen that λ must be very small in any practical case, and it is therefore clear that the unknown terms do not form any appreciable part of β ; hence with sufficient approximation we may calculate the critical value of the pressure difference, in the type of distortion specified by (23), from the following formula:

$$\Pi_1 - \Pi_2 = 2E \frac{h}{a} \left[\frac{a^4 \lambda^4}{k^4 (k^2-1)} + \frac{1}{3} \frac{m^2}{m^2-1} (k^2-1) \frac{h^2}{a^2} \right]. \quad (28)$$

The question now arises:—in the problem of the boiler-flue, where distortion is wholly or partially prevented at certain sections by the agency of “collapse rings,” what is the connexion between λ and the distance of these rings (or the effective length of the flue)? A purely ideal type of constraint may be imagined, which tends merely to maintain the *circularity* of the tube at certain sections, without restricting the slope of the tube-wall*; this would permit the occurrence of the distortion specified in (23), and the distance between constraints would be equal to $\frac{\pi}{\lambda}$. But in practice the end constraints will also tend to “clamp” the ends of the flue, and this effect will strengthen the tube, by an amount which it is not easy to determine exactly.

In any case we may say that

$$l \propto \frac{1}{\lambda},$$

$$\propto \frac{a}{q} \text{ (say),}$$

and we may illustrate the way in which the end effects die out by plotting $(\Pi_1 - \Pi_2)$ against the quantity $\frac{1}{a\lambda}$, or $\frac{1}{q}$. To do this we must take some definite value of the ratio $\frac{h}{a}$, and

* A thin disk, inserted in the tube but not fastened to it, would have approximately this effect.

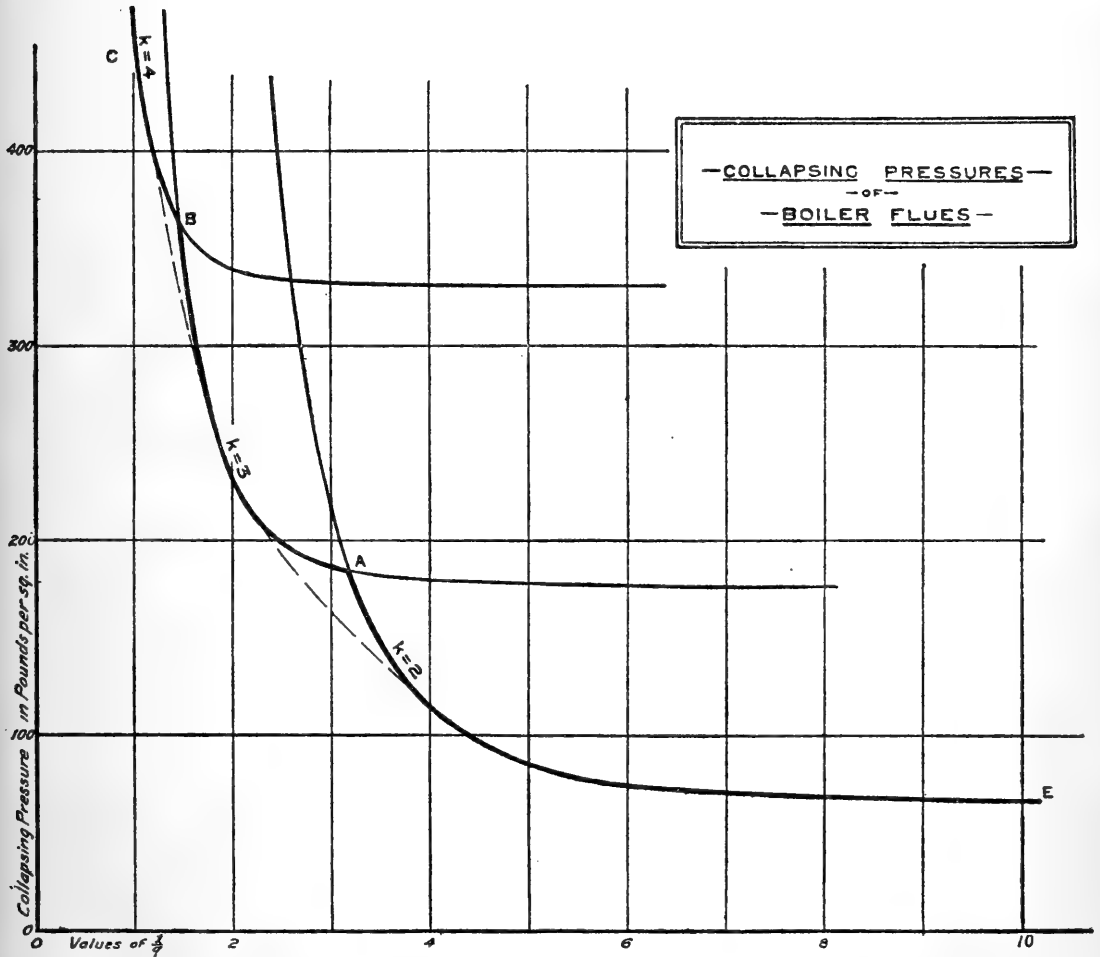
plot different curves for the values 2, 3, . . . etc. of k . This has been done in fig. 3, the following values being assumed for the constants :—

$$E = 3 \times 10^7 \text{ pounds per sq. inch,}$$

$$m = \frac{10}{3},$$

$$\frac{h}{a} = \frac{1}{100}.$$

Fig. 3.



From an inspection of these curves we see that long tubes will always tend to collapse into the 2-lobed form, since the curve for $k=2$ then gives the least value for the collapsing pressure, but that at a length corresponding to the point A the 3-lobed form of distortion becomes natural to the tube, and for shorter lengths still, of which the point B gives the

upper limit, the 4-lobed form requires least pressure for its maintenance. Thus the true curve connecting pressure and length is the discontinuous curve CBAE, shown in the diagram by a thickened line.

The changes in the form of the collapsed cross-sections, thus predicted, are clearly shown by experiments *, and the diagram (fig. 3) throws an interesting light upon the well-known formula of Fairbairn †, which makes the collapsing pressure inversely proportional to the length of the tube. This result is precisely what the present investigation would lead us to expect, if the experiments were restricted to short tubes, and if the possibility of discontinuities at points such as A and B in the curve of collapsing pressure were neglected ; for the hyperbolic curve

$$\Pi_1 - \Pi_2 = 464q$$

is an almost perfect envelope of the discontinuous curve CBAE down to the point at which the collapsing pressure reaches a sensibly constant value. Fairbairn, by expressing the whole range of his results in one formula, did neglect the possibility of discontinuities, and it is obvious that his experiments, since they show a steady fall of collapsing pressure with increase of length, must have been restricted to comparatively short tubes.

December 13th, 1912.

LXXI. *On Conformal Representation from a Mechanical Point of View.* By LORD RAYLEIGH, O.M., F.R.S.‡

IN what is called conformal representation the co-ordinates of one point x, y in a plane are connected with those of the corresponding point ξ, η by the relation

$$x + iy = f(\xi + i\eta), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f denotes an arbitrary function. In this transformation angles remain unaltered, and corresponding infinitesimal figures are similar, though not in general similarly situated. If we attribute to ξ, η values in arithmetical progression with the same small common difference, the simple square network is represented by two sets of curves crossing one another at right angles so as to form what are ultimately

* Cf. W. C. Unwin, 'Elements of Machine Design,' Part I. (1909) p. 113, and A. P. Carman, University of Illinois Bulletin, vol. iii. No. 7.

† Phil. Trans. Roy. Soc. cxlviii. p. 389.

‡ Communicated by the Author.

squares when the original common difference is made small enough. For example, as a special case of (1), if

$$x + iy = c \sin(\xi + i\eta), \quad . \quad . \quad . \quad (2)$$

$$x = c \sin \xi \cosh \eta, \quad y = c \cos \xi \sinh \eta ;$$

and the curves corresponding to $\eta = \text{constant}$ are

$$\frac{x^2}{c^2 \cosh^2 \eta} + \frac{y^2}{c^2 \sinh^2 \eta} = 1, \quad . \quad . \quad . \quad (3)$$

and those corresponding to $\xi = \text{constant}$ are

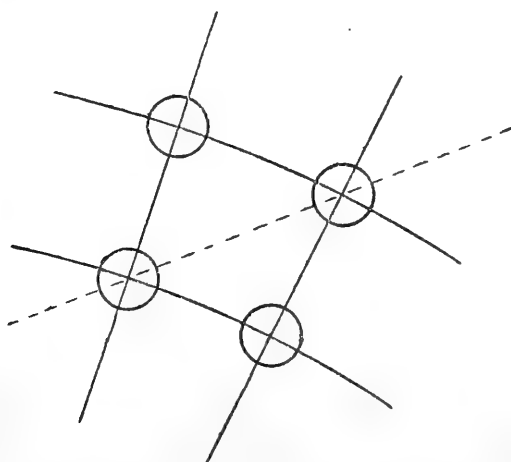
$$\frac{x^2}{c^2 \sin^2 \xi} - \frac{y^2}{c^2 \cos^2 \xi} = 1, \quad . \quad . \quad . \quad (4)$$

a set of confocal ellipses and hyperbolas.

It is usual to refer x, y and ξ, η to separate planes and, so far as I have seen, no *transition* from the one position to the other is contemplated. But of course there is nothing to forbid the two sets of co-ordinates being taken in the same plane and measured on the same axes. We may then regard the angular points of the network as moving from the one position to the other.

Some fifteen or twenty years ago I had a model made for me illustrative of these relations. The curves have their material embodiment in wires of hard steel. At the angular points the wires traverse small and rather thick brass disks, bored suitably so as to impose the required perpendicularity,

Fig. 1.



the two sets of wires being as nearly as may be in the same plane. But something more is required in order to secure that the rectangular element of the network shall be *square*. To this end a third set of wires (shown dotted in fig. 1) was

introduced, traversing the corner pieces through borings making 45° with the previous ones. The model answered its purpose to a certain extent, but the manipulation was not convenient on account of the friction entailed as the wires slip through the closely-fitting corner pieces. Possibly with the aid of rollers an improved construction might be arrived at.

The material existence of the corner pieces in the model suggests the consideration of a continuous two-dimensional medium, say a lamina, whose deformation shall represent the transformation. The lamina must be of such a character as absolutely to preclude *shearing*. On the other hand, it must admit of expansion and contraction equal in all (two-dimensional) directions, and if the deformation is to persist without the aid of applied forces, such expansion must be unresisted.

Since the deformation is now regarded as taking place continuously, f in (1) must be supposed to be a function of the time t as well as of $\xi + i\eta$. We may write

$$x + iy = f(t, \xi + i\eta). \quad . \quad . \quad . \quad . \quad (5)$$

The component velocities u, v of the particle which at time t occupies the position x, y are given by $dx/dt, dy/dt$, so that

$$u + iv = \frac{d}{dt} f(t, \xi + i\eta). \quad . \quad . \quad . \quad . \quad (6)$$

Between (5) and (6) $\xi + i\eta$ may be eliminated ; $u + iv$ then becomes a function of t and of $x + iy$, say

$$u + iv = F(t, x + iy). \quad . \quad . \quad . \quad . \quad (7)$$

The equation with which we started is of what is called in Hydrodynamics the Lagrangian type. We follow the motion of an individual particle. On the other hand, (7) is of the Eulerian type, expressing the velocities to be found at any time at a specified place. Keeping t fixed, *i. e.* taking, as it were, an instantaneous view of the system, we see that u, v , as given by (7), satisfy

$$(d^2/dx^2 + d^2/dy^2)(u, v) = 0, \quad . \quad . \quad . \quad . \quad (8)$$

equations which hold also for the irrotational motion of an incompressible liquid.

It is of interest to compare the present motion with that of a highly viscous two-dimensional fluid, for which the

equations are *

$$\rho \frac{Du}{Dt} = \rho X - \frac{dp}{dx} + \mu' \frac{d\theta}{dx} + \mu \left(\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} \right),$$

$$\rho \frac{Dv}{Dt} = \rho Y - \frac{dp}{dy} + \mu' \frac{d\theta}{dy} + \mu \left(\frac{d^2v}{dx^2} + \frac{d^2v}{dy^2} \right),$$

where $\theta = \frac{du}{dx} + \frac{dv}{dy}.$

If the pressure is independent of density and if the inertia terms are neglected, these equations are satisfied provided that

$$\rho X + \mu' d\theta/dx = 0, \quad \rho Y + \mu' d\theta/dy = 0.$$

In the case of real viscous fluids, there is reason to think that $\mu' = \frac{1}{3}\mu$. Impressed forces are then required so long as the fluid is moving. The supposition that p is constant being already a large departure from the case of nature, we may perhaps as well suppose $\mu' = 0$, and then no impressed bodily forces are called for either at rest or in motion.

If we suppose that the motion in (7) is *steady* in the hydrodynamical sense, $u + iv$ must be independent of t , so that the elimination of $\xi + i\eta$ between (5) and (6) must carry with it the elimination of t . This requires that df/dt in (6) be a function of f , and not otherwise of t and $\xi + i\eta$; and it follows that (5) must be of the form

$$x + iy = F_1\{t + F_2(\xi + i\eta)\}, \quad . \quad . \quad . \quad (9)$$

where F_1, F_2 denote arbitrary functions. Another form of (9) is

$$F_3(x + iy) = t + F_2(\xi + i\eta). \quad . \quad . \quad . \quad (10)$$

For an individual particle $F_2(\xi + i\eta)$ is constant, say $a + ib$. The equation of the stream-line followed by this particle is obtained by equating to ib the imaginary part of $F_3(x + iy)$.

As an example of (9), suppose that

$$x + iy = c \sin \{it + \xi + i\eta\}, \quad . \quad . \quad . \quad (11)$$

so that

$$x = c \sin \xi \cosh (\eta + t), \quad y = c \cos \xi \sinh (\eta + t), \quad . \quad (12)$$

whence on elimination of t we obtain (4) as the equation of the stream-lines.

* Stokes, Camb. Trans. 1850; Mathematical and Physical Papers, vol. iv. p. 11. It does not seem to be generally known that the laws of dynamical similarity for viscous fluids were formulated in this memoir. Reynolds's important application was 30 years later.

It is scarcely necessary to remark that the law of flow along the stream-lines is entirely different from that with which we are familiar in the flow of incompressible liquids. In the latter case the motion is rapid at any place where neighbouring stream-lines approach one another closely. Here, on the contrary, the motion is exceptionally slow at such a place.

LXXII. *On the Absorption of Short Electric Waves by Air and Water-Vapour.* By JAMES E. IVES, Ph.D., Associate Professor of Physics in the University of Cincinnati *.

IT is well known that Wireless Telegraph signals can be sent farther at night than in the day. One of the suggestions that has been made to explain this fact is, that the air may absorb more of the energy of the waves during the daytime than it does during the night; the absorption of the waves being supposed to be due to the ions produced, either in the lower or in the upper layers of the atmosphere, by the action of sunlight.

It was this fact and the suggested explanation of it which led to the research described in this paper.

Moser †, Thomson ‡, Tesla §, Remington ||, Ebert and Wiedemann ¶, and Wiedemann and Schmidt **, have investigated the ionization of a gas at low pressures by a powerful alternating electric field. They have shown that gases when ionized in this manner, and especially when glowing, become highly conducting, and indeed to such an extent that when placed between the source of the oscillating field and some other conducting body, they shield the latter from electrical disturbances.

Lecher ††, by using a double-walled glass vessel like a Bunsen calorimeter, placing a coil of wire within the inner tube and winding four turns of wire on the outer tube, has shown that if high frequency oscillations are set up in the outer coil, and the pressure of the air between the two tubes is reduced, the rarified air will absorb a large part of the energy of the outer coil. He found that the absorption was

* Communicated by the Author.

† *Comptes Rendus*, cx. p. 397 (1890).

‡ *Phil. Mag.* xxxii. pp. 321-336, 445-464 (1891).

§ *Elect. Eng.* xii. pp. 14, 15 (1891).

|| *Phil. Mag.* xxxv. pp. 506-525 (1893).

¶ *Ann. Phys.* xlix. pp. 32-49 (1893).

** *Ann. Phys.* lxii. pp. 460-467, 468-473 (1897).

†† *Phys. Zeitschr.* iv. pp. 32-38 (1902).

greatest between $\cdot 10$ and $\cdot 07$ mm. The two coils were separated by a distance of about 2.5 cm. The frequency of the current in the outer coil was about 107, which corresponds to a wave-length of about 30 metres.

In Lecher's experiment, then, the ionization was very intense, being of the nature of that accompanying a glow discharge, and the absorption of the electromagnetic energy took place in the immediate neighbourhood of the oscillating system. Such an absorption could not well be spoken of as an absorption of electric waves. In fact, the system used by Lecher to produce the oscillations was a closed system, which would not give off electric waves.

In the case of Wireless Telegraph waves, the ionization of the air which has to be considered is its natural ionization, that is, the ionization produced by light, the presence of radium, and other causes always present. It is not produced by the waves themselves since their electric field is too small to produce ionization.

In 1908 the author and R. E. C. Gowdy, in a paper read before the American Physical Society*, described some experiments made to detect the absorption of electric waves by air at different pressures. Waves having a wave-length of about 10 cm. were used, and sent through a tube 44.5 cm. long, so that there were at least four complete waves between the sender and the receiver. They stated that they thought that they had observed two maxima of absorption of short electric waves in air as the pressure was decreased from that of the atmosphere to something less than one millimetre of mercury. One maximum apparently occurred near the zero of pressure, and the other between 40 and 60 cm. of mercury.

As there seemed to be some question as to the reliability of these results, the work was continued by the senior author, and the original results were not confirmed by later experiments. In fact, it was found that the Duddell Thermo-galvanometer used in the earlier experiments was not sensitive enough to measure the disturbances due to the 5 cm. linear oscillator, and that the deflexions obtained must have been due to some other cause.

In the earlier experiments, the method adopted was to send waves from the same oscillator through two separate tubes, successively, one tube containing air at atmospheric pressure, and the other, air at any desired pressure. The waves were received by one and the same receiver. The

* See abstract published in the Physical Review, xxvi. pp. 196, 197 (1908).

two tubes were placed side by side on a carriage to which a horizontal motion could be given; first one tube being placed between the sender and receiver, and then the other.

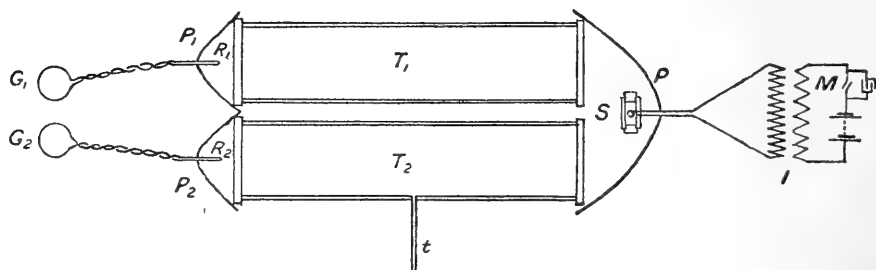
The difficulty with this method is that it is impossible to get waves of the same strength sent out from the sender twice in succession. As the absorption, if there is any, must be very small, it is necessary, when using this method, that the strength of the waves should be the same, or very nearly the same, each time. As is well known, when using an oscillator actuated by a spark-gap, it is impossible to attain this condition on account of the irregular action of the spark.

The only way to overcome this difficulty appeared to be to use a differential method.

In the experiments to be described in this paper, such a method was adopted, the waves being sent through both tubes *at the same time* from one and the same sender, and received on two separate receivers, one placed at the farther end of each tube. Each receiver contained a thermo-electric junction, and each junction was connected to one of the coils of a two-coil Siemens and Halske armoured galvanometer * in such a manner that the thermoelectric currents produced by the electric waves acted oppositely on the needle. By changing the position of the sender or of one of the receivers, or by partially covering one end of one of the tubes by a sheet of metal, the two disturbances of the galvanometer could be made to nearly neutralize each other, so that only a very small deflexion was obtained.

The arrangement of the apparatus is shown, diagrammatically, in fig. 1. T_1 and T_2 are two glass tubes both

Fig. 1.



Showing arrangement of apparatus.

exactly alike, 44.5 cm. long, and 10 cm. in diameter, and having pieces of plate glass sealed, with sealing-wax, upon their ends. The tubes were covered with tinfoil, so that the

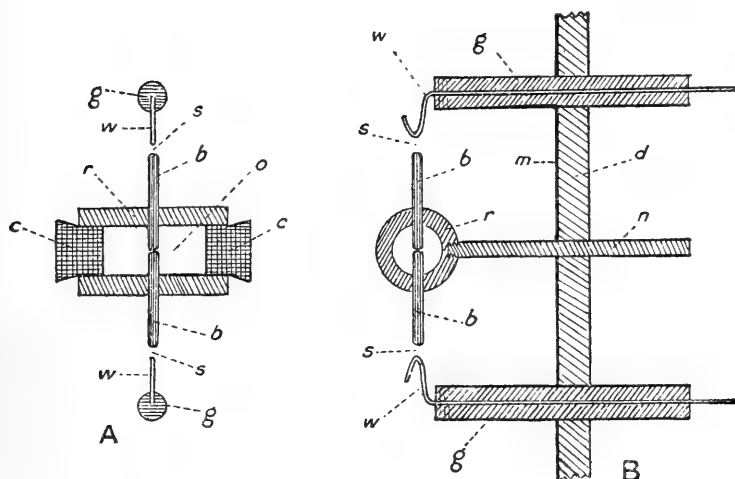
* This instrument is of the type designed by Du Bois and Rubens, and is described in the *Zeits. f. Instrumentenkunde*, Jahrg. 1900, p. 65.

disturbance in each tube would be confined to its own tube, and act only upon its own receiver. Covering them with tinfoil also got rid of disturbances due to the presence of neighbouring conductors. It was found that the excitation of the receivers was about five times as great when the tubes were covered with tinfoil as when not covered.

S is the sender. It consisted of two brass rods, placed end to end, each 2.5 cm. long. The rods were .25 cm. in diameter, rounded at the ends, and had a spark-gap .015 cm. long between them. The total length of the two rods together was therefore about 5 cm. It is one of the oscillators which I have fully described in my paper on the wave-length of the linear oscillator *, and it is the one that I have there called the 5-cm. sender. The brass rods were supported by a hard rubber cylinder, and the spark between them took place in kerosene oil. The oscillator was excited by two auxiliary sparks at the outer ends of the rods, each auxiliary spark being about 3 mm. long. The wave-length of this oscillator as previously determined † was about 10.2 cm.

The various parts of the sender are shown in cross-section in fig. 2; in A for a front view, and in B for a side view.

Fig. 2.



Sender. A, front view; B, side view.

bb are the brass rods; *r*, hard rubber cylinder; *cc*, corks closing the ends of the cylinder; *o*, space filled with kerosene oil; *ss*, auxiliary spark-gaps; *ww*, brass wires leading to secondary of induction-coil; *gg*, hollow glass rods supporting these wires; *n*, hard rubber rod supporting the hard

* *Physical Review*, xxx. pp. 199, 200 (1910).

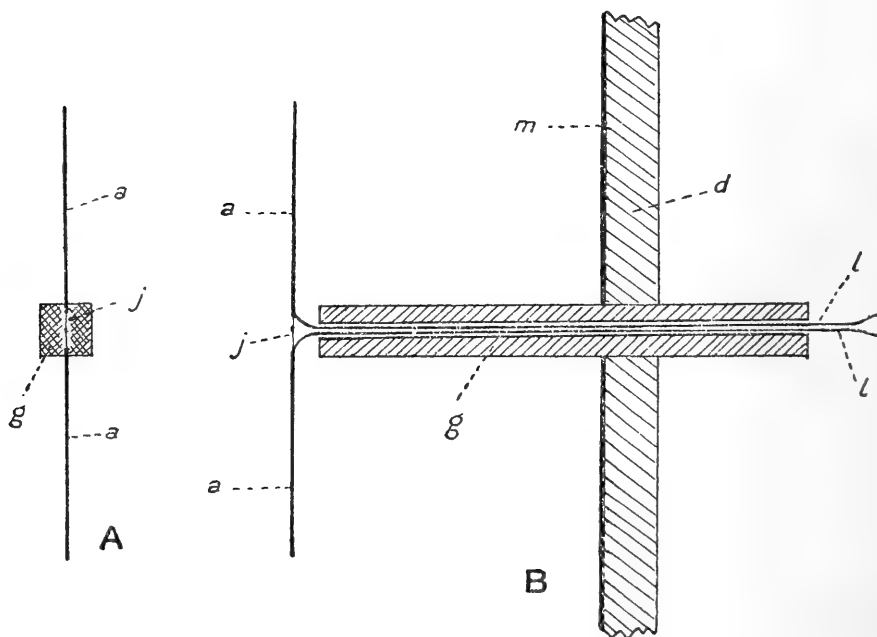
† *Physical Review*, xxxi. p. 214 (1910).

rubber cylinder; m , cross-section of parabolic mirror of sheet zinc; and d , the wooden support.

According to the experiments of Weber* and others, the wave-length of the waves emitted by the sender would be changed during their passage through the tubes, owing to the fact that a tube has a natural vibration of its own. According to Weber, the wave-length of the free vibrations in a tube is equal to 3.415 times the radius of the tube. In this case, therefore, the length of the waves due to the free vibrations of the tubes would be 17 cm. So that even if the length of the waves, due to the sender, was changed in passing through the tube, it would still be short.

R_1 and R_2 (fig. 1) were the receivers. They were each 4.4 cm. long, and made of two pieces of copper wire .0285 cm. in diameter joined together by a thermoelectric junction made of iron and constantan wires, each .0208 mm. in diameter, soldered at the junction. The wires going from the junction to the galvanometer were led out side by side through the centre of its wooden support. The fine wires forming the junction had a total length of about 4 mm.

Fig. 3.



Receiver. A, front view; B, side view.

The receiver is shown in detail in fig. 3, where A is a front view and B is a side view. aa are the copper wires

* *Ann. Phys.* viii. p. 743 (1902).

forming the linear receiver ; j , thermoelectric junction ; g , wooden rod supporting the receiver ; m , cross-section of parabolic mirror ; d , wooden support ; and ll copper wires leading to the galvanometer. The wires a and l are continuous, being made of one and the same piece of wire.

As already stated, each receiver was connected to one of the two coils, G_1 and G_2 (fig. 1), of the galvanometer, in such a manner that the thermoelectric currents passing through the coils produced nearly equal and opposite effects upon the needle of the galvanometer when the air in both tubes was at atmospheric pressure.

The tubes T_1 and T_2 were placed so that their axes were horizontal ; and the sender, S , and the receivers, R_1 and R_2 , were placed vertically and approximately in the focal lines of the cylindrical parabolic mirrors, P , P_1 , and P_2 respectively. The mirror P had a focal distance of about 3.7 cm. and an aperture of 24 cm. : P_1 and P_2 were of course alike, and each had a focal distance of about 3.0 cm. and an aperture of 13 cm. The mirrors were made of sheet zinc, and each was 20 cm. high. Each receiver was enclosed in a small box made of asbestos paper to protect it from changes of temperature.

I (fig. 1) is the induction-coil used to charge the sender, M is a rotating mercury interrupter, and t is a small glass tube leading from T_2 to a Gaede rotating mercury pump. The pressure within T_2 was read by one of three manometers : for high exhaustions by means of a MacLeod gauge ; for low exhaustions by means either of an open mercury manometer or of a closed U-shaped manometer. T_1 was not hermetically sealed, and therefore the air in it was always at atmospheric pressure.

The experiments were carried out as follows. The tube T_2 was filled either with air or with water-vapour. In some cases radium bromide in open vessels was placed within the tube. It was then slowly exhausted and readings taken of the pressure for every few centimetres, millimetres, or fractions of a millimetre.

Long series of readings were made, first with air alone, then with water-vapour alone, and then with air in the presence of radium.

When experimenting with water-vapour, the air was pumped out of the tube until what was left had a pressure of .0017 cm. Water-vapour was then introduced into the tube until the pressure had risen to 1.50 cm. The tube was then again gradually exhausted, and readings of the deflexions taken for decreasing pressures.

In no case was I able to detect, within the limits of accuracy of the experiment, any absorption of the waves.

Some of the typical results are given in Table I. The pressure is given in centimetres of mercury, and the galvanometer deflexion in centimetres. For every value of the pressure three independent readings of the galvanometer deflexion were taken when the waves were sent through the tubes. The mean of the three readings is the value given in the table.

The two thermoelectric junctions, as already stated, were so connected to the galvanometer that they produced nearly equal and opposite deflexions. The deflexion due to one junction alone was equal to about 2.5 cm. The deflexion due to R_1 was positive and slightly greater than that due to R_2 , which was negative. Consequently, if any absorption of the waves had taken place in T_2 , it would have been indicated by an *increase* of the differential deflexion of the galvanometer. It is evident, I think, from the table that a constant increase or decrease of the deflexion of .10 cm. could have been easily detected. Therefore the absorption, if it exists, must be less in all the cases examined than 4 per cent. of the whole radiation passing through the tube in a length of 44.5 cm., or less than one-tenth of one per cent. for a length of one centimetre, and we would probably be safe in saying that it must be less than half of this.

The variations which can be observed in the individual deflexions are probably due, in the main, to slight changes of temperature upsetting the balance between the two thermoelectric currents. It was for this reason that, after trying other arrangements, I finally placed the two tubes side by side, bringing the two receivers as close together as possible. As is well known, one of the difficulties in work with short electric waves is to obtain a receiver whose readings will be constant. The present experiment, in which the readings represent very small differences between two readings, presents unusual difficulties.

When the radium was used in the presence of air at different pressures, it was put in three watch-glasses placed at equal distances along the tube, so that it would be in direct contact with the air. In this way its ionizing effect was greatest. About one gram of radium chloride was used, having an activity of about 7000.

Before beginning the experiments on the effect of varying the density of air in the presence of radium, some preliminary experiments were made in the endeavour to detect some effect due to the presence of radium when the air was at

TABLE I.

Air alone.						Water Vapour.		Air in the presence of radium.			
Exp. 1.		Exp. 2.		Exp. 3.		Exp. 4.		Exp. 5.		Exp. 6.	
Pressure.		Pressure.		Pressure.		Pressure.		Pressure.		Pressure.	
Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.	
72.0	.05	75.4	.06	71.3	.09	.300	.19	.036	.11	.192	.30
72.3	.06	6.3	.09	7.25	.11	.152	.15	.031	.12	.145	.30
68.6	.04	3.7	.08	5.15	.10	.143	.14	.025	.12	.123	.20
63.7	.05	2.2	.10	4.05	.07	.128	.15	.021	.13	.112	.25
54.4	.05	1.4	.08	3.10	.10	.117	.15	.0150	.11	.095	.24
43.6	.06	0.8	.09	2.55	.12	.098	.15	.0110	.12	.083	.25
38.4	.05	1.5	.07	1.95	.11	.087	.10	.0065	.12	.066	.24
35.9	.05	7.7	.06	1.05	.11	.080	.09	.0080	.13	.052	.28
30.9	.10	5.7	.06	0.90	.12	.067	.07	.0067	.16	.028	.26
25.5	.06	4.8	.07	0.73	.10	.058	.04	.0057	.13	.0165	.30
21.7	.05	3.8	.09	0.65	.11	.049	.06	.0046	.13	.0130	.29
16.2	.06	2.9	.10	0.55	.13	.043	.07	.0034	.06	.0100	.30
10.2	.06	2.0	.09	0.35	.09	.034	.06	.0026	.03	.0085	.32
7.3	.05	1.6	.09	0.42	.10	.029	.10	.0020	.03	.0080	.30
6.0	.05	1.0	.07	0.22	.11	.021	.07	.0015	.10	.0073	.34
Mean	0.6	Mean	.08	Mean	.12	Mean	.11	Mean	.11	Mean	.29
Exp. 7.		Exp. 8.		Exp. 9.		Exp. 10.					
Pressure.		Pressure.		Pressure.		Pressure.					
Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.		Galvanometer deflexion.					
1.50	.16	70.6	.15	74.1	.10	72.4	.24				
1.20	.16	45.6	.15	.92	.08	.10	.26				
.70	.16	26.7	.13	.74	.11	.038	.32				
.40	.19	19.5	.16	.40	.10	72.5	.33				
.33	.17	7.5	.17	.24	.09	Mean	.29				
.20	.14	3.9	.15	.090	.09						
.10	.17	1.85	.16	Mean	.10						
.065	.17	1.40	.10								
.30	.20	.70	.13								
.015	.20	.44	.18								
Mean	.17	.29	.13								
		.143	.11								
		.120	.10								
		.097	.09								
		.076	.13								
		.060	.12								
		.041	.14								
		.024	.17								
		.0122	.20								
		.0075	.19								
		.090	.15								
		.090	.15								
		72.2	.16								
		73.0	.14								
		Mean	.14								

atmospheric pressure. To this end the plate covering the end of the tube T_2 nearest to the sender S was removed, and the radium in an open glass dish, a crystallizing dish, was alternately put in and taken out of the tube, and the deflexions observed in both cases. No difference in the deflexion for the two cases was found except that which was due to the presence of the glass dish itself. It was found that the dish itself obstructed the waves to a certain extent.

SUMMARY.

The results show that for electric waves about 10 cm. long passing through air at pressures ranging from 76 cm. to .001 cm. of mercury, and through water-vapour at pressures ranging from 1.50 cm. to .015 cm., the absorption of the energy of the waves by the air, if it exists, must be less than one-tenth of one per cent. per centimetre.

This was also found to be true when the air was ionized by radium chloride placed in open vessels within the tube. This would indicate that the ionization of the air by radium produces, if any, only a very small effect upon its absorbing power for electric waves about 10 centimetres long.

In conclusion, I wish to acknowledge the great aid received in this research from a grant from the Bache Fund of the National Academy of Sciences for the purchase of apparatus.

University of Cincinnati,
May 1912.

LXXIII. *The Existence of Uranium Y.*

By ALEXANDER FLECK, *B.Sc.**

THE only direct disintegration product of uranium that is actually known is uranium X, but Antonoff† described some experiments which, he thinks, show the existence of a new substance. As it is present in exceptionally small quantities he concludes that it is a branch product whose parent is uranium. The work, of which a short description is given below, was undertaken to attempt to confirm the existence of this new body.

Uranyl nitrate, which was known to have contained thorium but which was thought to have been purified by treating twice with excess of ammonium carbonate, was employed to repeat Antonoff's experiments as nearly as

* Communicated by F. Soddy, F.R.S.

† Antonoff, *Phil. Mag.* [6] xxii. p. 431 (1911).

possible. It was not possible to repeat his experiments by what he called the "ferric method," which consisted in boiling a uranium solution which contained a small quantity of an iron salt. According to Antonoff the iron should be precipitated as hydroxide and should contain uranium X and the new substance, uranium Y.

If, however, uranium X was removed with iron* by boiling a solution, in excess of ammonium carbonate, of uranium containing iron, the product when measured in an electroscope with a 0.0034 mm. thick aluminium base gave an effect very similar to the one described by Antonoff. When measured in an electroscope with a 0.1 mm. thick aluminium base, the activity of this product decayed normally with the period of uranium X. Attempts were now directed to obtaining this quickly decaying substance free from uranium X, and it was found that by precipitating lead as lead sulphide in an acid solution of the active product of the ammonium carbonate treatment, the precipitate contained active material which, on examination, was shown to be thorium B. When the iron in the filtrate was reprecipitated as carbonate, it contained uranium X which decayed normally.

Efforts were made to purify the uranium salt from thorium (a) by shaking the uranium containing water of crystallization with ether and separating the aqueous from the ethereal layer, (b) by precipitating with dilute oxalic acid and allowing to stand overnight, and (c) by precipitating with ammonium sulphide and shaking the precipitate with dilute hydrochloric acid. After these various methods of treatment and allowing time for any quantity of thorium X which had collected to decay, the presence of thorium B could still be detected, although of course in much smaller amount.

After this, uranyl nitrate which had been separated by Soddy† from uranium X, and therefore from any thorium initially present, and which had been through the ammonium carbonate treatment many times, was used, and no rapid initial decay in the uranium X preparation was observed.

An attempt was then made to concentrate the substance by an experiment which does not seem to have been made by Antonoff. According to him, uranium Y is precipitated in ferric carbonate but not in barium sulphate. If, then, we have uranium X and Y in ferric carbonate, dissolve both in dilute acid, add a trace of barium and precipitate that with sulphuric acid, then, all the uranium X, in the absence

* Crookes, *Proc. Roy. Soc.* lxi. p. 409 (1900).

† Soddy, *Phil. Mag.* [6] xviii. p. 858 (1909).

of thorium, will be adsorbed * in the barium sulphate, whilst the uranium Y will be left in solution. If it exists it ought to be obtained in a pure condition on reprecipitating the iron as carbonate. When this was done, only a small residual activity due to uranium X was obtained, and no trace whatever was found of any substance producing either soft β or α rays whose period was 1.5 days.

These experiments were repeated many times under varying conditions, but never was anything observed which would lead to the conclusion that a short period body existed whose parent was either uranium 1 or 2.

Conclusion.

All attempts to confirm the existence of the substance called uranium Y were unsuccessful.

I wish to take this opportunity of thanking Mr. F. Soddy, F.R.S., for his interest and advice throughout the course of the work.

Physical Chemistry Department,
Glasgow University.
March, 1913.

LXXIV. *The Growth of Radiothorium from Mesothorium 2.* *By JOHN A. CRANSTON, B.Sc., Robert Donaldson Scholar †.*

THE object of this research was to establish whether or not there exists an intermediate body between mesothorium 2 and radiothorium ‡. Additional interest is lent by the fact that radiothorium corresponds with ionium, the parent of which is experimentally unknown. The growth of α activity from a quantity of pure mesothorium 2 was observed.

A theoretical curve for this was calculated, making the following assumptions :—

- (1) That mesothorium 2 gives no α rays.
- (2) That mesothorium 2 disintegrates directly into radiothorium.
- (3) That during the course of the experiment (1 month) the amount of radiothorium present does not decrease appreciably by its own disintegration.
- (4) That thorium X, thorium emanation, and thorium A disintegrate together.
- (5) That thorium B and thorium C disintegrate together.

* Fleck, Journ. Chem. Soc. 103. p. 381 (1913).

† Communicated by F. Soddy, M.A., F.R.S.

‡ Hahn, *Phys. Zeit.* ix. p. 246 (1908).

The percentage of the total ionization due to one α ray of each of the series was calculated from Geiger's * formula, the figures being corrected for the magnet electroscope used—the equivalent of 1.5 cm. of air being subtracted from the range.

At a distance x along the range, the ionization i is

$$i = a(R - x)^{\frac{1}{2}}$$

where a is a constant.

Then

$$I_{1.5}^R = k(R - 1.5)^{\frac{3}{2}}.$$

This gives for the series :—

RaTh	14.2	} 58.3
ThX	16.5	
ThEm	19.6	
ThA	22.2	
ThC	6.0	} 27.5
ThC'	21.5	

The α radiation is thus proportional to

$$14.2\lambda_2 B + 58.3\lambda_3 C + 27.5\lambda_5 E,$$

where B , C , and E are the amounts, and λ_2 , λ_3 , and λ_5 are the radioactive constants of RaTh, ThX, and ThC respectively. By calculating the amount of B , C , and E present at any time in terms of their exponential functions we get the ionization given by

$$I = k[57.6 - 7.6e^{-\lambda_1 t} - 55.6e^{-\lambda_3 t} + 5.6e^{-\lambda_4 t}],$$

where k is a constant and λ_1 , λ_3 , and λ_4 the radioactive constants of MesoTh 2, ThX, and ThB respectively.

The mesothorium 2 was obtained in the following manner :—The chemical methods were worked on the basis of its analogy to actinium †. To a solution containing mesothorium 1 associated with about 100 gms. of barium chloride a few drops of thorium nitrate were added in acid solution and the thorium precipitated out again by ammonia. This brought down the mesothorium 2, the radiothorium, and the thorium B and C present. The thorium and the radiothorium were removed by dissolving the precipitate in the smallest quantity of acid, neutralizing, and adding

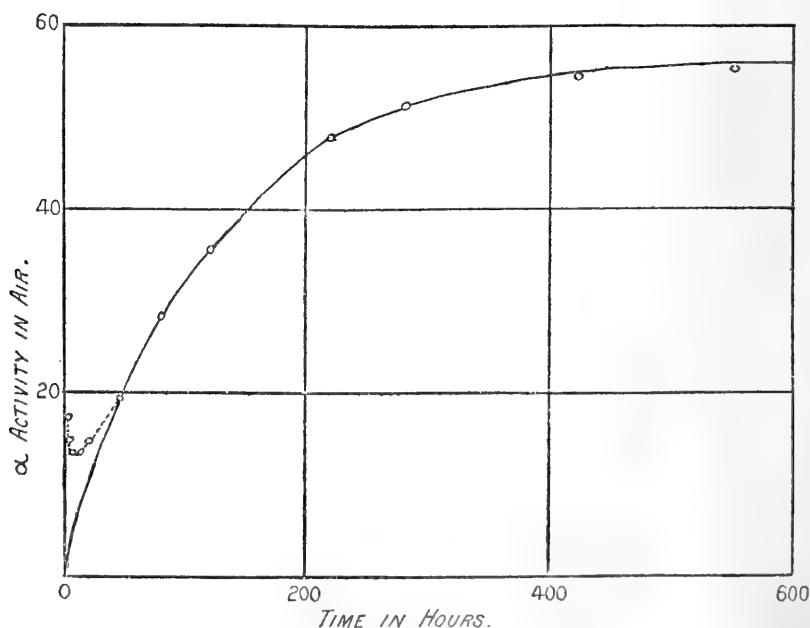
* Proc. Roy. Soc. A. lxxxiii. p. 513 (1910).

† Fleck, Trans. Chem. Soc. ciii. p. 381 (1913).

hydrogen peroxide. The value of various reagents in effecting this separation was found as follows :—

Reagent.	Percentage of Mesothorium 2 separated.
Ammonia	16
Methylamine	11
m-Nitro-benzoic Acid . . .	100
Ammon. Hydrazoate . . .	74
Hydrogen Peroxide	100

The hydrogen peroxide removes most of the ThB and part of the ThC, but the last traces of these were removed by adding lead and bismuth and precipitating out with H_2S several times. The filtrate was then evaporated down to dryness and the ammonium salts ignited, leaving on a silver tray a film of pure mesothorium 2. This tray was placed between the poles of an electromagnet above which was an electroscope. The brass base of the electroscope had a slot cut out of it the size of the tray (7.7 cm. \times 1.4 cm.). A sheet of aluminium foil (thickness .00035 cm.) covered the slot. The electroscope was provided with a mica screen which could be slipped over the slot so as to absorb all the α rays without appreciably affecting the β or γ activity. The difference between two measurements made, one with the mica off and one with the mica on (both being made with the magnet on to deflect the β rays) gave the α activity.



The variation of the α activity with time is shown in the figure, experimental points being indicated by the circles.

The scale of the α activities was chosen so that the experimental point 220 hours from the start lay on the theoretical curve. It will be seen that, while the curves do not agree for the first few hours, the subsequent close agreement establishes the fact of the direct growth of radiothorium from the mesothorium 2.

Earlier experiments showing a greater initial drop in the activity were shown by the absorption-curves to be due largely to ThB and ThC present. Further observations were made of the activity during the first few hours after precipitation, when the electroscope was filled with hydrogen. This minimized the effect of the large quantity of β and γ rays present, and increased the effect of the small α present. The curve obtained showed an initial activity relatively slightly less than that obtained in air, but was otherwise similar.

The difference-curve being approximately an exponential curve with the period of mesothorium 2, suggests the possibility of some of the atoms of mesothorium 2 disintegrating with the emission of an α ray. The number of these, however, must be very small, and is shown by these curves to be less than 3 in 10,000. Owing to the similarity of period of mesothorium 2 and thorium B, it is difficult to make quite sure that the initial decay of the α rays occurs with the same period as that of mesothorium 2, and the point is left open for further examination.

I desire to thank Mr. F. Soddy, M.A., F.R.S., for suggesting this research, for the interest he has shown in it, and for the use of materials employed in carrying it out.

Physical Chemistry Laboratory,
Glasgow University.

LXXV. *The Relative Visibility of the Different Colours of the Spectrum. Being a Report of a Committee on that subject appointed by the Physical Society of Glasgow University**.
By R. A. HOUSTOUN, Ph.D.†

IT is well known that light in the middle of the spectrum is much brighter than light at the ends for the same intensity of radiation in ergs/sq.cm.sec. The brightness of

* The Physical Society of Glasgow University is a students' society. The experiments described in the above paper were taken up by a committee, and the work was done by the following:—Miss Margt. B. Moir, M.A., B.Sc., and Messrs. A. R. Brown, M.A., B.Sc., John Brown, M.A., B.Sc., F. F. S. Bryson, M.A., and A. S. Morrison, M.A., B.Sc.

† Communicated by Dr. R. A. Houstoun.

any part of the spectrum in candles/sq.cm. divided by the intensity of radiation in ergs/sq.cm.sec. may be defined as the visibility of that part. To determine the relative visibility of the different parts of the spectrum we must determine the luminosity curve of the spectrum, and the distribution of energy throughout it. This paper * describes the first determination that has been made of the relative visibility of light of different colours to the average human eye. Previous observers have contented themselves with luminosity curves alone, without specifying the distribution of energy in the spectrum (Sir Wm. Abney), or if all the data have been given, it is only for one observer (Prof. A. König's results reduced by P. G. Nutting†). The relative visibility of the different colours of the spectrum is of course important with reference to heterochromatic photometry and the definition of light‡.

The number of people who made complete tests was 52, most of whom were honours students in physics. The experimental work fell into two parts: (1) the taking of the luminosity curves for each person tested, and (2) the determination of the distribution of energy in the spectrum, which had only to be done once for all.

A considerable time was spent choosing an apparatus for taking the luminosity curves. Abney's well-known method was experimented with and rejected, because it is very wasteful of light, and requires an arc or Nernst filament as source, and these sources were not considered constant enough for a long series of tests such as was contemplated. Then a spectroscope was employed with its eyepiece removed and an aperture substituted. The eye of the observer looking in then saw a face of the prism illuminated in monochromatic light; the lower part of the prism was covered with a white card illuminated from the side, and the intensities of the card and prism were matched by altering the width of the slit. This method was tried also with a Thorp diffraction grating instead of a prism, but was rejected owing to its not being accurate enough. Finally, the following original method was employed and satisfied all requirements:—

A Hilger constant deviation spectroscope was taken, and two little total reflecting prisms were mounted in the eye-

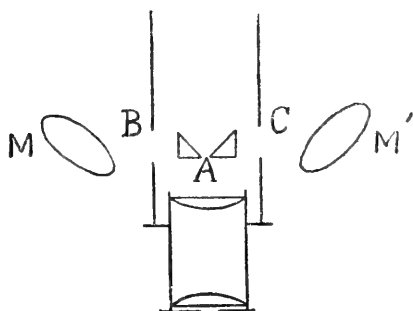
* Since this paper was written a series of articles by Mr. H. E. Ives with the same purpose has appeared in the *Phil. Mag.* This and the following sentence are consequently not true.

† *Bull. Bureau of Standards*, vii. p. 238 (1911).

‡ R. A. Houstoun, *Proc. Roy. Soc. A*, lxxv. p. 275 (1911).

piece, as shown in the figure (fig. 1). The edges A were ground extremely sharp, and were slightly less than $\frac{1}{10}$ mm. apart.

Fig. 1.



B and C are holes in the tube, and opposite these holes were little plane mirrors with universal motion, which reflected on to the prisms the rays from a white comparison surface situated above and beyond the spectroscope prism. The eyepiece was focussed on the two edges. An eye looking into the eyepiece saw, therefore, a strip of spectrum bounded sharply on each side by white surfaces. The luminosity of the strip of spectrum was measured by closing the slit until it was equally bright with the two white patches on each side of it. The strip of spectrum subtended at the eye an angular height of about 9° and a breadth of about 1° .

The spectroscope prism was covered with a cardboard case to keep out stray light, and the slit supplied with the instrument was replaced by a better quality micrometer one. Also it was found necessary to insert screens in the telescope and collimator tubes to stop reflexion at grazing incidence from the sides of these tubes; this was at first a source of trouble when work was done at the ends of the spectrum.

For sources of light two 125 volt, 16 candle-power, carbon glow-lamps were taken. They were run in parallel off storage-cells, and the voltage was always checked before every test. One of these lamps, which we shall call A, was enclosed in a box with a ground-glass window immediately in front of the spectroscope slit; the other, lamp B, was used for illuminating the white comparison surface, and was placed in a gauze screen 92 or 155 cm. behind the latter.

The luminosity curves obtained were those of lamp A as modified by the spectroscope employed. Under this modification is included the different absorption undergone by the different colours of the spectrum in passing through the glass of the instrument, and also the different extension of the

various parts of the spectrum, because the latter of course was not a normal one.

The lamp A was compared with a Hefner lamp at its normal voltage by means of a spectrophotometer, and the final results are expressed in the second column of the following table. This column gives ratio of lamp A to Hefner lamp, and we see that lamp A is stronger at the blue end. The distribution of energy in the spectrum of the Hefner lamp has been determined by K. Ångström*, and he has represented his results by the formula

$$\lambda^{-5} e^{-\frac{7.85}{\lambda}},$$

where λ is measured in μ . This function is given in the third column of the table. On multiplying the second and third columns we get the original distribution of energy in the spectrum of lamp A. To allow for the different absorption of light in the spectroscope the slit and eyepiece of the latter were removed, and a beam of light which passed through the spectroscope and an additional lens and ground glass was compared by the spectrophotometer with another beam from the same source, which was twice reflected by mirrors, and passed through a similar ground glass. The results are shown in the fourth column. The figures are proportional to the percentage transmitted, and they show that the blue end of the spectrum is absorbed to a greater degree than the red end. The figures in the fourth column are of course not quite beyond question, as the one beam went through an additional lens instead of the eyepiece, and the other beam was probably slightly affected by the two mirrors, but there was no other way of measuring this quantity, and the absorption almost all takes place in the prism. It should be noticed that it is only the relative values, not the absolute values of the figures in the second, third, and fourth columns that have any meaning.

To allow for the spectrum being prismatic we have to make the "slit-width" correction, *i. e.*, multiply the distribution of energy by $\frac{d\lambda}{ds}$, which gives the inclination of the tangent to the calibration curve of the spectroscope. The spectroscope was one of the earlier ones not furnished with a wave-length scale, and s was the reading of the prism drum in hundredths of a revolution. The fifth column gives $\frac{d\lambda}{ds}$, and the sixth column gives the product of the

* Phys. Rev. xvii. p. 312 (1903).

second, third, fourth, and fifth columns, that is, the distribution of the energy in the spectrum as seen through the eyepiece of the spectroscope.

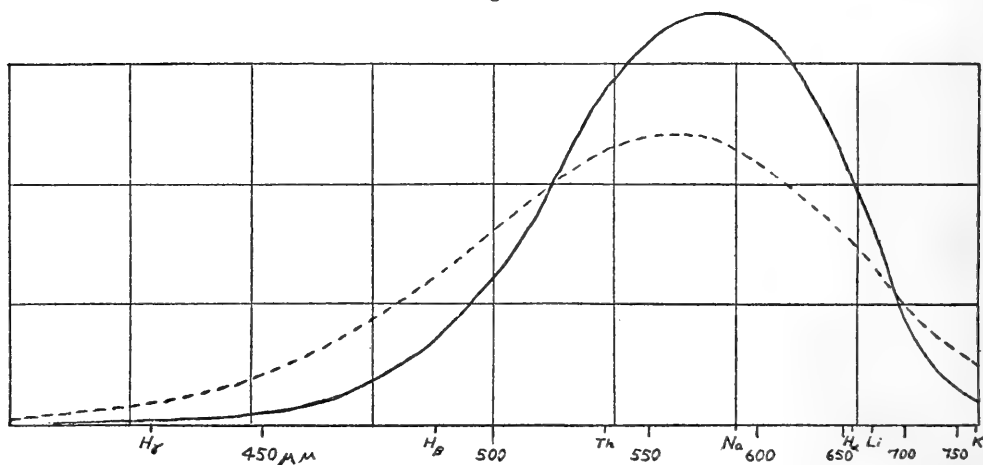
470 $\mu\mu$	2.08	2.57	1.58	.44	3.74
490	1.87	4.17	1.63	.57	7.27
530	1.67	9.33	1.80	.80	22.4
570	1.59	18.2	1.98	1.00	57.3
610	1.50	30.9	2.03	1.14	107
650	1.46	51.3	2.15	1.33	215

In order to measure the influence of the Purkinje effect luminosity curves were taken at two intensities for every observer. The procedure on making a test was as follows. First of all the gentleman supervising the test saw that the voltage on the two lamps was right, that the instrument was in adjustment, that the lamp B was in the first standard position 92 cm. from the white comparison surface, and that the lamp A was in its box in a standard position near the ground glass. The intensity of the illumination falling on the eye was then about one half metre-candle. The slit was then set in succession at four standard widths, and for each of these widths, on each side of the brightest part of the spectrum, wave-lengths were sought for which the intensity of the spectrum matched the intensity of the white surfaces. Thus eight points were obtained on the luminosity curve. Then for a wave-length midway between the middle points already obtained the width of the slit was diminished until the intensities matched, and an additional point thus obtained. This whole procedure was then repeated twice for two other positions of the lamps A and B, for which the intensity of illumination was $\frac{1}{600}$ metre-candle, and finally was repeated a fourth time for the original intensity, so that in all four luminosity curves were obtained each with nine points on it, two for a strong intensity and two for a weak intensity. At the end of every test the position of the sodium line was read. The observations were entered on cyclo-styled sheets and the curves plotted to a standard scale, strong intensity in black and weak intensity in red. The complete set of readings took three hours or more.

In order to get the average luminosity curves the mean of each observer's two "strong" and the mean of each

observer's two "weak" curves was taken, and the reciprocal of slit-width plotted against s , the drum reading. This gave two prismatic luminosity curves for each observer. These curves were integrated and then replotted, with their ordinates shortened or lengthened, so as to make their areas the same. This was done so that they would all contribute in the same degree to the average. The average of all the strong intensity curves and of all the weak intensity curves was then taken, and they are shown in the following diagram (fig. 2):—

Fig. 2.



The full curve is for the illumination of $\frac{1}{2}$ and the broken curve for the illumination of $\frac{1}{6.00}$ metre-candle.

The diameter of the pupil of the eyepiece was 7 mm.

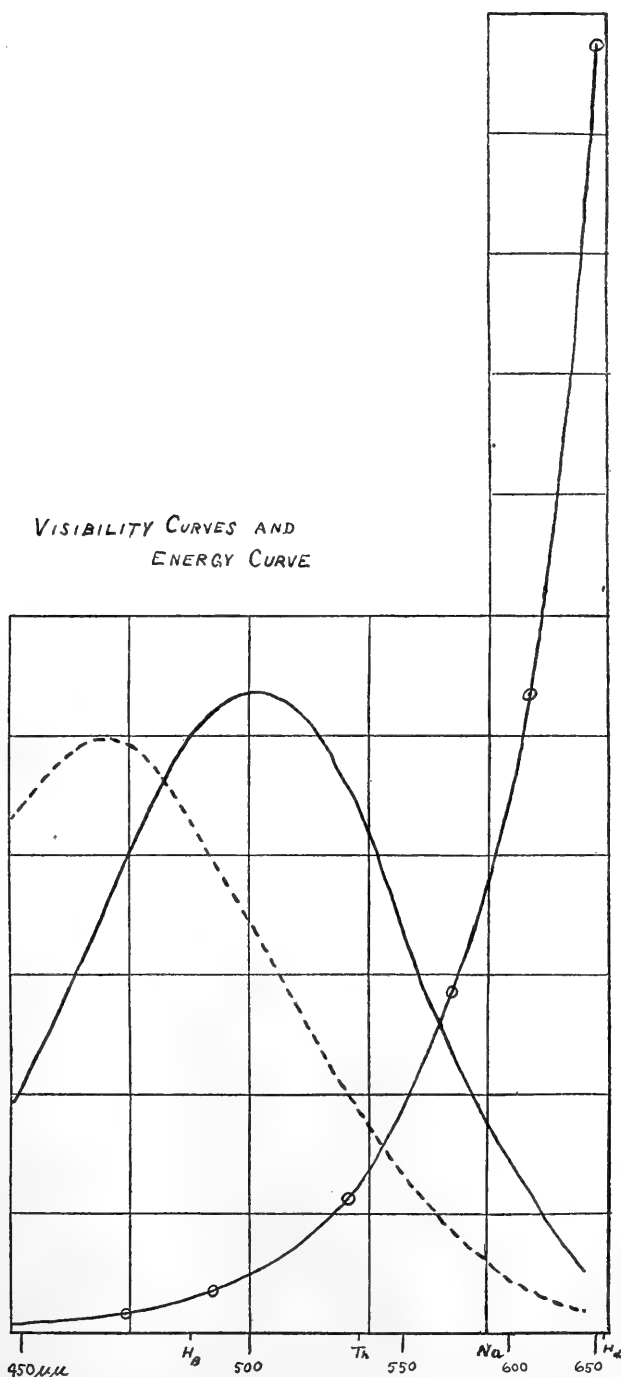
The extreme red is not given, as it was found in the course of the tests that the readings on the drum were not reliable for that part of the spectrum, owing to the spring for rotating the prism becoming slack there. The maxima of the curves are situated at 576 and 560 $\mu\mu$.

The sixth column of the preceding table was then plotted as a function of s , the drum reading, and the ordinates of the energy curve thus formed divided into the corresponding ordinates of the two luminosity curves. The result gave the two visibility curves shown in the next diagram (fig. 3). To determine the shape of these curves was the purpose of the investigation.

The broken curve is for the weaker intensity, and is plotted only on half the scale of the stronger intensity curve. The maxima for both curves was further towards the violet than had been anticipated, and the energy curve had to be extrapolated in the violet. However, extrapolation gives as great

accuracy in this region as measurements would give, because it was found impossible to get figures for the second and fourth columns of the preceding table for this region.

Fig. 3.



According to our results, then, at an illumination of $\frac{1}{2}$ metre-candle, the maximum visibility is at 502 $\mu\mu$, and at

an illumination of $\frac{1}{600}$ metre-candle the maximum visibility is at 466 $\mu\mu$.

Three hours was not long enough to obtain regular luminosity curves from one observer. Hence, although the mean was certainly accurate for the average eye, the individual curves were only approximate for the individual eyes.

All the observers tested had normal colour vision. Two had the shape and position of the "strong" and "weak" luminosity curves exactly the same. This is supposed to denote no rod vision. The women students tested, of whom there were nine, showed no systematic difference from the men.

LXXVI. *The Analysis of the Gamma Rays from Radium B and Radium C.* By PROFESSOR E. RUTHERFORD, F.R.S., and H. RICHARDSON, B.Sc., Graduate Scholar, University of Manchester*.

IT has long been recognized that the penetrating γ rays emitted by a γ ray salt were complex in character. The examination of the radiation has been made by the electric method in two ways :

(1) by measuring the absorption of the γ rays in different materials over a wide range of thickness ;

(2) by an examination of the absorption of the secondary and scattered γ rays which appear when γ rays traverse matter.

Initial experiments on the absorption of the γ rays of radium by different materials were made by Rutherford† and McClelland‡. These were extended by later investigations of Eve§, Tuomikoski||, Wigger¶, and S. J. Allan**. The experiments showed that the absorption of the γ rays in lead rapidly decreased for the first two centimetres of thickness, but became approximately exponential for greater thicknesses. The whole question was re-examined with great detail and thoroughness by Mr. and Mrs. Soddy and A. S. Russell††, who determined the absorption of the

* Communicated by the Authors.

† Rutherford, *Phys. Zeits.* iii. p. 517 (1902).

‡ McClelland, *Phil. Mag.* viii. p. 67 (1904).

§ Eve, *Phil. Mag.* xvi. p. 224 (1908) ; xviii. p. 275 (1909).

|| Tuomikoski, *Phys. Zeit.* x. p. 372 (1909).

¶ Wigger, *Jahrb. Radioakt.* ii. p. 430 (1905).

** Allan, *Phys. Rev.* xxxiv. p. 311 (1912).

†† Soddy and Russell, *Phil. Mag.* xviii. p. 620 (1909) ; Mr. and Mrs. Soddy and Russell, *Phil. Mag.* xix. p. 725 (1910) ; Russell, *Proc. Roy. Soc. A.* lxxxvi. p. 240 (1911).

γ rays in a number of materials and investigated the effect of different arrangements on the apparent value of the absorption coefficient. They found that the absorption of the γ rays by lead was accurately exponential for a very wide thickness, viz. from 2 to 22 cm., and concluded that over this range of thickness the γ rays were to be considered as homogeneous in type. These results were confirmed and extended by Russell, who showed that the γ rays from radium were absorbed by mercury over a range of thickness from 1 to 22.5 cm. strictly according to an exponential law. Over this range of thickness the intensity of the ionization current in the testing vessel, which served as a measure of the intensity of the γ rays, varied in the ratio of 360,000 to 1.

From an examination of the quality of the secondary γ rays set up in different materials by the γ rays, Kleeman* considered that the primary γ rays from radium could be divided into three types of widely different penetrating power. In similar experiments Madsen† found evidence of two types. On the other hand, Florance‡, who examined the character and intensity of the secondary and scattered γ rays from radiations of different materials at various angles for the primary beam, concluded that the γ rays were very complex in character and that no definite evidence could be obtained by this method of the existence of distinct groups of primary rays.

It was at first supposed that the penetrating γ rays emitted by a radium salt arose entirely from the transformation of its product radium C. Moseley and Makower§, however, showed in 1912 that radium B also emitted γ rays, although weak in intensity and penetrating power compared with those emitted from radium C. Even if radium C emitted only one type of radiation, it was clear from this result that the γ rays from a radium salt must contain at least two types of γ rays. In the meantime, the work of Barkla on X rays had shown conclusively that each of the elements emitted one or more types of characteristic or fluorescent radiations when X rays of suitable penetrating power traversed them. In some of the elements two types of characteristic radiations were observed. J. A. Gray|| extended these results to γ rays, for he found that the γ rays emitted by radium E were able to excite the characteristic

* Kleeman, *Phil. Mag.* xv. p. 638 (1908).

† Madsen, *Phil. Mag.* xvii. p. 423 (1909).

‡ Florance, *Phil. Mag.* xx. p. 921 (1910).

§ Moseley and Makower, *Phil. Mag.* xxiii. p. 312 (1912).

|| Gray, *Proc. Roy. Soc. A.* lxxxvii. p. 489 (1912).

radiations of certain elements. His results showed, as had long been supposed, that the γ rays were identical in general properties with X rays and possessed the fundamental property of exciting characteristic γ rays. In a paper entitled "The origin of β and γ rays from radioactive substances," Rutherford* put forward the view that the γ rays from radioactive substances were to be regarded as the characteristic radiations of the respective elements set up by the escape of α or β rays from them. On this basis an explanation was given of the numerous groups of homogeneous β rays emitted by radium B and C, and their connexion with the γ rays was outlined. If this were the case, each type of characteristic radiation emitted should be absorbed according to an exponential law by an absorbing substance of low atomic weight like aluminium.

The present experiments were undertaken with a view of testing this hypothesis. It will be seen that this analysis brings out that the γ radiation from radium B consists of at least two and possibly of three distinct types, and from radium C of a single type, probably corresponding in penetrating power to the characteristic radiations to be expected from elements of their atomic weight.

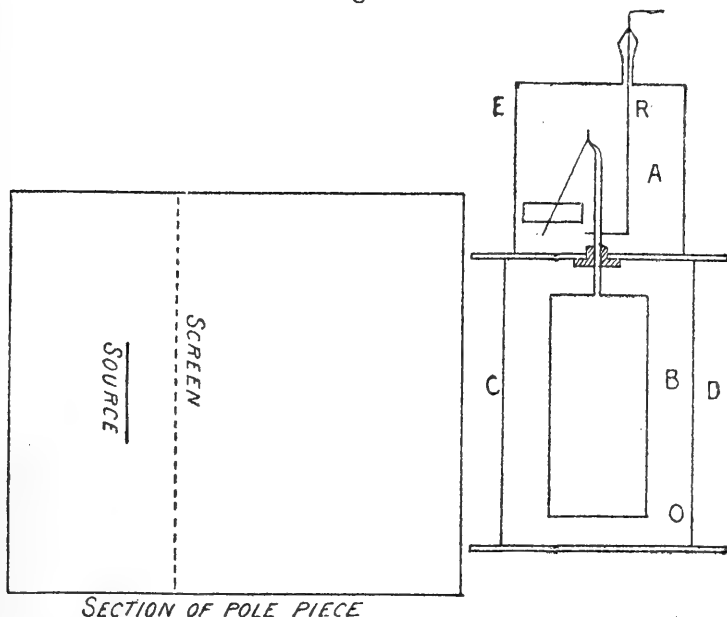
Experimental Arrangement.

In the preliminary investigations the source of γ rays consisted of about 50 millicuries of radium emanation enclosed in an α ray tube with thin walls. The thickness of glass was equal in stopping power for α rays to about 2 cm. of air. In order to get rid of the effect of the primary β rays, the source was placed between the pole-pieces of a powerful electromagnet. The γ rays passed horizontally into a thin-walled ionization vessel ($3 \times 5 \times 7$ cm.) CD, fig. 1, placed at the side of the electromagnet, in which the ionization was measured in the usual way by means of an exhausted electroscope E of dimensions $5 \times 5 \times 5$ cm. The ionization produced by the γ rays in the electroscope E was negligibly small compared with that produced in the ionization vessel CD. The sides of the vessel CD, through which the γ rays passed, consisted of thin sheets of mica equivalent in stopping-power for the α particles to about 2 cm. of air. This was done in order to increase relatively the ionization due to the softer γ rays that might be present. The inside of the vessel was lined throughout with aluminium. In most experiments the pole-pieces of the electromagnet were about 2 cm. apart.

* Rutherford, Phil. Mag. Oct. 1912.

The source of γ rays was in all cases more than 9 cm. distant from the vessel CD. The absorbing metal screens were placed between the pole-pieces of the magnet close to the source. The β rays escaping from the absorbing material

Fig. 1.



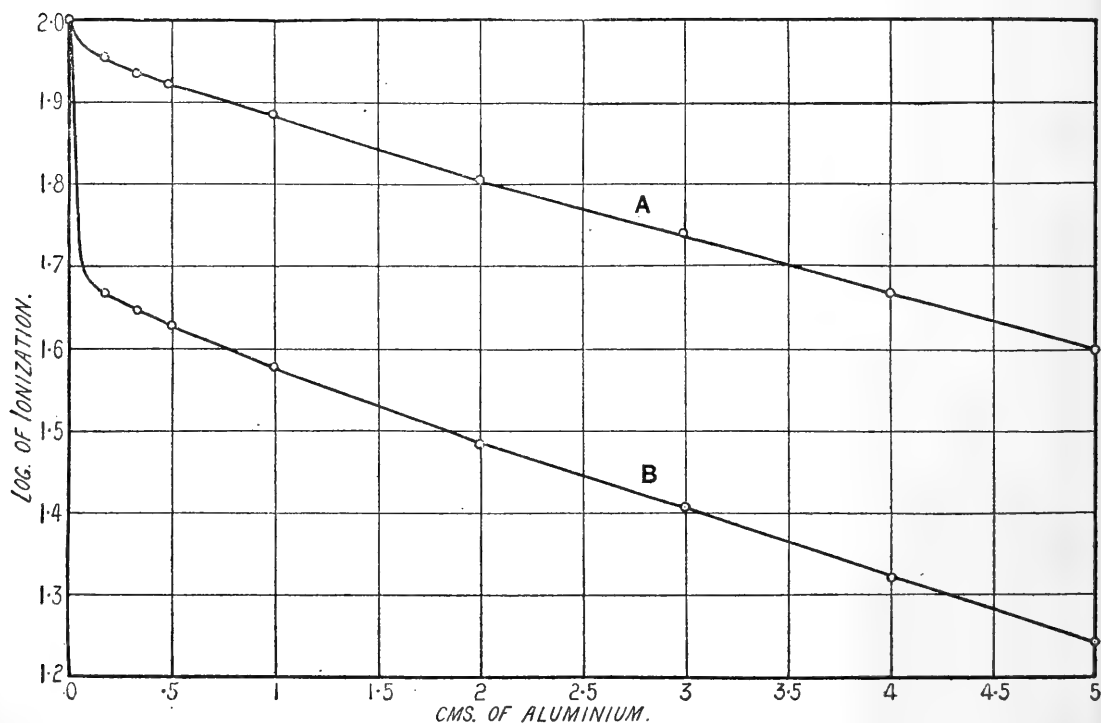
were removed by the magnetic field before entering the ionization vessel. The γ rays which entered the ionization vessel passed nearly normally through the absorbing screens, so that no correction for obliquity was necessary in determining the absorption coefficient of the rays.

Preliminary experiments showed that if the ionization vessel were filled with air, the effect of the penetrating γ rays from radium C was large compared with that due to the softer types of radiation that were present. When air was used, the reduction of the ionization by using absorbing screens of aluminium of different thicknesses is shown in fig. 2 A (p. 726), where the logarithms of the ionization are plotted as ordinates and the thickness of aluminium as abscissæ. It will be observed that in this case there is a rapid drop of the ionization corresponding to about 10 per cent. of the whole effect.

In order to bring out prominently the effect of the softer types of γ radiation present, the vapour of methyl iodide was used instead of air. As it was impossible to exhaust the ionization vessel on account of the thin mica covering of

the sides, the vapour was introduced by means of a slow current of hydrogen which bubbled through the liquid. Under these conditions, the ionization vessel was filled with a mixture of hydrogen and vapour of methyl iodide at atmospheric pressure. The ionization in the vessel was almost entirely due to the methyl iodide, and for the hard γ rays from radium C was usually about three times as great as for air at atmospheric pressure. Some difficulty was at first experienced on account of the absorption of the vapour by the wax used in fixing the mica plates and in sealing the

Fig. 2.



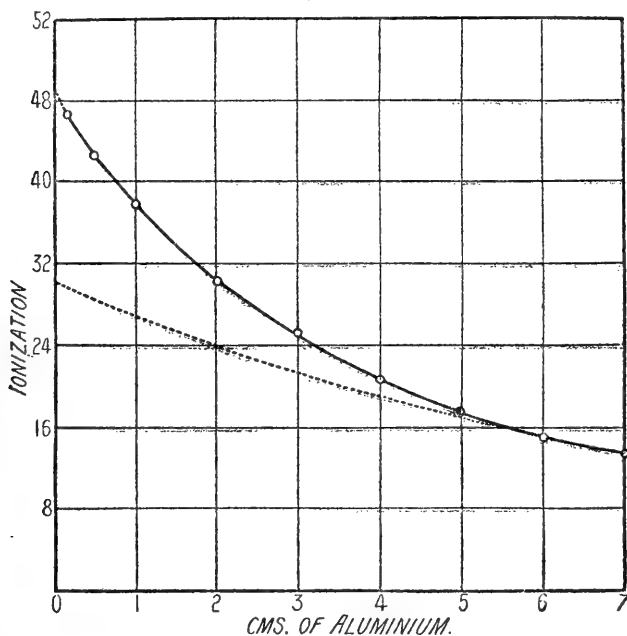
various parts of the vessel. This effect was got rid of by reducing the amount of wax to a minimum, and covering it with a non-absorbing layer of gum. This was kindly prepared for us by Dr. Lapworth, F.R.S., by special treatment of the ordinary gum sold commercially. By this method the absorption of the vapour was so much reduced that measurements extending over several hours could be made with certainty and accuracy.

The absorption curve using methyl iodide instead of air is shown in fig. 2 B. An absorbing screen of 1.6 mm. of aluminium reduced the ionization to about 50 per cent. It will also be seen that the latter part of the absorption curves A and B are not linear and are not parallel to one another.

This will be shown to be due to the fact that two penetrating types of radiation are present, the relative ionizations of which differ in air and in methyl iodide.

After passing through about 6 cm. of air, the absorption curves, both for air and methyl iodide, became exponential with a value of the absorption coefficient $\mu=0.115$, or $\mu/D=0.0424$, where D is the density. This is practically identical with the absorption coefficient found by Russell and Soddy for the γ rays from radium C after passing through 2 cm. of lead. The absorption curve of the γ rays for thicknesses of aluminium between .05 and 7 cm. is shown in fig. 3, where the ionization itself is plotted as ordinates.

Fig. 3.

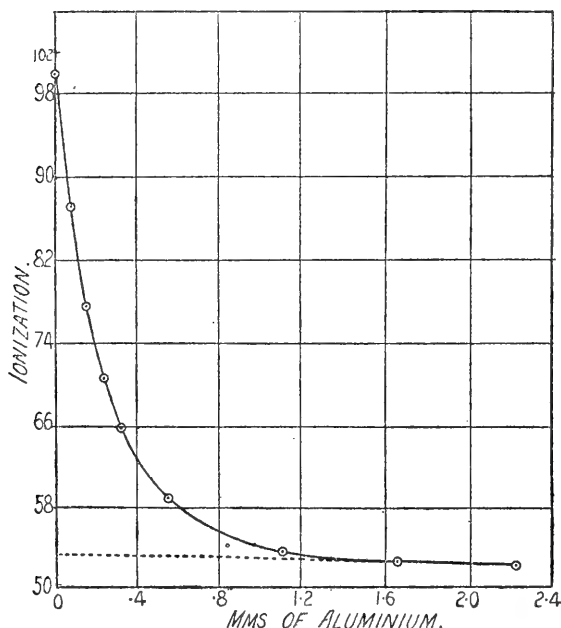


After 6 cm. of aluminium the curve is exponential with a value of $\mu=.115$. It will be shown later that the absorption curve in aluminium of the γ rays from radium C is practically exponential from the beginning with a value of $\mu=0.115$. Consequently, if the curve is produced backwards from a thickness of 6 cm. corresponding to radiations for which $\mu=.115$, it gives the ionization due to the γ rays from radium C alone. This is shown in the dotted curve fig. 3. If the difference between the ordinates of these curves be plotted, it is found to be an exponential curve with a value of $\mu=0.51$ in aluminium. This radiation is undoubtedly due to radium B. A similar result was obtained when air was used instead of methyl iodide, but the effect due to this radiation is relatively smaller compared with that from radium C.

Analysis of the soft radiation.

In order to find the absorption coefficient of the very soft radiation, which is shown so prominently in fig. 2 B, sheets of aluminium $\cdot 042$ and $\cdot 084$ mm. thick were used. The curve obtained is shown in fig. 4. In deducing the ionization due to these soft rays, it is necessary to subtract the

Fig. 4.
Absorption of γ rays from radium B+C. Initial portion of curve $\lambda=40$.



ionization due to the harder rays. This can easily be done since the absorption of the harder rays over the thickness of 1.51 mm. of aluminium is practically linear. The difference curve is exponential and gives an absorption coefficient in aluminium $\mu=40$. The source of γ rays in this case was about 15 cm. from the ionization chamber. In these experiments, the pole-pieces were covered with thick cardboard in order to reduce the excitation of secondary γ rays to a minimum. With the bare pole-pieces close together, the radiation entering the ionization vessel was distinctly softer with a value of μ between 40 and 45.

Attempts to detect very soft γ radiation.

Special experiments were made to examine whether radium B or radium C emitted any very soft types of γ radiation in addition to the type already discussed for which $\mu=40$. In the experiments with the emanation tube, the γ rays before entering the ionization vessel passed through

absorbing material equivalent in amount to about 14 cm. of air. Any very soft type of γ radiation which might be present would be largely absorbed in traversing this material. It is essential, however, in the experiments to use sufficient absorbing material to stop completely the α rays from radium C, which have a range of 7 cm. in air. Since it is well known that, for equal masses, X rays pass with much less absorption through elements of small atomic weight, arrangements were made to absorb the α rays mainly by hydrogen and carbon. The source of radiation was the active deposit of radium deposited from the emanation on both sides of a very thin mica plate. This was placed in a brass vessel which was closed at one end by a thin mica plate equal in stopping power to 1.5 cm. of air. This mica plate also formed one side of the ionization chamber, shown in fig. 1. The active matter was deposited on mica to avoid the excitation of detectable characteristic X rays. For a similar reason, the inside of the brass vessel was lined entirely with thick cardboard. A continuous current of hydrogen was sent through the brass vessel. Sheets of india-paper were interposed in the path of the rays of just sufficient thickness to stop entirely the α rays. The ionization in the detecting vessel filled with methyl iodide was then carefully examined when thin aluminium screens were introduced. It was found that the ionization at first decreased more rapidly than corresponded to an exponential law of absorption of the radiation for which $\mu=40$ in aluminium. This initial drop could be accounted for by assuming the presence of a very soft γ radiation for which $\mu=230$ about in aluminium. Since the ionization in methyl iodide due to this radiation corresponded to only 10 per cent. of the total effect, the initial slope of the curve could not be determined with much certainty. It is difficult to decide whether this soft radiation has an independent existence, or whether it is due to an initial drop in the absorption curve of the radiation corresponding to $\mu=40$. It will be seen later that a rapid initial drop of the absorption curve is always observed when lead is used as an absorbing material. It is possible that aluminium may show a similar effect for a comparatively soft radiation.

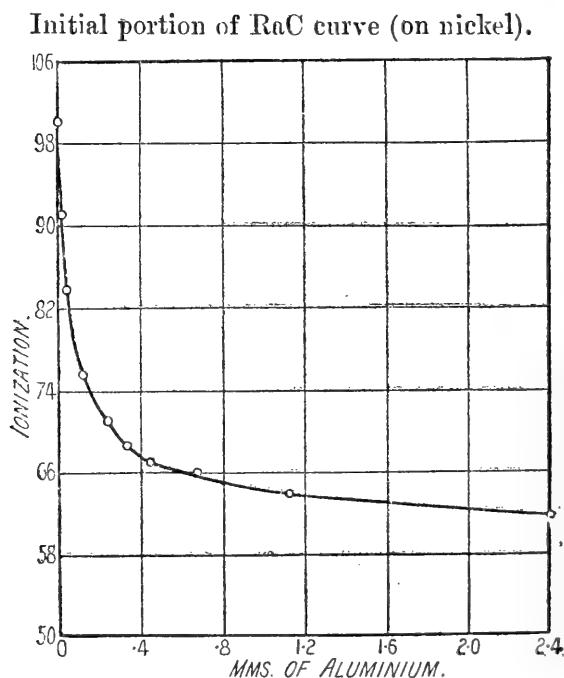
From the rate of decay of this very soft radiation it was clear that it arose from radium B. It was always proportional in amount to the radiation $\mu=40$. It should be pointed out that decay of the active deposit measured under these experimental conditions is initially far more rapid than that calculated by Moseley and Makower (*loc. cit.*). This is

due to the fact that radium B initially provides about 70 per cent. of the total ionization due to radium B + C instead of the 12 per cent. observed by Moseley and Makower under their experimental conditions with air in the testing vessel.

Analysis of the rays from radium C.

Experiments were next made to settle which of the types of γ radiation were to be ascribed to radium B and which to radium C. It is not convenient to use radium B itself as a source, as there is a rapid growth of radium C from it. By von Lerch's method, however, it is possible to obtain a strong deposit of pure radium C on a metal plate placed in an acid solution of the active deposit radium B + C. Since radium C loses half its activity in 19.7 minutes, a large number of experiments were necessary to determine with accuracy the absorption curves for the γ rays emitted from it. The type of curve obtained with radium C on nickel is shown in fig. 5.

Fig. 5.



It is seen that a very soft γ radiation is present, but after passing through two millimetres of aluminium the absorption is exponential with a value of $\mu = .115$. This soft radiation was much more readily absorbed than the γ radiation, $\mu = .40$, obtained when the emanation was used as a source. It thus seemed probable that this soft radiation was excited in the nickel by the radiation from the radium C deposited on it.

This conclusion was confirmed by using a deposit of radium C on silver instead of nickel. A sufficiently active preparation was obtained by using the method outlined by v. Hevesy* of placing a silver plate in a silver nitrate solution containing the radium B + C in solution. With the silver plate, no appreciable amount of soft radiation was observed, but the absorption curve in aluminium was exponential from the beginning with a value of $\mu = \cdot 115$.

There appears to be no doubt that this soft radiation from nickel consists mainly of the "characteristic X radiation" of nickel excited probably by the α rays, although some rays of a more penetrating type were also present. It was observed that the amount of this soft radiation varied markedly with the orientation of the nickel plate, and was much less when the plate was parallel to the face of the pole-pieces than when it was perpendicular. Chadwick† first showed that γ rays were excited by α rays traversing different materials. The method employed by him, however, was not suitable for the detection of such a soft type of γ radiation. It is intended to make further experiments by the method outlined in this paper to examine whether the characteristic radiations of all elements are excited under similar conditions.

A number of experiments were made to test whether radium C itself emitted more than one type of radiation. For this purpose, the absorption curve in aluminium was very carefully examined over a thickness of aluminium from 0.2 to 4 cm. Over this range the absorption of the γ rays appeared to be exponential within the margin of possible experimental error with a value of $\mu = \cdot 115$. No evidence was obtained that a radiation for which $\mu = \cdot 5$ about was present. At the same time, it should be pointed out that it would be very difficult by direct measurement to detect with certainty the presence of a few per cent. of this radiation mixed with the more penetrating type for which $\mu = \cdot 115$.

Absorption of the γ rays by Lead.

In the experiments so far described aluminium has been used as an absorbing material. Since it is well known that the absorption of γ rays in a heavy element like lead is abnormal, it was thought desirable to determine the absorption curves for this material.

The curve obtained for pure radium C on nickel is shown in fig. 6, Curve B. The soft radiation from the nickel was first

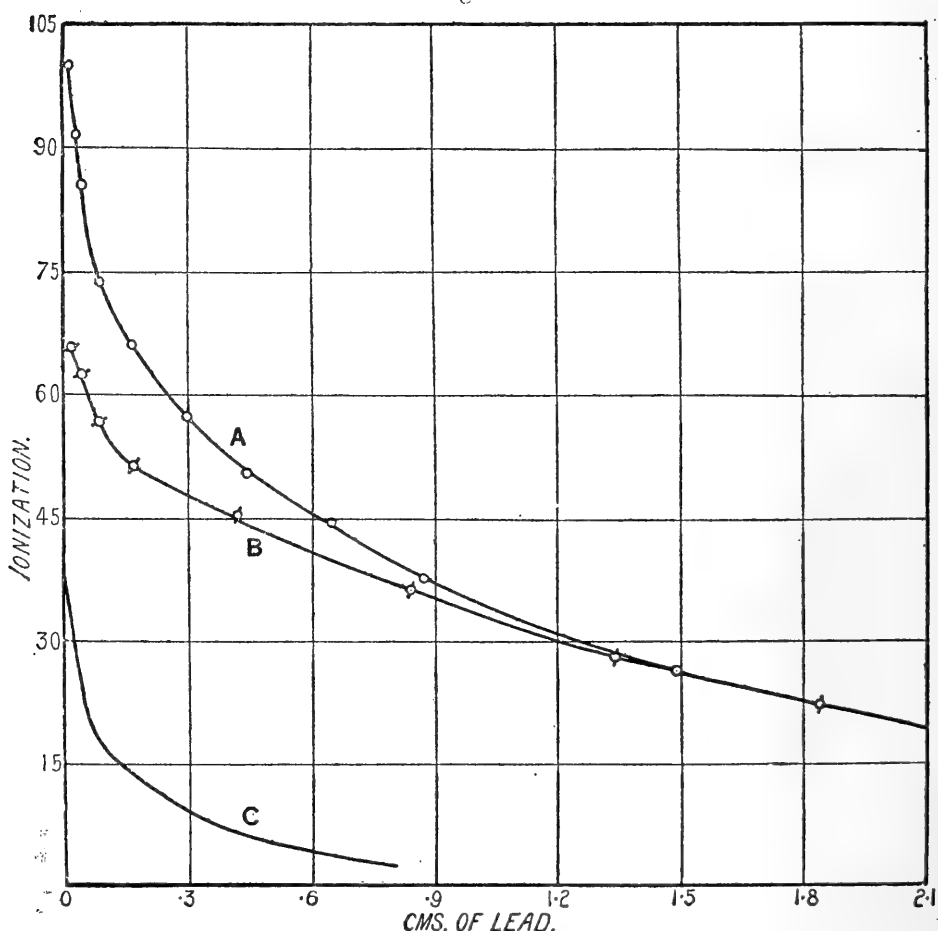
* Hevesy, *Phil. Mag.* xxiii. p. 628 (1912).

† Chadwick, *Phil. Mag.* xxv. p. 193 (1913).

cut out by a thin sheet of lead. The ionization initially fell more rapidly than was to be expected for an exponential law of absorption, but after traversing 1 cm. of lead the absorption of the rays in lead became accurately exponential with a value of $\mu=0.50$.

The absorption of the γ rays, using the emanation tube as a source, was also determined. In this case, before beginning the measurements, a thickness of lead was used sufficient to absorb completely the γ rays for which $\mu=40$ in aluminium. The curve obtained is shown in fig. 6, Curve A. After a thickness of 1.5 cm. of lead the absorption became exponential with a value of $\mu=0.50$. Since the radiation $\mu=0.50$ comes entirely from radium C, the curve B (fig. 6) represents the

Fig. 6.



part of the γ radiation due to radium C alone. The difference curve C given in fig. 6 shows the absorption in lead of the γ rays from radium B. It is seen that the curve shows a rapid initial drop, which is far more marked than in the case of radium C. The value of the absorption

appears to vary from $\mu=11$ to $\mu=2\cdot8$ about, but it is difficult by this method to fix the values with much accuracy. These results are in general agreement with the experiments of Moseley and Makower, who showed that the absorption coefficient of the γ rays from radium B for lead varied between $\mu=6$ and $\mu=4$ about.

It is thus seen that the two types of γ radiation which are exponentially absorbed by aluminium both show irregular absorption curves when lead is used as absorbing material. It is intended in a later paper to discuss in more detail the relative absorption curves in lead and aluminium, and their bearing on the question of the homogeneity of the radiations concerned.

General discussion of results.

The results of the analysis of the γ radiation from radium B and radium C are included in the following table. The density D of the aluminium was taken as $2\cdot71$.

	Absorption coefficient in aluminium.	Mass absorption coefficient in aluminium.	Absorption coefficient in lead.
Radium B.....	$\left\{ \begin{array}{l} 230 ? \\ 40 \text{ (cm.)}^{-1} \\ 0\cdot51 \text{ ,} \end{array} \right.$	$\left\{ \begin{array}{l} 14\cdot7 \text{ (cm.)}^{-1} \\ 0\cdot188 \text{ ,} \end{array} \right.$	<p>varying from 11 to $2\cdot8 \text{ (cm.)}^{-1}$.</p>
Radium C.....	$0\cdot115 \text{ ,}$	$0\cdot0424 \text{ ,}$	$0\cdot50 \text{ (cm.)}^{-1}$ after traversing 1 cm. of lead.

It is seen that radium C emits essentially only one type of γ radiation, while radium B certainly emits two, and possibly three. In a previous paper, one of us pointed out that the rays from radium C correspond in penetrating power to the "characteristic X radiation" of the K series to be expected from an element of atomic weight 214. The soft radiation from radium B ($\mu/D=14\cdot7$) undoubtedly corresponds closely in penetrating power to the radiation of the L series to be expected from an element of atomic weight 214. For example, Chapman* found that the value of μ/D in aluminium for the characteristic X radiation from bismuth (atomic weight 208·5) was 16·1, while the value of μ/D for thorium (atomic weight 232) was 8·0. It seems reasonable to suppose that the second type of γ radiation from radium B ($\mu/D=188$) also corresponds to a type of characteristic radiation from heavy elements which has not so far been

* Chapman, Proc. Roy. Soc. A. lxxxvi. p. 439 (1912).

observed with X rays on account of the difficulty of obtaining X rays of sufficient penetrating power to excite it. It is of interest to note that Chadwick and Russell* have found that three types of radiation were excited by the α rays in ionium. Two of these types, $\mu/D=8.35$ and $\mu/D=0.15$, appear to be analogous to the two types of radiation from radium B, but it is doubtful whether the very soft type ($\mu/D=400$) observed by them in ionium is given out by radium B or radium C, although, as we have seen, careful experiments have been made to test this point. There appears to be little room for doubt that the γ rays at any rate from radium B+C are to be regarded as types of characteristic radiation from these elements. It is of interest to note that the energy of the soft γ radiation from radium B is very small compared with the energy of the more penetrating types of γ radiation from radium B and radium C. Chadwick and Russell, on the other hand, found that the soft types of γ rays excited by the α rays in ionium were relatively far more prominent. The bearing of these results on the general theory of the connexion between β and γ rays which led to these experiments will be discussed in detail in a later paper.

Summary.

The γ rays from radium B consist of at least two distinct groups, each of which is absorbed exponentially in aluminium with absorption coefficients $\mu=40$ and $\mu=0.51$ (cm.)⁻¹ respectively. The first group of γ rays is much less penetrating than the X rays excited in an ordinary focus-tube. The γ rays from radium C consist essentially of one type which are absorbed exponentially in aluminium with a value $\mu=0.115$. No evidence was obtained of the emission from radium C of the groups of radiation observed from radium B. The absorption of the rays by lead does not follow an exponential law.

The general evidence indicates that these radiations are to be regarded as types of characteristic radiation from the elements in question analogous to the characteristic X radiations excited in elements by X rays.

Experiments are now in progress to analyse by the methods outlined in this paper the γ radiations from all the radioactive elements which emit β and γ rays. The analysis of the γ radiation from α ray products is being undertaken by Chadwick and Russell in this Laboratory.

University of Manchester,
March 6, 1913.

* Chadwick and Russell, Proc. Roy. Soc. A. lxxxviii. p. 217 (1913).

LXXVII. *On the Carriers of the Negative Thermionic Current in a Vacuum.* By GWILYM OWEN, M.A., D.Sc., and ROBERT HALSALL, B.Sc., *University of Liverpool* *.

IT has long been known that electricity of both signs is discharged from incandescent bodies. The current so obtained from a charged wire to the surrounding electrode is called by O. W. Richardson a thermionic current, and the carriers are called thermions. Workers in this field are not yet agreed as to the nature of the positive thermions, but it has been established by various observers that the negative carriers in a vacuum are mainly free electrons. Sir J. J. Thomson† in 1899 measured e/m for the negative thermions from a carbon filament at low pressure and obtained the value 10^7 . Values of the same order have since been obtained by Wehnelt‡ for the negative thermions from hot lime, and by Owen for those from platinum§ and the Nernst filament||.

Now it is well known that metal wires contain considerable quantities of absorbed gases which are evolved at a high temperature. Moreover, some substances—carbon and palladium, for example—disintegrate¶ rapidly when raised to incandescence at a low pressure. The question therefore arises: Is the negative thermionic current conveyed solely by electrons or by an admixture of electrons and heavy gaseous or metallic ions?

This point was investigated, in the case of platinum, by one of the writers in 1904 (*Proc. Camb. Phil. Soc. loc. cit.*). The results then obtained led to the conclusion that at temperatures below 1000° C. the negative thermionic current is conveyed solely by electrons, while at higher temperatures there appeared evidence of the presence in the discharge of a small percentage (about 5 per cent.) of heavy ions.

The writers have recently re-examined this question as to the presence of heavy ions in the negative thermionic current, and the present paper is a short account of the results obtained. The metals studied have been palladium, pure and commercial platinum, and iridium, and were in the form of wires about 0.4 mm. diameter. The method of investigation was, in the main, identical with that used

* Communicated by the Authors.

† Thomson, *Phil. Mag.* [5] vol. xlviii. p. 547 (1899).

‡ Wehnelt, *Ann. d. Phys.* vol. xiv. p. 425 (1904).

§ G. Owen, *Proc. Camb. Phil. Soc.* vol. xii. p. 493 (1904).

|| G. Owen, *Phil. Mag.* [6] vol. viii. p. 230 (1904).

¶ J. H. T. Roberts, *Phil. Mag.* February 1913.

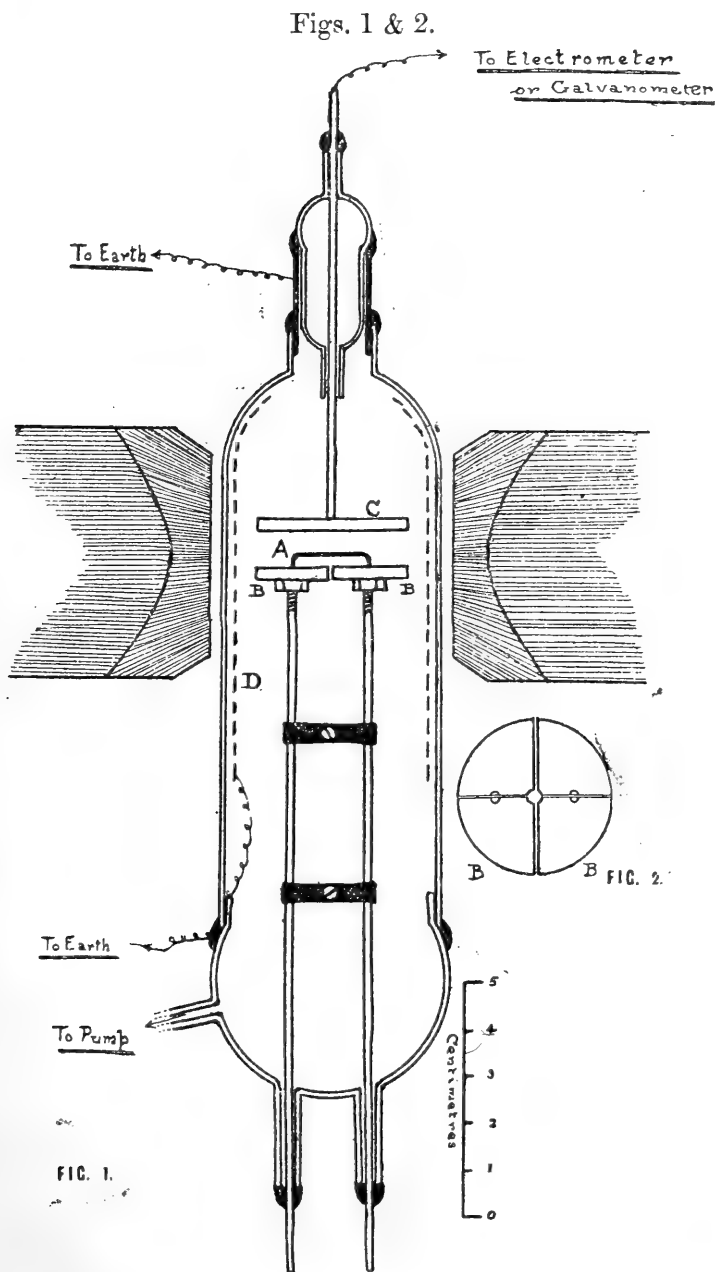
previously—namely, the retardation of the discharge by a transverse magnetic field. This method, which is due to Sir J. J. Thomson, is too well known to require full description. It will be sufficient to say that if charged particles starting from rest from the plane $x=0$ be subjected simultaneously to an electric field X , and a magnetic field Y at right angles to X , then the paths of the particles are cycloids, and the greatest distance d they get to from their plane of origin is given by

$$d = \frac{2X}{H^2} \cdot \frac{m}{e}.$$

Hence, if an insulated electrode be situated at a distance greater than d from the plane $x=0$, none of the particles will reach it. It is obvious that the magnetic field which just prevents an electron from reaching the electrode, will be far too weak to produce an appreciable deflexion of any charged particles of atomic dimensions that might be present. Thus, by measuring the thermionic current to a distant electrode with and without the magnetic field, information can be obtained as to the relative proportions of electrons and heavy ions in the discharge.

The experimental tube used in our investigation is shown in fig. 1. A is the hot wire charged generally to about 200 volts. The method of supporting the wire is shown more clearly in fig. 2, where the disk BB is shown in plan; the object of this disk was to obtain a fairly uniform electric field between the wire and the insulated electrode C . The latter was connected to an electrometer by screened wires and keys in the usual way. When experimenting at high temperatures the electrometer was replaced by a sensitive d'Arsonval galvanometer provided with suitable shunts, so that currents over a wide range could be measured. D is a cylinder of wire gauze connected to earth. This cylinder is necessary to prevent the inside walls of the glass tube from becoming charged up by the stream of deflected electrons. If this precaution be omitted, the magnetic field has but little retarding effect on the discharge. The distance of the hot wire from the insulated plate ranged in the different experiments from 6 mm. to 2 mm. At the latter distance, with 240 volts on the wire (iridium), a magnetic field of 300 units produced an appreciable effect on the negative thermionic current. [This gives 1.33×10^7 for the value of e/m for the electrons from iridium.] Generally, however, magnetic fields of intensity 800 or 1000 were applied, and, on occasion, fields of 2000 units. The wire was heated by

the current obtained from the secondary of a small transformer connected to an alternating dynamo, and the temperature was varied as desired by altering the relative positions of the primary and secondary, the latter being supported on a platform capable of slow motion to and fro along the axis of the primary.



The following table contains some representative observations made on the four metals mentioned. The currents

are given in purely arbitrary units, and as the sensitiveness of the electrometer or of the galvanometer was altered continually to suit the varying magnitudes of the thermionic currents at the different temperatures, it is only numbers in the same horizontal line in columns 3 and 4 that are to be compared. It should also be explained that 0·1 in the fourth column means a deflexion on the scale of one-tenth of a millimetre. In the experiments with platinum and iridium the vacuum was maintained by means of charcoal in liquid air.

Metal.	Temperature.	Negative thermionic current in arbitrary units.		Proportion of heavy ions to electrons.
		Magnetic field off.	Magnetic field on.	
Palladium (pure)	Dull red.	1'00	<0·1	<1 in 14000
	Bright red.	45000	3	1 in 15000
	Yellow.	800	<0·1	<1 in 8000
	Bright yellow.	7000	2	1 in 3500
Platinum (pure)	Bright yellow.	200	<0·1	<1 in 2000
	Almost white hot.	500	<0·1	<1 in 5000
	Nearly melting.	33000	3	1 in 11000
Platinum (commercial) {	Bright yellow.	600	<0·1	<1 in 6000
	Very bright yellow.	2600	1	1 in 2600
	White hot.	4200	1·5	1 in 2800
Iridium (pure)	Bright yellow.	580	<0·1	<1 in 5800
	White hot.	1500	<0·1	<1 in 15000
	Nearly melting.	5400	1	1 in 5400

In every case control tests were made by charging the wires positively, when it was found that the strongest magnetic field we could apply (about 3000 units) was entirely without influence on the positive carriers.

The above table shows clearly that the proportion of heavy ions to electrons in the negative thermionic current is exceedingly small at all temperatures for the metals investigated. This fact is specially interesting in the case of palladium, which metal, as has been mentioned, volatilizes rapidly in a vacuum. Since in every case the thermionic current with the magnetic field on could only produce

deflexions of the order of 1 scale-division (1 mm.), too much weight must not be attached to the absolute values of the ratios in the last column of the table. It should perhaps be pointed out that the very small deflexions obtained with the magnetic field do not prove conclusively the presence of heavy ions in the discharge. Similar results would be observed if a few electrons were shot out of the wire with a considerable velocity, or if a few rebounded on to the insulated electrode after striking the earthed gauze cylinder.

It remains to consider why heavy ions to the extent of 5 per cent. and more were apparently detected in some cases in the earlier work on this subject (Owen, *Proc. Camb. Phil. Soc. loc. cit.*). In the experimental tube used then, the insulated electrode consisted of two vertical brass disks, 8 mm. apart, and connected together by a single thin bar of brass screwed into them at the extreme end of horizontal diameters. The hot wire was situated midway between the disks, and the magnetic field was arranged so as to deflect the electrons along a vertical diameter. Owing to non-uniformity of the electric and magnetic fields, it is possible that when the thermionic currents were large (as at high temperatures) some of the electrons were caught by the bar connecting the two disks. In the experimental arrangement described in the present paper this possible source of error is absent. Moreover, the electromagnet used in these later experiments produced a strong uniform magnetic field over a space much larger than that occupied by the wire and the electrode, and was in this respect greatly superior to that at disposal in the earlier work. These considerations probably account for the fact that in the earlier experiments some electrons succeeded in reaching the electrodes in spite of the magnetic field.

Summary.

The nature of the carriers, in a vacuum, of the negative thermionic currents from palladium, pure and commercial platinum, and iridium has been studied. It is found that the carriers consist almost entirely of free electrons. If any of the discharge is carried by heavy ions, then the proportion of heavy ions to electrons is, for all temperatures, certainly less than one part in two thousand, and probably less than one part in ten thousand.

Holt Physics Laboratory,
University of Liverpool.
March 14, 1913.

LXXVIII. *A Quantitative Relation between the Range of the α Particles and the Number of Charges emitted during Disintegration.* By A. VAN DEN BROEK *.

IN 1907 Rutherford † observed that there appeared to be a relation between the period of transformation of a product and the velocity of the α rays expelled from it. In 1911 Geiger and Nuttall ‡ showed that in the great majority of cases the range of the α particle increased with the decrease of the period of transformation. Plotting the logarithm of the range of the α particle against the logarithm of the constant of transformation, the products of the uranium and radium series lie nearly on a straight line. In the thorium and actinium series again most of the products lie approximately on a straight line parallel with the line showing the relation for the uranium-radium series. As Rutherford § remarks, "The relation found by Geiger is of exceptional interest, for it supplies undoubted evidence that a connexion exists between two of the fundamental magnitudes in radioactive transformation."

Similar relations were given by Swinne || and H. A. Wilson ¶.

Between the velocity of the α rays and the number of charges expelled there appears also to be a similar relation. Plotting the logarithm of the initial velocity of the α particle against the number of charges expelled, the products of all series lie nearly on a straight line. As the values for all series, but not for analogous products in each, are the same, the initial value for each series can be chosen to fit in well. Of course it is not known if these are really the first.

Two difficulties immediately arise. Firstly, Ra C and Th C (or B) were proved by Fajans ** and by Marsden and Barratt †† to give off two branches of products. It seems, however, that for one branch the relation holds good, while for the other a reversal, and probably a regular one, seems to take place. In this case, on the Ra series one product more for each branch ought to be introduced; for the thorium series, however, more.

* Communicated by the Author.

† Phil. Mag. xiii. p. 110 (1907).

‡ Phil. Mag. xxii. p. 613 (1911); xxiii. p. 439 (1912); xxiv. p. 647 (1912).

§ 'Radioactive Substances and their Radiations,' p. 609, Cambridge 1913.

|| Phys. Zeitsch. xiii. p. 14 (1912).

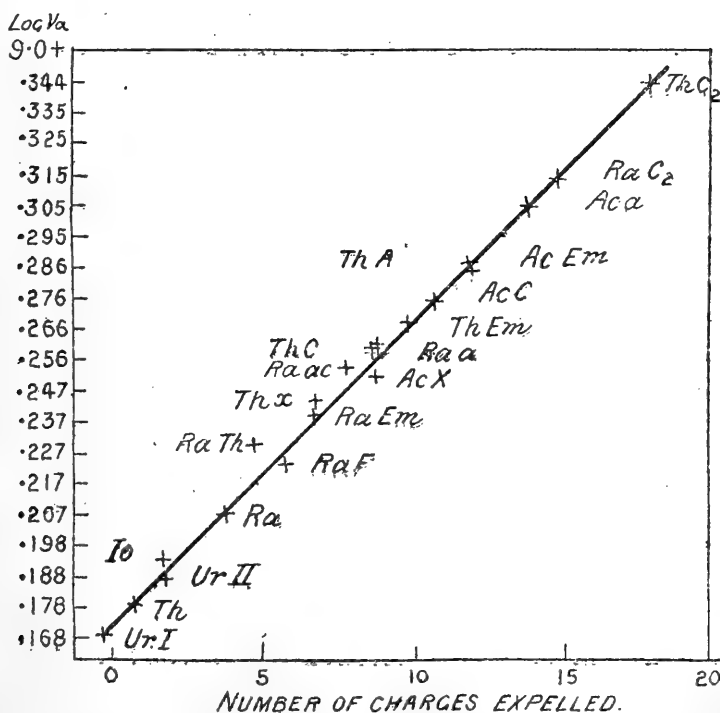
¶ Phil. Mag. xxiii. p. 981 (1912).

** Phys. Zeitsch. x. p. 697 (1909).

†† Proc. Phys. Soc. xxiv. p. 8 (1911).

The actinium series, too, must then be complex as the same reversal exists here. Indeed, Mlle. Blanquies* found some evidence that the α rays emitted from actinium C are complex.

That uranium, too, is complex was observed by Antonoff †, The branch product Ur Y emits soft β rays, and some evidence was found that it emitted α rays. As Rutherford ‡ remarks, "The possibility of a branch product of uranium is of great interest, as affording a possible explanation of the origin of actinium." If now we suppose Ur Y—as emitting $\alpha + \beta$ rays—to consist of two products, one emitting α rays, the other emitting β rays (and the same must be supposed for Ra, Th X, Ac X, Ra Ac—which all emit both α and β rays), then the product of Ur Y 2 falls together with Act. and might be identical with it.



If we accept for Ur II the value given by Geiger and Nuttall, then the uranium series cannot unite in the radium series, as the values for U II and Io are nearly identical. If, however, the range 2.90 cm. is attributed to Ur Y and in part that of 2.50 to Ur II also, while the range ± 1.6 cm. found by Friedmann § is attributed to Ur also as emitting two α rays of

* C. R. cli. p. 57 (1910); *Le Radium*, vi, p. 230 (1909), vii, p. 159 (1910).

† Phil. Mag. xxii. p. 419 (1911).

‡ Loc. cit. p. 45.

§ Wien. Ber. cxx. p. 1361 (1911).

different range for the two different branches, then also the radium series can be deduced from the uranium series. Of course, such a deduction is very hypothetical.

Recently von Hevesy *, and also Fajans †, proved that a relation exists between the expulsion of α and β rays and the change in chemical properties. As the atomic weight of the products also depends on the number of α particles expelled and finally "a relation of a similar though not nearly so definite a character as that found by Geiger for the α rays appears to hold between the velocity of expulsion of β particles and the period of transformation of the product concerned" ‡, it seems not improbable that all radioactive constants depend on the number of charges expelled only.

Summary.

The following relations seem to exist, first, between the initial velocity of the α rays and the number of charges expelled during disintegration: $\log V_{\alpha} = A + nB$, and second, between the period of transformation and the number of charges expelled: $\log \lambda = C + nD$, where B and D are general constants, A and C special constants for each series, and n the number of charges expelled.

Noordwyk-Zee, Duinhoeve,
February 1913.

LXXIX. *The Effect of Interionic Forces on the Osmotic Pressure of Electrolytes.* By S. R. MILNER, D.Sc., Lecturer in Physics, The University of Sheffield §.

THE osmotic pressure of dilute solutions of inorganic electrolytes, as determined from the lowering of the freezing-point, is always nearly, but not quite, as great as it would be if the dissociation of the electrolyte were complete. The explanation given by Arrhenius in 1887 that in such electrolytes an appreciable fraction of the molecules remains undissociated, is still the one which is generally accepted. This theory is strongly supported by the agreement of the values of the dissociation calculated from freezing-point and from conductivity measurements, but it gives results for its variation with the concentration which are, as is well known, wholly at variance with the law of mass-action; and although many attempts have been made to explain this discrepancy

* *Phys. Zeitsch.* xiv. p. 50 (1913).

† *Phys. Zeitsch.* xiv. p. 137 (1913).

‡ *Loc. cit.* p. 610.

§ Communicated by the Author.

none is wholly satisfactory*. Now both the formula of Arrhenius, giving the dissociation in terms of the freezing-point lowering, and the law of mass-action in its usual form depend on the assumption that the osmotic pressure of the ions, as well as that of the molecules, obeys the law for perfect gases, and both will require modification in case any deviation from the gas law is produced by the relatively large electrical forces which exist between the ions. In a previous paper† in this Magazine I have shown that a completely dissociated mixture of ions possesses a finite virial, and have calculated its approximate value by what is I think a strict mathematical method. In the application to solutions it follows that the osmotic pressure of the ions of an electrolyte differs from that of a perfect gas in a calculable way. In the present paper the virial calculation is applied to determine the theoretical osmotic pressure, and hence the lowering of the freezing-point at different concentrations of an assumed completely dissociated binary electrolyte. A comparison of the result with experiment leads to the conclusion that the freezing-point lowering at all dilute concentrations in monovalent salts can be completely accounted for by the effect of the interionic forces in reducing the osmotic pressure below that given by the gas law on the assumption that the dissociation is complete throughout.

The view that so-called "strong" (or strongly dissociated) electrolytes are completely dissociated at all concentrations is not of course a new one. It has been proposed on other grounds—in particular by Sutherland‡—but the hypotheses on which it has been based seem somewhat speculative, and indeed the view is not one which is generally accepted. The argument for the view which follows from the result of this paper, however, seems to me to stand on a different footing from any previously advanced. The interionic forces certainly exist, and their effect on the osmotic pressure and the freezing-point is a purely mathematical deduction from the known facts. Further, the magnitude of the theoretical effect is determined absolutely in terms of known quantities, no arbitrary constants being involved. The effect must thus be admitted, if the deduction is correct, on the recognized theory of electrolytes, and allowed for before any conclusion can be drawn from the freezing-point

* A summary of the various explanations which have been suggested up to 1910 is given by Partington, Journ. Chem. Soc. xcvi. p. 1158 (1910).

† Phil. Mag. xxiii. p. 551 (1912).

‡ Phil. Mag. iii. p. 161 (1902); xii. p. 1 (1906)

determinations as to the fraction of the electrolyte which is dissociated. Finally, the calculated effect is of just the right magnitude to account for the observed depressions in a completely dissociated electrolyte.

The view that an electrolyte is completely dissociated at all concentrations gets over the long outstanding difficulty of the want of agreement between the observed freezing-point variation and the law of mass-action, for the latter law clearly does not now come into the matter at all. On the other hand, at first sight an equally great new difficulty is raised by the existence of a variation in the molecular conductivity with the concentration, for this can now no longer be ascribed to incomplete dissociation. However, the interionic forces in a completely dissociated electrolyte may be expected to produce an effect on the conductivity as well as on the osmotic pressure, and I hope to show in a later paper not only that such is the case, but also that the theoretical effect is in good accord with experiment.

It was proved in the paper on the virial referred to above, that in a gaseous mixture of $N+$ and $N-$ ions confined in a volume V the ions will not be distributed at random in the volume, but that the ions of opposite sign will be on the average slightly nearer together, and those of like sign on the average slightly farther apart, than they would be on a purely random distribution. It is because of this deviation from the random distribution, which is brought about by the action of the interionic forces, that there exists a finite virial for the mixture, for the virial of a purely random distribution of the ions would be zero. The virial* we are concerned with is defined as

$$\overline{E} = \overline{\sum \pm q^2/r},$$

where q is the ionic charge, and r is the distance apart of any pair of ions. The summation is to be extended with appropriate sign over every pair which can be formed out of the $2N$ ions in the volume, and then averaged over every possible configuration of the system, due regard being paid to the probability of occurrence of each configuration. It was found that \overline{E} could be expressed in the form

$$\overline{E} = Nwh\phi(h). \quad . \quad . \quad . \quad . \quad (1)$$

In this equation

$$w = \frac{RT}{\nu},$$

where ν is the number of molecules in a gram molecule;

* Boltzmann's definition of the virial as $\overline{\sum Rr}$ has been employed in this and the preceding paper. Some authors define the virial as $\frac{1}{2}\overline{\sum Rr}$.

w is the most probable, or two-thirds of the average, kinetic energy of translation possessed by an ion or a molecule at the temperature T ,

$$h = \left(\frac{4\pi}{3} \cdot \frac{2N}{V} \right)^{\frac{1}{2}} q^2 / w. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

h is a pure number, being the ratio of a potential energy to the kinetic energy w ; the potential energy is that of two ions at a distance apart equal to the radius of the sphere in which on a random distribution the average number of ions contained would be one. $\phi(h)$ is a function of h the value of which is theoretically determinate, and of which approximate numerical values for a few different values of h were calculated.

In equation (1) the interionic forces are reckoned + when repulsive, and \bar{E} is a negative quantity, $\phi(h)$ being always negative. It will be more convenient for our present purpose to deal with a positive quantity for the virial. Put $W = -\bar{E}$ and $f(h) = -\phi(h)$, then

$$W = Nwhf(h)$$

is positive and may be called the attractive virial. If the volume V contains 1 gm. mol. of the associated ions, as we shall henceforward assume, then $N = \nu$, and $w = RT/N$, whence

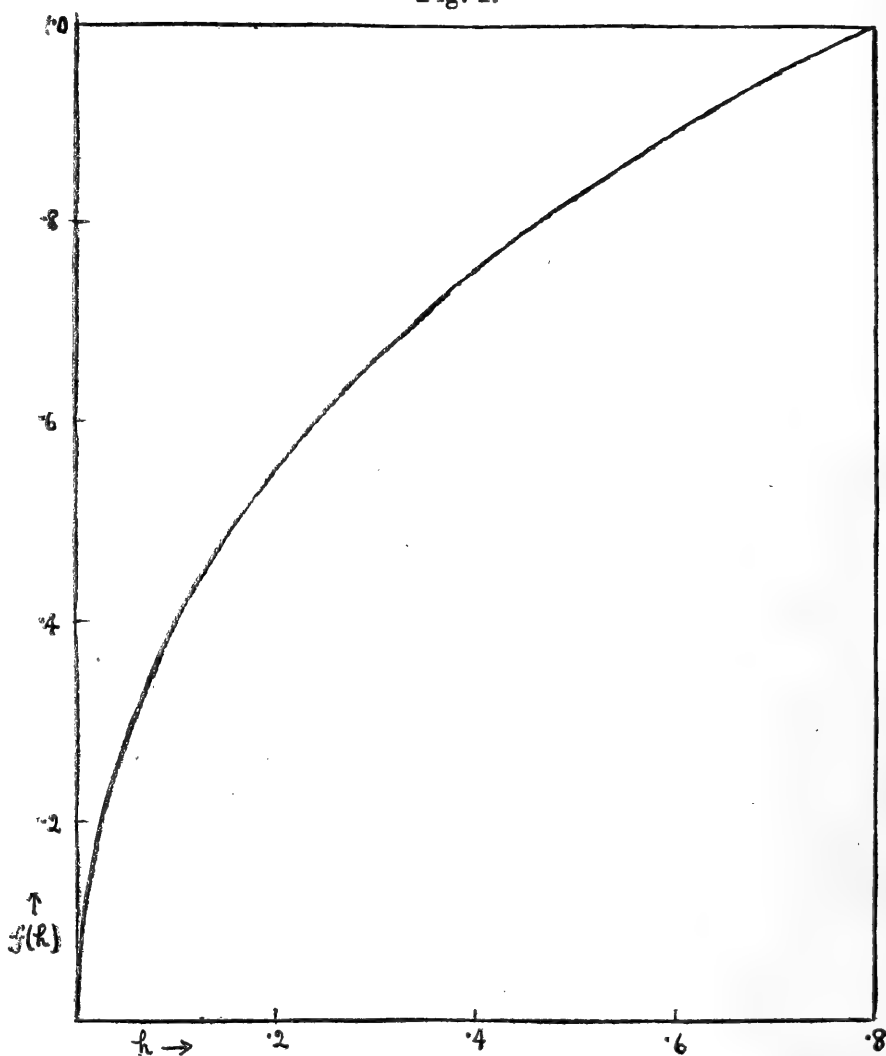
$$W = RT hf(h). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

A curve showing the approximate course of $f(h)$ with h is here appended (fig. 1, p. 746).

Strictly, the result (3) only holds if the ratio h is a small number, the chief reason being that the assumption is made in the calculation that association of the ions due to electrical forces is negligible, and this would become less and less true as h increases. Also to simplify the expressions the virial was calculated for an assumed gaseous mixture, the forces between a pair of ions being put q^2/r^2 . Under these conditions, however, h comes out to be quite a large number, thus the result is evidently not applicable to an actual gaseous mixture of ions which have the ordinary ionic charges. This conforms with the fact that a gaseous mixture of ions initially dissociated is not in equilibrium, but undergoes spontaneously an almost complete association. The case is, however, different when we apply the result to electrolytes. We do not know what will be the exact effect on the interionic forces of the water molecules between the electrolytic ions; it is doubtless a very complicated one, but it will certainly diminish the forces very considerably. In the

absence of complete knowledge, we can only assume that the effect is the same as would be produced if the ions were immersed in a continuous medium of S.I.C. equal to that, K , of water in mass.

Fig. 1.



If we do this, the same expression (3) for the virial will apply if in place of (2) for h we substitute the value

$$h = \left(\frac{8\pi N}{3V} \right)^{\frac{1}{3}} \frac{q^2}{Kw} \cdot \cdot \cdot \cdot \cdot \cdot (4)$$

To obtain the numerical value of h for a solution of given concentration, let C be the concentration in gm. mols. per litre, ϵ the charge per gm. ion of a monovalent ion, then substituting in (4) $V = 1000/C$, $N = \epsilon/q$, and $w = RTq/\epsilon$, we get

$$h = \frac{1}{10} \left(\frac{8\pi}{3} \right)^{\frac{1}{3}} \frac{q^{\frac{3}{2}} \epsilon^{\frac{4}{3}}}{KRT} \cdot C^{\frac{1}{3}}.$$

Putting

$$q = 4.77 \times 10^{-10} \text{ E.S.U.}, \quad \epsilon = 9654 \times 3 \times 10^{10} \text{ E.S.U.},$$

$$R = 8.31 \times 10^7 \text{ erg/deg. C.}, \quad T = 273, \quad K = 87 \text{ at } 0^\circ \text{ C.},$$

$$\text{we get} \quad h = 1.203 \text{ C}^{\frac{1}{2}}.$$

Given the virial we can, if we may treat the electrolyte as we should a gas, at once obtain the pressure by using the equation of Clausius, which states that pressure \times volume = $\frac{2}{3}$ (kinetic energy) $-\frac{1}{3}$ (virial). Applied to a completely dissociated electrolyte this gives, since there are two gram ions present in the volume V ,

$$PV = 2RT - \frac{1}{3}W$$

$$\text{or} \quad \frac{PV}{RT} = 2 - \frac{1}{3}hf(h). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It may not, however, appear quite legitimate to apply without question formulæ deduced from the concepts of the kinetic theory of gases directly to the complex phenomenon which the osmotic pressure of an electrolyte undoubtedly is. The same formula is therefore deduced below in another way.

When, as is the case in the system we are considering, the internal forces vary according to the inverse square law, the virial bears a simple relation to the internal potential energy of the system. If we measure the internal energy, U , of the solution at the volume V by the work which would be done by the electrical forces if the ions of opposite sign were allowed to collapse on each other in pairs from the positions which they occupy in the volume V ,—or in other words by the heat which would be produced if complete association of all the ions were brought about—and if U_∞ stands for the corresponding energy of the system at infinite dilution, then $U_\infty - U$ is easily seen to be the average value of the summation of $-\left(\pm \frac{q^2}{Kr}\right)$ for all pairs of ions in the solution. This is the attractive virial W , and, in fact,

$$\begin{aligned} U &= U_\infty - W \\ &= U_\infty - RThf(h) \end{aligned}$$

We can now apply the general thermodynamical relation

$$\frac{dU}{dV} = T \frac{dP}{dT} - P \quad . \quad . \quad . \quad . \quad . \quad (6)$$

to determine the osmotic pressure P . If $\frac{dU}{dV}$ were zero, (6) would be satisfied by

$$P = \frac{2RT}{V},$$

the gas law for a completely dissociated electrolyte. When $\frac{dU}{dV}$ is not zero, we may therefore take P to be of the form

$$P = \frac{2RT}{V} + \phi(V, T), \quad \dots \quad (7)$$

and determine the function ϕ . Substituting (7) in (6) gives

$$T \frac{d\phi}{dT} - \phi = \frac{dU}{dV} = -RT \frac{d}{dV} [hf(h)],$$

whence

$$\phi = -RT \int^T \frac{d}{dV} [hf(h)] \frac{dT}{T},$$

there being no constant of integration since ϕ vanishes with h . This expression can always be integrated when, as is here the case *, h is of the form $F(V)/T$, for take the $\frac{d}{dV}$ outside the \int , and substitute $-\frac{dh}{h}$ for $\frac{dT}{T}$, when we get

$$\begin{aligned} \phi &= RT \frac{d}{dV} \int^h f(h) dh \\ &= RT \frac{dh}{dV} \cdot \frac{d}{dh} \int^h f(h) dh \\ &= RT \frac{dh}{dV} f(h). \end{aligned}$$

* Since K the s.r.c. of water, varies to some extent with the temperature, h is not strictly proportional to $1/T$. If, however, we were to try to take into account here the variation of K with T , it would lead to a discrepancy between the expressions for the pressure obtained by the kinetic and by the thermodynamical calculations. Such a discrepancy cannot, however, really exist, for the virial equation is consistent with thermodynamics. The fact is that K has already virtually been assumed constant in determining the virial (if it were not constant the electrical force between two ions would depend on their kinetic energies as well as on their positions), and to obtain agreement the same assumption must be made here also.

But by (4) $\frac{dh}{dV} = -\frac{1}{3} \frac{h}{V}$, whence

$$\phi = -\frac{1}{3} \frac{RT}{V} hf(h),$$

which gives the same equation (5) for the osmotic pressure as before.

Effect on the Freezing-Point.—The thermodynamical relation between the osmotic pressure of a solution and the lowering t of its freezing-point below 0°C. , reduces in dilute solutions to

$$\frac{PV}{RT} = \frac{t}{1.86 \text{ C}} = \frac{\tau}{1.86},$$

where C is the concentration (gm.mols./litre) and $\tau = t/C$ the molecular lowering. This relation is practically independent of whether the osmotic pressure obeys the gas law or not. By combining it with (5), we get for the variation of τ with the concentration in a completely dissociated electrolyte

$$\tau = 1.86 \left\{ 2 - \frac{1}{3} hf(h) \right\} \quad . \quad . \quad . \quad . \quad (8)$$

The appended table shows values of h and $\frac{1}{3}hf(h)$ for various concentrations :—

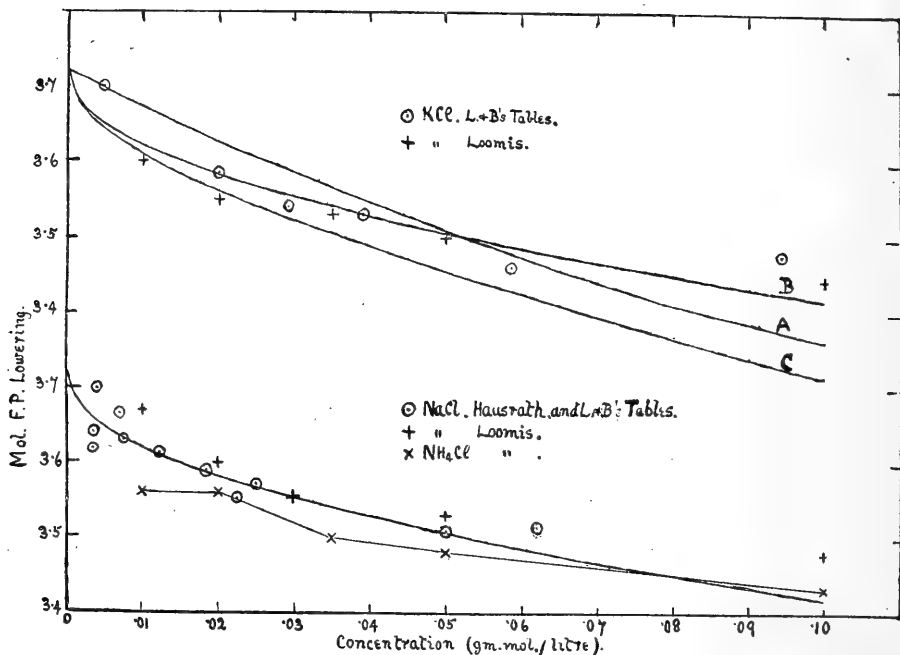
C.	h .	$\frac{1}{3}hf(h)$.
·0001	·0559	·0056
·001	·120	·0175
·002	·152	·0245
·005	·206	·038
·01	·259	·053
·02	·327	·074
·05	·443	·115
·1	·559	·162
·2	·704	·224

In fig. 2 (p. 750) are plotted the experimental values of τ for KCl, NaCl, and NH_4Cl . KCl and NaCl are probably among all substances those for which the lowerings have been most accurately determined at dilute concentrations. In the figure Loomis' results* are indicated by crosses, the \odot 's give all the values of other observers collected in Landolt

* Loomis, *Ann. d. Phys.* li. p. 500 (1894); lvii. p. 495 (1896).

and Börnstein's Tables (3rd ed., 1905), for NaCl Hausrath's* observations in addition have been plotted. The three curves in the top figure show the theoretical variations of τ with C under different assumptions. A is calculated on the

Fig. 2.



assumption that the gas law is obeyed by the ions, and that the whole effect on τ is due to partial association. This gives

$$\tau = 1.86 \left\{ 1 - \frac{K}{2C} + \frac{1}{2} \sqrt{\frac{K^2}{C^2} + \frac{4K}{C}} \right\}.$$

In the curve K is arbitrarily put $\cdot 350$, a value chosen to give agreement with experiment at $C = \cdot 05$ normal. As is well known, this type of curve does not even approximately fit the experimental numbers. B represents the theoretical curve (8) in which the variation is ascribed entirely to the effect of interionic forces in a completely dissociated electrolyte. In each of the salts there is a close agreement of the experimental numbers with B. The agreement becomes still more striking when we remember that the theoretical curve is given absolutely by the calculation—there are thus no arbitrary constants involved by the adjustment of which a possibly spurious agreement might have been obtained. The curve C represents approximately the way in which we

* Hausrath, *Ann. d. Phys.* ix. p. 547 (1903).

LXXX. *Notices respecting New Books.*

Optique géométrique. By J. BLEIN. Pp. vi+263. Paris: O. Doin et Fils, 1912. 5 fr.

Geometrical Optics. By ARCHIBALD STANLEY PERCIVAL. Pp. vi+132. London: Longmans, Green & Co., 1913.

THE former of these two books, which forms one of the volumes of the *Encyclopédie scientifique*, is an excellent summary in very small space of the fundamental principles and methods employed in connexion with this subject. It leads in the end to a consideration of the various methods based upon the characteristic function of Hamilton (employed by Maxwell) and upon the several functions derived from it which avoid the difficulties involved in the employment of the characteristic function itself. These have been employed by Lord Rayleigh, Bruns, Schwarzschild, and Pelletan. The account given of Schwarzschild's method is a most luminous one.

An English reader will probably regret that the author has not included a reference to the paper by Professor Sampson (*Royal Society Transactions*, 1912) which deals with aberrations of the fifth order and which extends Seidel's five conditions to seven.

The second of the two volumes is written primarily for medical students. It is rather difficult to guess for whom it is really intended. The preface states that the text embodies all that can reasonably be demanded in any preliminary examination in science. We must assert definitely that scarcely any medical student with whom we have become acquainted (and their total number is very large) would be able to cope with the volume in the very short time which he has at his disposal.

The book itself has many excellent features when viewed apart from the use to which it is intended to be put. The author has an original way of expressing himself; many of the old familiar statements appear here in a new dress. The question of cardinal points is dealt with in a very simple manner indeed. If only a large number of *senior* students can be induced to study the book carefully it will place ophthalmic science in a very different position from that which it is in to-day.

LXXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 660.]

January 8th, 1913.—Dr. Aubrey Strahan, F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Geological History of the Malay Peninsula.' By John Brooke Scrivenor, M.A., F.G.S., Geologist to the Government of the Federated Malay States.

This paper is an attempt to present briefly and in a connected form all the information bearing on the geological history of the

Malay Peninsula that has been gathered during the course of economic work since 1903.

The main points are as follows:—

During the Mesozoic Era earth-movements took place in a part of the crust which is now the site of the Malay Peninsula. These movements resulted in the formation of two large anticlinal folds. The folding admitted of the intrusion of two masses of granite, and the intrusion was accompanied by faulting of the rocks in the folds, and by 'magmatic stoping' on a large scale.

The rocks affected by the folding are the Raub Series of calcareous rocks, and the Malayan Gondwana rocks, resting unconformably on the Raub Series, and in many places faulted down against that series.

The palæontological evidence afforded by small collections from the Raub Series cannot be reconciled with the field evidence. No fixed horizon has been discovered in these rocks, which may be either Carboniferous or Permo-Carboniferous. Associated with the Raub Series are volcanic rocks, which are evidence of contemporaneous submarine eruptions. The eruptions continued into later times.

At the base of the Gondwana rocks are glacial deposits that may be referred to the same horizon as the late Palæozoic glacial deposits of Peninsular India, the Salt Range, Australia, and South Africa, but this horizon cannot be defined exactly in the terms of the European sequence. Its presence shows that the Raub Series must be older than the *Productus* Beds of the Salt Range, or equivalent to the shales below the boulder-bed in the trans-Indus section of the Salt Range.

The glacial deposits are succeeded by littoral deposits, and far to the east of the glacial deposits a Rhætic horizon has been described in them by Mr. R. B. Newton, and named by him the Myophorian Sandstone. To account for the apparent discrepancy in age between the climatic horizon afforded by the glacial deposits and the Myophorian Sandstone, an hypothesis has been adopted to the effect that the Malayan Gondwana rocks were deposited on the Gondwanaland coast-line as it moved slowly eastwards, probably with many checks and oscillations.

The glacial deposits show that this portion of the Gondwanaland coast contained stanniferous granite and also much corundum. This granite is called 'the Palæozoic Granite,' as distinguished from 'the Mesozoic Granite': it is not known *in situ*. The glacial deposits are, therefore, part of a Palæozoic tin-field, now being worked at the same time as the stanniferous deposits derived from the Mesozoic Granite.

Denudation has brought to light the two great anticlinal folds and the granite masses upon which they now rest. On the west is the Main Range Anticline, on the east the Benom Anticline. The eastern limb of the former and the western limb of the latter meet in the Main Range Foothills. The eastern limb of the Benom Anticline is formed by the main Gondwana outcrop, which includes the highest peak in the Peninsula (Gunong Tahan, altitude 7188 feet).

It is believed that this main Gondwana outcrop is continued through the Peninsula to Singapore, and on to Banka and Billiton, where it may turn so as to enter Western Borneo, forming an inner arc roughly parallel with the outer volcanic arc of the Malay Archipelago and the Philippines.

The igneous rocks of the Benom Anticline are less acid than those of the Main Range Anticline, and there is a corresponding difference in mineral products. The area of the Benom Anticline coincides with the 'gold-belt' of the Peninsula. The products of the Main Range Anticline are tin and wolfram.

Tertiary coal-measures, unconformable on the Gondwana rocks, are known in Selangor. Their exact age cannot be determined, since the flora resembles the existing jungle-flora; and the same may be said of floras in Borneo coal-measures that are believed to date back to the Eocene Period. An arrangement based on the percentage of moisture in the coal, however, points to the possibility of their being Miocene.

Evidence has been found in the Peninsula supplementing the biological evidence described by Dr. A. R. Wallace, of changes in the Archipelago in Tertiary times. When the land-connexion that allowed the migration of the fauna of the Archipelago from the north was destroyed by submergence, the subsidence continued until the Peninsula became an island or group of islands. Subsidence then gave place to elevation, which restored the Peninsula and is continuing at the present day.

Interesting recent deposits are deposits of lignite in 'cups' formed by solution in the limestone of the Raub Series, and torrential deposits made up of 'core-boulders' derived from weathered granite.

2. 'On a Mass of Anhydrite in the Magnesian Limestone at Hartlepool.' By Charles Taylor Trechmann, B.Sc.

The harbour of Hartlepool owes its existence to the erosion of a mass of anhydrite of great thickness, proved by boring and other evidence to exist in close proximity to the Upper Magnesian Limestone upon which the towns of Hartlepool and West Hartlepool are built.

The anhydrite is shown to be included in, and to represent the time-equivalent of part of, the Middle and the greater part of the Upper Limestones. The contrary view, that the anhydrite belongs to the overlying red beds here faulted down, is shown to be erroneous.

The former presence of sulphates in the Magnesian Limestone is discussed. This formation, wherever protected by overlying comparatively impervious beds, proves to be more or less gypsiferous throughout its thickness. Evidence is brought to show that very large quantities of anhydrite were originally deposited with the Magnesian Limestone, the subsequent hydration and removal of which is chiefly responsible for the collapse, degradation, brecciation, and other alterations that are such obvious features of the formation in its present condition.

The distribution of organisms in the Magnesian Limestone was largely influenced by the quantity of sulphates present in the surrounding water. The Shell Limestone is shown to be a chain of reef-knolls, in the building up of which a limited number of forms take part, probably induced by current-action in the Permian Sea and lying more or less parallel with the old Permian shore-line. The increasingly unfavourable conditions prevailing towards the top of the Shell Limestone bring about a dwarfing and gradual extinction of the typical Shell-Limestone fauna.

The curious distribution and present position of the Upper Magnesian Limestones in Durham is noticed, and an explanation offered.

The Permian succession is shown to be more complete in the southern than in the northern area of the county.

Various sections in the Upper and Upper Middle Limestones in the Hartlepool area are described, among them the recent sinking for Blackha'l Colliery, where all the series were pierced, including the full thickness of the Shell Limestone.

February 26th, 1913.—Dr. Aubrey Strahan, F.R.S., President,
in the Chair.

The following communications were read :—

1. 'The Geology of Bardsey Island (Carnarvonshire).' By Charles Alfred Matley, D.Sc., F.G.S.; with an Appendix on the Petrography by John Smith Flett, M.A., D.Sc., F.G.S.

Bardsey, an island a mile and three-quarters long, lies off the promontory of the Llyn (Western Carnarvonshire), and forms the isolated extremity of the strip of pre-Cambrian rocks that borders the western coast of the Llyn from Nevin south-westwards.

The rocks are principally gritty schistose slates, with many thin and some thick bands of grit, quartzite, and limestone; and they contain an horizon of variolitic lava and tufaceous shale, which indicates that a volcanic episode took place during their formation. Sills of albite-diabase also occur, as well as one or more sills of a crushed granite.

The rocks have been subjected to intense earth-pressure acting mainly from the north-west, and are mostly in a cataclastic condition, the harder rocks being almost always torn up into lenticles. The beds are shown to be arranged on the whole in a number of isoclinal folds, complicated by overthrusting, shearing, and brecciation. Stages in the formation of crush-conglomerates are described. From the nature of the brecciation and the comparatively small amount of mineral alteration that the beds have undergone, it is inferred that the load of superincumbent rock at the time of the principal earth-movements was not great.

The rocks are correlated with the lower portion of the Llanbadrig Beds and with the Llanfair y'nghornwy Beds of Anglesey, and they agree also with their Anglesey representatives in the manner in which they have been affected by earth-movement.

Some post-movement dykes of olivine-dolerite occur, with a north-west to south-east trend. They are probably of Tertiary age.

Glacial striæ and boulders indicate that the island was invaded by a portion of the Irish Sea ice-sheet which, after crossing Anglesey to the west of Red Wharf Bay in a south-westerly direction, was deflected in Carnarvon Bay and traversed Bardsey in a south-easterly direction. This deflexion is tentatively attributed to the pressure of ice radiating from Ireland.

There are doubtful indications of a post-Glacial raised beach at 18 to 20 feet O.D.

In an Appendix Dr. J. S. Flett describes the petrographical characters of the granites, the pillow-lavas and their tuffs, and the diabases.

2. 'The Loch Awe Syncline (Argyllshire).' By Edward Battersby Bailey, B.A., F.G.S.

Mr. J. B. Hill's classification of the sedimentary schists of the district, into the Loch Awe Group above, and the Ardrishaig Group below, is accepted. So also is his reading of the Loch Awe Syncline. This syncline is a comparatively shallow trough, with well-marked fan-structure due to small-scale isoclinal folding, in which the limbs of the folds are vertical along the axial belt of the syncline, and inclined outwards on either side.

There are, however, two modifications of Mr. Hill's original interpretation, both of them already dealt with, in part, by Dr. B. N. Peach and the author in the Geological Survey Memoir describing the southernmost portion of the region (Sheet 28). One of the proposed alterations is concerned with the numberless igneous rocks folded along with the sedimentary schists. Many of these are obvious intrusions; but some, as Dr. Peach showed in 1903, are certainly lavas. In the present paper, Dr. Peach's volcanic zone is traced throughout the whole district, where it maintains a constant horizon in the Loch Awe Group. This brings us to the second suggested modification, affecting, as it does, details of the stratigraphy of the Loch Awe Group, for which the following sequence is proposed:—

Loch Avich Green Slates and Grits (volcanic rocks in the lower part).

Tayvallich Black Slates and Limestones (volcanic rocks throughout).

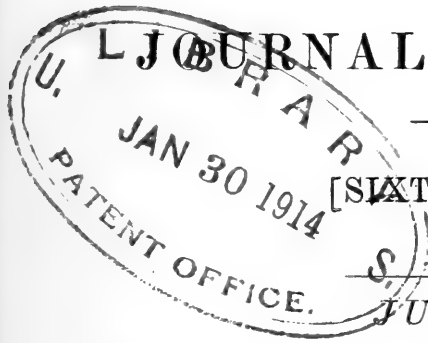
Crinan Grits and Quartzites.

Shira Limestone, constituting a passage-zone down into the Ardrishaig Phyllites.

Attention is drawn to evidence, already published, that the order of superposition of the sediments in the Loch Awe Syncline corresponds with the original order of sedimentary superposition. Finally, a recent suggestion of Mr. Hill's is adopted, in which he correlates the extremely low grade of metamorphism of the rocks of the central part of the Loch Awe Syncline with their high structural position. The hypothesis is that these rocks were not deeply covered during their metamorphism, and accordingly were never raised to any very high temperature.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND

JOURNAL OF SCIENCE.
[SIXTH SERIES.]
JUNE 1913.



LXXXII. *On a Dynamo for maintaining Electrical Vibrations of High Frequency. With some notes on the Transmission of Waves in Wireless Telegraphy.* By Sir OLIVER LODGE*.

I DESIRE not so much to put on record, since that has in some sort been already done, but to welcome the achievement of what many physicists in years past desired to attain, namely the construction of an alternating arrangement capable of maintaining electrical vibrations of sufficiently high frequency to give a continuous train of waves of moderate length; comparable for instance to four miles or even less. It may be that this problem will give way, as problems so often do, in several directions at once; and that the result may be—possibly has been—achieved by several different methods. At present, however, my attention has been called to the ingenious device introduced by Dr. Goldschmidt of Berlin, an ex-Professor of Electrotechnics at Darmstadt.

A method of achieving the desired end by a series of alternating dynamos had already been suggested, and will be found referred to in Professor G. F. FitzGerald's *Collected Papers*, page 280, where a discussion between himself and Dr. Sumpner, involving also Professor Trouton, is reported as having occurred at the Physical Society of London on 22nd January, 1892; with myself, as it happened, in the chair. It is reported also in *Nature*, vol. xlv. p. 358.

The plan then mooted was to use the alternating current from one dynamo to excite the field magnets of another, that

* Communicated by the Author.

other to excite a third, and so on. By this means it was clearly perceived that the frequency could be made to mount up in arithmetical progression with the number of machines. But the obvious cumbersomeness and wastefulness of the arrangement, although it was true that all the dynamos might run on the same shaft, caused the idea to be promptly abandoned.

Dr. Goldschmidt, however, has now made the interesting discovery that all these steps can be taken in a single machine, with some manifest and some unexpected advantages, and apparently with sufficient economy for practical purposes even at high power, so long as the final frequency does not exceed say 50,000 per second.

The fact that iron is used, and to all appearances necessarily used, in attaining this result, although its magnetization should not be pushed beyond a permeability of 100 or something below the steep part of a magnetization curve, necessitates many instrumental precautions, much careful design, and considerable constructive skill; but designers of the Firm of Messrs. C. Lorenz, and Engineers of the Firm of Messrs. Bergmann, both in Berlin, have been able to execute machines which certainly work in the way expected.

So far as I am aware Physicists in this country have not made themselves generally acquainted with the device employed, and inasmuch as its ingenuity commands admiration, I venture

- (1) to expound the principle briefly,
- (2) to attempt a theory.

The features of the machine and the laws utilised may be all considered known when taken separately, some of them well known; and yet, in combination, they work in a way which at first sight seems puzzling and might readily have been pronounced fanciful.

The separate points on which the invention is based may be thus stated:—

- (1) That when the field magnet of an alternating dynamo, with a number of poles distributed round a circle, is itself excited by an alternating current, its field may be considered as revolving equally in two opposite directions; *i. e.*, its magnetism revolves although the iron is mechanically stationary. This is merely because each North pole changes sinuously into a South pole, and each South pole into a North; thus virtually changing places in a continuous cyclical manner.

(2) The second point is that an armature revolving in front of such a field magnet, which if the magnet were steady would have the frequency q generated in it, will, when the field magnet itself is excited by an alternating current of frequency p , be subject to the resultant frequencies $p - q$ and $p + q$.

For if the armature stood still, the induced frequency would be p ; and if it revolves, its own frequency q is superposed upon this; in one direction running after and perhaps overtaking the frequency p , and in the other direction running away from and thereby virtually increasing the relative magnetic velocity.

If the two frequencies are equal, being both generated by the highest rate of rotation mechanically safe, the two resultant frequencies will be 0 and $2p$.

This is the principle which it was proposed to utilise in the series of machines mentioned above as under discussion in 1892.

(3) This is not real doubling, but an addition of one to one, as can be proved by continuing the process and employing the frequency $2p$ as again a field magnet exciter; for, when an armature is revolving in front of that, the frequencies generated in that new rotor are $3p$ and p respectively (the sum and difference). Hence the progression is merely arithmetical, not geometrical. If, still further, the $3p$ is used as exciter, the frequencies appearing in a new rotor will be $4p$ and $2p$; and so on.

(4) The frequency 0 in the first rotor is of course not a current at all—though it sounds like a continuous current—but it is static magnetism, and may be said to correspond with the natural reaction between field magnet and armature, like that between a magnet and its keeper, when both are stationary.

(5) The $2p$ generated in the second armature as the difference between stator and rotor frequencies is likely to be opposite in phase to the $2p$ generated in the same armature as the sum of rotor and stator frequencies; and the two may therefore partially cancel each other. Similarly with other intermediate frequencies in the chain, each of which occurs twice over. The only unique currents will be the first and the last—the steady current in the magnets of the original exciter, and the highest frequency currents in stator and in rotor at the other end of the chain.

(6) The self-induction of the different coils, which would naturally cause lag and entail considerable complication and impedance, can be neutralised for any desired frequency by

the insertion of capacity in series ; so that the general equation for a circuit, with i as current,

$$L\ddot{i} + Ri + \frac{u}{S} = E \cos pt$$

becomes simplified, when the current is properly attuned to the driven frequency, *i. e.* tuned in such a way that $p^2 LS = 1$. It then, after a brief moment of growth, assumes the simple form

$$\dot{i} = \frac{E}{R} \cos pt ;$$

because the first and third terms neutralise each other under tuned conditions ; since then $\ddot{i} + p^2 u = 0$.

(7) If a current is started and stopped in such a circuit, its rise and fall are governed by the customary laws ; for it must be remembered that there are free oscillation terms in the complete solution which control the initial and final stages of such a maintained current, and that these are discarded from the permanent theory as being too rapidly evanescent to deserve much notice. The initial (and final) free oscillations are rapidly killed out of the complete solution of the above equation by an exponential time-coefficient involving $R/2L$, and forced oscillations alone survive. But the free are not wholly to be ignored, and in some cases may be found to give trouble. The current starting from zero, when it is attuned to the maintained oscillations and not over-damped, rises to its final stage according to the equation

$$\dot{i} = \frac{E}{R} (1 - e^{-\frac{Rt}{2L}}) \cos pt,$$

as clearly explained in Lord Rayleigh's 'Sound,' vol. i. §§ 47, 48. Hence, to attain rapid response, it may even be desirable to introduce a little extra resistance into some of the circuits, so as to diminish the time-constant $2L/R$ by which these momentary perturbations are regulated. It may be noted, as a practical consequence of the completer theory, that the frequency factors should be chosen with capacity large and inductance small ; for it is the latter factor alone that retards the attainment of the permanent state.

Of course a current takes time to develop in a circuit, even without any self-induction,—the velocity of light must be involved and a travelling wave-front ; but in ordinary practice these can safely be ignored.

(8) The current and the E.M.F will be in the same phase, and lag will be obliterated, if the precise frequency is maintained.

(9) The system is not self-exciting but requires an initial starting current or an excited magnet, without which the whole is inactive. The initial current supplies no energy however, and, if no variations were wanted, its place might be taken by a permanent magnet. All the effective energy of the system is derived from the mechanical rotation; and signalling can be managed by varying the exciting current.

(10) The original exciter may be either a steady current or a comparatively slowly alternating one, say of acoustic frequency. It might for instance be supplied through a microphone and be carved into fluctuations by speech, which could thus apparently be effectively magnified and indirectly transmitted to a distance. The frequency of the exciting stimulus is of no consequence so long as it is incomparably slower than any of the really high frequencies to which the circuits are tuned.

An exciting current of acoustic frequency, say 500 a second, is practically a steady stimulus of slowly varying strength during each half period; but the result of employing such a current as the stimulus may be the powerful emission of a note of 1000 per second, when the perfectly inaudible electric waves are collected and reinterpreted by some device.

(11) The neutralisation of self-induction by capacity applies not only to the whole of a circuit but to any part of it for which the condition corresponding to $p^2LS=1$ is satisfied; and the only obstacle in that part of a circuit is then its ohmic resistance, subject of course to any throttling or skin effect due to the most favourable automatic distribution of current in the substance of the conductor; a distribution which can be made virtually uniform by adequate subdivision, as by employing a cable composed of fine insulated wires. In so far as iron is used, the resistance term will contain eddy-current losses and hysteresis, which must be guarded against in known ways.

(12) That if to a circuit with one L and S in series, another L and S pair is added also in series, the natural frequency is unaltered; for though the resulting inductance is doubled, the resulting capacity is halved, and the product remains the same. The advantage of such a doubly-tuned circuit is that its parts are connected by nodes, to which anything can be attached without disturbance; for a pair of

nodes might even be short-circuited without altering the frequency of vibration.

(13) A tuned or resonant circuit can be maintained in vibration with very little power, the only expenditure of energy being that concerned with the dissipation term RC^2 , together with a similar expression for the energy radiated away which in the case of an open circuit may become important.

In some cases wave radiation is the thing desired, and in that case the expenditure in this way is useful dissipation, and the greater its proportional amount the higher the efficiency of the arrangement.

(14) That in an alternating dynamo, consisting of a rotor and a stator, so far as mutual action is concerned it does not matter which is which ; we are only concerned with the relative motion between the two, and each can react on the other by mutual induction.

Putting all these simple principles together, and providing both the rotor and the stator with as many tuned branch circuits as are required, Dr. Goldschmidt has designed his dynamo, whereby by mutual action and reaction between stator and rotor the frequency mounts to a level such that unavoidable hysteresis and other iron losses make further additions to it uneconomical or impracticable. And the highest frequency can be used for emission of waves.

In a machine which now exists at Slough, the revolutions being about 4000 a minute, the frequency attained directly by multiple poles and high speed rotation is 12,000 per second ; and this by action and reaction is multiplied by 4 ; thus emitting a wave from the aerial $6\frac{1}{4}$ kilometres or about 4 miles long.

A skeleton diagram of Dr. Goldschmidt's ingenious arrangement can be given thus : without any statement that those precise arrangements are necessarily adhered to. The rotor connexions are supposed to be made with slip rings as usual : the whole rotor, and whole stator, being of course connected up, and not a portion only as in the diagram.

An explanation is hardly necessary, since each branch circuit is labelled with the frequency-constant to which it is attuned, and nodes are plainly provided for the attachment

of capacity in series so as to raise the frequency in some branches.

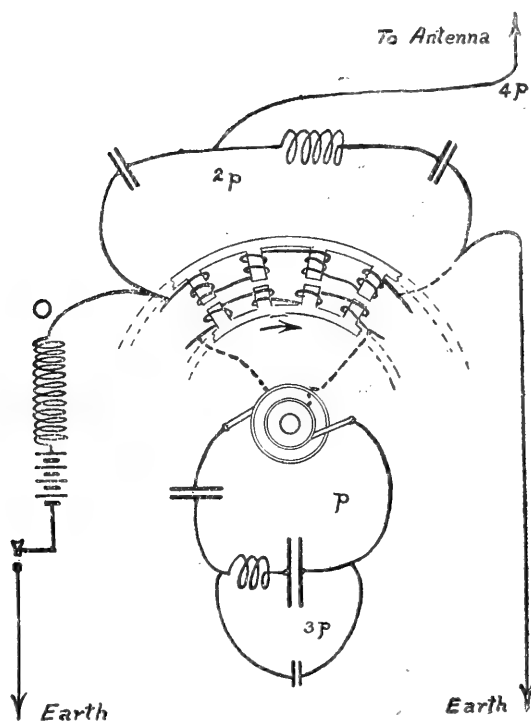


Diagram to illustrate principles used in the Goldschmidt Dynamo, not any actual arrangements.

Theory of the Goldschmidt Dynamo.

The theory as verbally explained in the preceding pages appears to be expressible by the two following equations, subject always to satisfaction of tuning conditions in every circuit so that the self-inductance and capacities neutralise each other throughout.

$$x = \frac{M}{R} \frac{d}{dt} (y \cos pt) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$y = y_0 + \frac{M}{R'} \frac{d}{dt} (x \cos pt), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x is the current in the rotor, y in the stator, and M is the amplitude of the mutual induction between them, *i. e.* the value when the poles are opposite each other. At other times the mutual induction is $M \cos pt$.

And since the currents are variable too, the above equations are justified. They look simple enough, but to solve

them generally is not easy ; though it appears physically necessary that

x must develop into a series of circular functions of odd multiples of pt , while

y develops into a similar series with even multiples of the same quantity.

The series may be stopped at any stage by ceasing to provide resonating circuits and permitting radiation and dissipation of energy.

To prove the above equations—remembering that they only have that simple form when tuned circuits are provided for every intended frequency—write the number of lines of force from stator to rotor as N ; and from rotor to stator as N' ; then the E.M.F. generated is dN/dt or dN'/dt respectively.

But $N=my$, and $N'=mx$,

and $m=M \cos pt$, *i. e.* is a sinuous function of time as the armature revolves.

Hence, if the rotor circuit resistance is R , while that of the stator is R' , and if the conditions of § (6) are satisfied,

$$x = \frac{E}{R} = \frac{1}{R} \frac{dN}{dt} = \frac{1}{R} \frac{d}{dt} (my) = \frac{M}{R} \frac{d}{dt} (y \cos pt).$$

Similarly, if y_0 is the stimulating current initially supplied to the stator, the current in it is

$$y = y_0 + \frac{M}{R'} \frac{d}{dt} (x \cos pt).$$

So they are proved. I have not yet succeeded in solving them generally, but it is not difficult to proceed by stages.

Working out of the Equations.

To deal with these equations easily, take them piecemeal, and apply them to say four provided branch circuits beside the original exciting circuit of stator. Two of these tuned circuits are connected to rotor, with resistances R_1 and R_3 , two with the stator, with resistances R_2 and R_4 . The latter circuit involves useful dissipation by radiation as well as all hysteresis and ohmic losses.

The initial current in stator being y_0 , the current first generated in rotor is

$$x_1 = \frac{1}{R} \frac{dN}{dt} = - \frac{pM}{R_1} y_0 \sin pt.$$

The current generated by reaction from this, back into the stator, is

$$\begin{aligned} y_2 &= \frac{M}{R_2} \frac{d}{dt} (x_1 \cos pt) \\ &= \frac{p^2 M^2}{R_1 R_2} y_0 \sin^2 pt - \frac{p^2 M^2}{R_1 R_2} y_0 \cos^2 pt \\ &= -\frac{p^2 M^2}{R_1 R_2} y_0 \cos 2pt. \end{aligned}$$

The current which this now generates in the rotor is

$$\begin{aligned} x_3 &= \frac{M}{R_3} \frac{d}{dt} (y_2 \cos pt) \\ &= \frac{p^3 M^3}{R_1 R_2 R_3} y_0 \cos 2pt \sin pt + \frac{2p^3 M^3}{R_1 R_2 R_3} y_0 \sin 2pt \cos pt \\ &= \frac{p^3 M^3}{R_1 R_2 R_3} y_0 \{\sin 3pt + \sin 2pt \cos pt\} \\ &= \frac{p^3 M^3}{R_1 R_2 R_3} y_0 (1\frac{1}{2} \sin 3pt + \frac{1}{2} \sin pt). \end{aligned}$$

The current which x_3 now generates in the stator is

$$\begin{aligned} y_4 &= \frac{M}{R_4} \frac{d}{dt} (x_3 \cos pt) \\ &= \frac{M}{R_4} \cos pt \cdot \frac{dx_3}{dt} - \frac{pM}{R_4} x_3 \sin pt \\ &= \frac{p^4 M^4}{R_1 R_2 R_3 R_4} y_0 \left\{ 4\frac{1}{2} \cos 3pt \cos pt + \frac{1}{2} \cos^2 pt - \sin 3pt \sin pt \right. \\ &\quad \left. - \sin 2pt \cos pt \sin pt \right\} \\ &= A \{ 4\frac{1}{2} \cos 3pt \cos pt - \sin 3pt \sin pt + \frac{1}{2} \cos^2 pt - \frac{1}{2} \sin^2 2pt \}. \end{aligned}$$

Employing the identity $\cos^2 A - \sin^2 B = \cos (A+B) \cos (A-B)$ this becomes

$$\begin{aligned} y_4 &= A (4 \cos 3pt \cos pt + \cos 3pt \cos pt - \sin 3pt \sin pt) \\ &= A (4 \cos 3pt \cos pt + \cos 4pt) \\ &= A \{ 2(\cos 4pt + \cos 2pt) + \cos 4pt \} \\ &= \frac{p^4 M^4}{R_1 R_2 R_3 R_4} y_0 (3 \cos 4pt + 2 \cos 2pt). \end{aligned}$$

Hence the *total* current in rotor is

$$x = x_1 + x_3 = y_0 \left\{ \frac{p^3 M^3}{R_1 R_2 R_3} \cdot \frac{3}{2} \sin 3pt + \frac{pM}{R_1} \left(\frac{p^2 M^2}{2R_2 R_3} - 1 \right) \sin pt \right\}; \quad (3)$$

and the *total* current in stator is

$$y = y_0 + y_2 + y_4 = y_0 \left\{ \frac{p^4 M^4}{R_1 R_2 R_3 R_4} 3 \cos 4pt + \frac{p^2 M^2}{R_1 R_2} \left(\frac{2p^2 M^2}{R_3 R_4} - 1 \right) \cos 2pt + 1 \right\}$$

Thus y_0 , the original exciting current, is a simple factor throughout; and the circular functions of even and odd multiples of pt , which on general grounds were expected, are obvious.

A rather more general treatment.

On showing this to my brother, Alfred Lodge, of Charterhouse, late of Coopers Hill, he pointed out that the neatest substitution would be

$$\theta = pt + \frac{1}{2}\pi,$$

so as to throw everything into the cosine form and get a general method of formation; subsequent re-interpretation being as follows:—

$$\cos \theta = -\sin pt; \quad \cos 3\theta = \sin 3pt;$$

$$\cos 2\theta = -\cos pt; \quad \cos 4\theta = \cos 4pt.$$

The terms in the pt formulæ will all be of the same sign, all the x series being in sines, and all the y series in cosines of multiples of pt ; while the θ formulæ are all in cosines, the signs of successive terms being alternately $+$ and $-$.

If all the coefficients affected with the $+$ sign are added together, their sum will always exceed the sum of the $-$ coefficients by unity; a fact which furnishes a check on arithmetical correctness.

To calculate successive x 's and y 's proceed thus:—

Write

$$\theta = pt + \frac{1}{2}\pi.$$

Then

$$x_1 = \frac{M}{R_1} \frac{d}{dt} (y_0 \cos pt) = \frac{pM}{R_1} \frac{d}{d\theta} (y_0 \sin \theta)$$

$$= c_1 y_0 \cos \theta.$$

$$y_2 = \frac{pM}{R_2} \frac{d}{d\theta} (\sin \theta \cdot x_1) = c_1 c_2 y_0 \frac{d}{d\theta} \left(\frac{1}{2} \sin 2\theta \right)$$

$$= c_1 c_2 y_0 \cos 2\theta.$$

$$\begin{aligned} x_3 &= \frac{pM}{R_3} \frac{d}{d\theta} (\sin \theta \cdot y_1) = c_1 c_2 c_3 y_0 \frac{d}{d\theta} (\sin \theta \cdot \cos 2\theta) \\ &= c_1 c_2 c_3 y_0 \cdot \frac{1}{2} \frac{d}{d\theta} (\sin 3\theta - \sin \theta) \\ &= \frac{1}{2} c_1 c_2 c_3 y_0 (3 \cos 3\theta - \cos \theta). \end{aligned}$$

Let us ignore $c_1 c_2 c_3 \dots y_0$ for the present. They evidently come in as multiples only.

$$\begin{aligned} y_4 &= \frac{1}{2} \frac{d}{d\theta} (\sin \theta \cdot 3 \cos 3\theta - \sin \theta \cos \theta) \\ &= \frac{1}{4} \frac{d}{d\theta} (3 \sin 4\theta - 4 \sin 2\theta) \\ &= \frac{1}{4} (3 \times 4 \cos 4\theta - 4 \times 2 \cos 2\theta) \\ &= 3 \cos 4\theta - 2 \cos 2\theta. \end{aligned}$$

Now suppose this is $A_4 \cos 4\theta - B_4 \cos 2\theta$.

$$\begin{aligned} x_5 &= \frac{d}{d\theta} \sin \theta (A_4 \cos 4\theta - B_4 \cos 2\theta) \\ &= \frac{1}{2} \frac{d}{d\theta} \{A_4 \sin 5\theta - (A_4 + B_4) \sin 3\theta + B_4 \sin \theta\} \\ &= \frac{1}{2} \{5A_4 \cos 5\theta - 3(A_4 + B_4) \cos 3\theta + B_4 \cos \theta\} \\ &= \frac{1}{2} (15 \cos 5\theta - 15 \cos 3\theta + 2 \cos \theta). \end{aligned}$$

Call this $A_5 \cos 5\theta - B_5 \cos 3\theta + C_5 \cos \theta$, and note that this makes $A_5 - B_5 + C_5 = A_4 - B_4 = 1$.

Similarly

$$\begin{aligned} y_6 &= \frac{1}{2} \{6A_5 \cos 6\theta - 4(A_5 + B_5) \cos 4\theta + 2(B_5 + C_5) \cos 2\theta\} \\ &= 3A_5 \cos 6\theta - 2(A_5 + B_5) \cos 4\theta + (B_5 + C_5) \cos 2\theta \\ &= \frac{1}{2} (45 \cos 6\theta - 60 \cos 4\theta + 17 \cos 2\theta). \end{aligned}$$

Also

$$\begin{aligned} x_7 &= \frac{1}{4} \{45 \times 7 \cos 7\theta - 105 \times 5 \cos 5\theta + 77 \times 3 \cos 3\theta - 17 \cos \theta\} \\ &= \frac{1}{4} \{315 \cos 7\theta - 525 \cos 5\theta + 231 \cos 3\theta - 17 \cos \theta\}, \end{aligned}$$

and

$$\begin{aligned} y_8 &= \frac{1}{8} \{315 \times 8 \cos 8\theta - 840 \times 6 \cos 6\theta + 756 \times 4 \cos 4\theta \\ &\quad - 248 \times 2 \cos 2\theta\} \end{aligned}$$

$$= 315 \cos 8\theta - 630 \cos 6\theta + 378 \cos 4\theta - 62 \cos 2\theta,$$

with multiplier $c_1 c_2 c_3 c_4 c_5 c_6 c_7 c_8 y_0$.

Note that $315 + 378$ exceeds $630 + 62$ by unity ; also that

$$A_8 = 1 \times \frac{3}{2} \times 2 \times \frac{5}{2} \times 3 \times \frac{7}{2} \times 4 = 8 \div 2^7.$$

Continuing, we find that the positive coefficients for x_9 are the halves of 2835, 5040, and 62 ; while the negative ones are the halves of 6615 and 1320.

For y_{10} the positive coefficients are the halves of 14175, 34965, and 1382 ; while the negative ones are the halves of 37800 and 12720.

The law of formation of the terms is fairly simple :—
Thus let

$$u_{n-1} = A_{n-1} \cos (n-1)\theta - B_{n-1} \cos (n-3)\theta \\ + C_{n-1} \cos (n-5)\theta - + \dots,$$

then

$$u_n = \frac{1}{2} \{ A_{n-1} \cdot n \cos n\theta - (A_{n-1} + B_{n-1})(n-2) \cos (n-2)\theta + \\ = A_n \cos n\theta - B_n \cos (n-2)\theta + - \dots$$

multiplied in each case by $y_0 c_0 c_1 c_2 \dots$; the last factor being c_n in the case of y_n . Also $A_n = n! \div 2^{n-1}$.

A few minor considerations applicable in a 4 circuit machine.

In first writing down the general equations (1) and (2) for the arrangement diagrammatically illustrated above, the fact that the different branch circuits may have different resistances was ignored. No principle is thus neglected, and general solution is made easier. The only resistance which is not unimportant or unessential from the point of view of radiation is the last of the series, R_4 , which ought to be large compared with the others.

The constant which characterizes every expression is of the form pM/R , the frequency-constant multiplied by the mutual time-constant of each circuit. There are 4 circuit branches altogether, besides the steady exciting-current circuit of the stator ; the circuits of the rotor have been called R_1 and R_3 , those of the stator have been called R_2 and R_4 ; the latter circuit involves useful dissipation by radiation as well as all hysteresis and ohmic losses.

Thus to summarise sufficiently, ignoring differences in R for the moment, call $pM/R=c$, for all four circuits.

$$x=y_0\{\frac{3}{2}c^3 \sin 3pt + c(\frac{1}{2}c^2-1) \sin pt\} \quad . \quad . \quad (3')$$

$$y=y_0\{3c^4 \cos 4pt + c^2(2c^2-1) \cos 2pt + 1\}. \quad . \quad (4')$$

There are really four characteristic constants

$$\frac{pM}{R_1}, \quad \frac{pM}{R_2}, \quad \frac{pM}{R_3}, \quad \frac{pM}{R_4},$$

which we may denote by c_1, c_2, c_3, c_4 , respectively, and so can write the values

$$x=c_1y_0\{\frac{3}{2}c_2c_3 \sin 3pt + (\frac{1}{2}c_2c_3-1) \sin pt\} \quad . \quad . \quad (3'')$$

$$y-y_0=c_1c_2y_0\{3c_3c_4 \cos 4pt + (2c_3c_4-1) \cos 2pt\}. \quad . \quad (4'')$$

To cancel the p frequency, c_2c_3 must equal 2, or $p^2M^2=2R_2R_3$.

To cancel the $2p$ frequency, c_3c_4 must equal $\frac{1}{2}$, or $p^2M^2=\frac{1}{2}R_3R_4$.

To cancel both, $2R_2R_3$ must equal $\frac{1}{2}R_3R_4$, or $R_4=4R_2$.

It is not likely that these cancelling conditions can be satisfied; nor is it at all certain that it would be desirable to satisfy them, since possibly if any intermediate step were omitted the graduated rise of frequency might cease. But the partial cancelling of merely auxiliary currents is of interest, and ought to have some effect in reducing unnecessary iron losses. The highest frequency losses are inevitable, and the limit of practicable frequency will be reached when hysteresis and other such losses become too prominent in comparison with what is available for radiation. But it must always be remembered that the shorter the wave the more powerful is the emission; and so, presumably, the shorter the wave the more vigorous would be the reception at a distance, save for difficulties connected with transmission and accidents by the way.

PART II. ON THE TRANSMISSION OF WAVES IN AIR.

The rate of emission of energy from an aerial was calculated by FitzGerald for a magnetic radiator in 1883, and by Hertz for an electric one in his great paper of 1888. Hertz's

result is that the loss of energy per half swing is

$$\frac{8\pi^4 e^2 l^2}{3K\lambda^3}$$

and the loss per second therefore

$$\left(\frac{2\pi}{\lambda}\right)^4 \cdot (el)^2 \cdot \frac{v}{3K} = \text{energy radiated per second}$$

by an electric radiator of moment el . It is easy to get this by integrating the flow of energy per unit area, $EH/4\pi$, all over the surface of a large sphere.

For a magnetic or closed circuit radiator, of moment μnAC , a similar expression can be written with v/μ instead of v/K .

This may be thrown into various convenient forms (see Lodge and Howard, *Phil. Mag.* July 1889), and the form I prefer in practice is in terms of the mean square of current supplied to the aerial :

$$\begin{array}{l} \text{Radiation Power} \\ \text{in kilowatts} \end{array} = 4 (\text{amperes})^2 \left(\frac{\text{height}}{\text{wave-length}} \right)^2 \dots (5)$$

because the current in an aerial can be measured with an ammeter—if necessary a sensitive hot-wire instrument heavily shunted,—and the radiation power can thus be calculated. Another way of measuring the current would involve the use of a flowing-water calorimeter; which I propose to try for this purpose.

The main uncertainty about the data is an estimate of the effective height of the upper capacity area which shall properly enter as a factor into the aerial's electric moment el ; unless indeed there is also a lower capacity area thoroughly insulated from the ground: for the effective height must partly depend on the perfection or imperfection of the earth-connexion and the quality of the soil. If the earth were a perfect conductor the effective height would be twice the apparent height. In practice there is generally some intermediate value characteristic of the circumstances of the station.

To establish the above very handy expression for the energy actually radiated per second, proceed thus:—

The magnetic field close to a linear Hertz oscillator is

$$H = \frac{eln}{r^2} \cos nt \sin \theta;$$

which corresponds to an oscillating current of strength $en \cos nt$ and length l .

The current amplitude is therefore

$$C_0 = en = \frac{2\pi e}{T} = \frac{2\pi ev}{\lambda}.$$

The average current depends on how it is measured ; its square may be $\frac{1}{2}C_0^2$. But if it is considered as the quantity passing in half a swing, $C = e/\frac{1}{2}T$, the radiation expression becomes

$$\frac{16\pi^4 e^2 l^2 v}{3K\lambda^4} = \frac{4\pi^4 C^2 l^2}{3Kv\lambda^2} = \frac{400 \mu v C^2 l^2}{3\lambda^2} = \frac{400 \times 10^{10} \mu C^2 l^2}{\lambda^2} \text{ ergs per sec.}$$

But in electromagnetic measure the unit of current is 10 amperes, and 10^{10} ergs per second is a kilowatt, so the formula for radiation power is proved; and the true radiation (subject to correction for the numerical factor) is

$$4 \times (\text{mean amperes})^2 \times \frac{l^2}{\lambda^2} \text{ kilowatts, . . . (5)}$$

l being the effective height, or linear factor of the electric moment, of the radiator.

There are many circumstances which it would seem necessary to take into account besides those which appear in this formula. Capacity, for instance, and self-induction, and arrangement of antenna generally. But they are all implicitly involved in the wave-length, and there is no need specially to attend to them except in considering the design of an antenna. For that purpose it must be remembered that in true waves the electric and magnetic energies are equal, and in any region where they are not equal the excess of one is useless for wave emission. At great distances the electric and magnetic intensities are necessarily and automatically equal, because any other part of the energy has returned to the oscillator and is promoting persistence of vibration, which in the case of shock-excitation is a useful thing to do.

But to determine the conditions which assist radiation we may calculate separately the electric and magnetic intensities at points on the equator fairly near the oscillator, within say a quarter wave-length ; or perhaps most simply at the critical distance $r = \lambda/\pi\sqrt{2}$, characterized by $m^2 r^2 = 2$, the place at which progressive radiation really begins.

It is manifest that the shorter the wave-length the stronger will these intensities be, and hence the stronger the radiation, other things being equal ; for the radiation through unit area at every place is by Poynting's theorem $\text{EH}/4\pi$.

Consider therefore the circumstances on the equator of a

Hertz oscillator in general. The electric field is there all axial, and is given by

$$E = \frac{el}{Kr^3} \left\{ (1 - m^2 r^2) \sin (mr - nt) - mr \cos (mr - nt) \right\},$$

which may be written with a phase angle $(mr - \phi)$ and a clearly expressed amplitude, thus:—

$$E = \frac{el}{Kr^3} \sqrt{(1 - m^2 r^2 + m^4 r^4)} \sin \{nt - (mr - \phi)\},$$

where $\tan \phi = \frac{mr}{1 - m^2 r^2}.$

The magnetic intensity at the same place lies along the equator and is

$$H = \frac{elmn}{r} \left\{ \sin (mr - nt) + \frac{\cos (mr - nt)}{mr} \right\};$$

or, rewriting it,

$$H = \frac{eln}{r^2} \sqrt{(1 + m^2 r^2)} \sin \{nt - (mr + \phi')\},$$

where $\tan \phi' = \frac{1}{mr}.$

So at a distance $r = \lambda/\pi\sqrt{2}$, or $\lambda/4.4$, the amplitude of the electric intensity is

$$E_0 = \frac{el}{Kr^3} \sqrt{(1 - 2 + 4)} = \frac{el\sqrt{3}}{Kr^3},$$

while the magnetic amplitude is

$$H_0 = \frac{eln}{r^2} \sqrt{(1 + 2)} = \frac{enl\sqrt{3}}{r^2}.$$

Expressing these in terms of current amplitude, whose value may be written alternatively

$$C_0 = en = \frac{2\pi e}{T} = \frac{2\pi ev}{\lambda} = emv,$$

we get, at a distance such that $mr = \sqrt{2}$ or $r = \lambda/\pi\sqrt{2}$,

$$H_0 = \frac{\sqrt{3} \cdot C_0 l}{r^2} = \frac{\sqrt{12} \cdot \pi^2 l C_0}{\lambda^2},$$

$$E_0 = \frac{\sqrt{3} \cdot l}{Kr^3} \cdot \frac{C_0}{mv} = \frac{\sqrt{3} \cdot l \cdot m^2 C_0}{2^{\frac{3}{2}} K v} = \frac{\sqrt{6} \cdot \pi^2 l \mu v C_0}{\lambda^2}.$$

To express C_0 in magnetic units we take μ as 1, and to express E_0 in electrostatic units we divide by v .

Consequently, in the units most convenient,

$$E_0 = \sqrt{\frac{3}{2}} \cdot \frac{C_0 l}{r^2}$$

while $H_0 = \sqrt{3} \cdot \frac{C_0 l}{r^2}.$

Thus for a simple vertical linear oscillator, the magnetic force somewhat exceeds the electric in the region where waves begin. Hence anything which tends to increase the electric force, such as a tilted capacity area or the like, will assist radiation in one general direction:—as initiated by Dr. de Forest in 1904, introduced by Mr. Marconi in 1905, and described by him to the Royal Society on 22 March, 1906 (Proc. Roy. Soc.).

Design of Aerial.

The necessity for superposed electric and magnetic fields, and the fact that radiating power is their vector product, at right angles to the plane of both, explains the main behaviour of directive antennæ. A linear Hertz vibrator, for instance, gives no axial radiation for two reasons, (1) because there is no magnetic field at the axis, and (2) because the electric force there is “end-on,” so to speak, and could not contribute to axial radiation anyhow. So also in the case of a closed-circuit oscillator, say a large plane coil of one turn; though the magnetic force along the axis is strong, its direction prevents its contributing to axial radiation. Hence if a linear and a closed-circuit oscillator are combined, as they practically are in a Γ shaped aerial, especially when the upper arm is very long, the fore and aft radiation in the plane of the Γ , notably that in front of the vertical part, will be copious compared with that in a perpendicular direction; and the interesting figure-of-8 equal-intensity region, detected by Mr. Marconi and his staff, is a consequence.

All increase of capacity combined with height, in the aerial, goes to increase both the electric and the magnetic fields at a distance, and therefore will be advantageous (though expensive) notwithstanding the concurrent increase of wave-length. In fact free capacity and height afford two separate means of increasing wave-length without diminishing the power of emitting radiation; while both together increase that power; for radiation is proportional to the square of SVl/λ^2 , and λ^2 is proportional to S and also to l if the radiator is straight.

But insertion of inductance coils in the aerial will have
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the effect of lengthening the wave without strengthening the field at a fixed distance, and so must act deleteriously on radiation intensity; though such coils will promote persistent oscillation and tuning, and may therefore be advantageous up to a point. Their use will always be of the nature of a compromise; and this whether they are actually inserted in the aerial or are inductively associated with it: so they should be kept to a reasonable minimum.

In an umbrella aerial whose ribs approach the ground, charge from the region of greatest capacity has to ascend before descending; wherefore it fails to exert full magnetic force at a distance, and conserves some energy which it might radiate, thereby becoming more capable of tuning. The amount of potential tuning necessary or desirable in an antenna must depend on the method of excitation. With shock-excitation some amount of it is essential; with maintained waves it appears to be unnecessary; and accordingly in the latter case the more closely an antenna can approach to a simple Hertz oscillator—a copious radiator and absorber—the better; some kind of directivity being a still further improvement when circumstances allow.

A practical remark may here be interpolated:—The importance of great height for the upper capacity area is so striking, and the trouble and expense of securing it by artificial structures so obvious, that I doubt if sufficient attention has been paid—in the selection of a long-distance site—to the possibility of finding a mountain or rock of sufficiently non-conducting material to serve as the supporter of the upper part of an antenna for a station at its base. Experience would be necessary to ascertain whether the surgings in such a hill, or pair of twin hills, need be any more deleterious to efficient radiation and reception than they are in the iron of the Eiffel Tower, for instance.

Magnetic Radiation.

A magnetic radiator only differs from an electric radiator in having as moment a current area instead of a pair of separated charges; *i. e.* μAC instead of el .

So if the value of C is made to correspond with en , which would usually mean a very strong current since n is very great, the two radiators would be equally effective when AC in magnetic measure equals el in electric; in other words when

$$2\pi A = l\lambda,$$

i. e. in the case of a Γ aerial, when the efficient length of upper arm equals $\lambda/2\pi$.

To see what $C=en$ means. Write $e=SV$.

Let S be comparable to Kl' , that is let it correspond to a capacity area not greatly differing from the height of the aerial in linear dimensions, and let V correspond say to nearly an inch spark, say 60,000 volts or 200 electrostatic units. Then

$$\begin{aligned} C &= nSV \\ &= \frac{2\pi}{T} \cdot \frac{l'}{v^2} \cdot 200 v \text{ magnetic units} \\ &= \frac{4000 \pi l'}{\lambda} \text{ amperes.} \end{aligned}$$

If l' is 200 metres and $\lambda = 4$ kilometres, $C=600$ amperes.

It is noteworthy, though now familiar, how strong a current amplitude is readily produced by a disruptive discharge.

Arguments for use of long waves.

Although short waves have so many advantages, they need not be as efficient as long ones at really great distances if they have to overcome obstructions or opacities in the atmosphere. For when it comes to transmitting waves near the surface of the earth, the simple theory of unimpeded etherial transmission is no longer sufficient. Earth conduction and air conduction become of the essence of the phenomenon, and many complications may happen to the waves, some of which have attracted the attention of mathematicians—notably at present Professor Zenneck, who has dealt elaborately with the problem of earth and sea conduction in his important paper in the *Annalen der Physik*, vol. xxiii. page 846, 1907; summarised or translated by Professor Fleming in 'Engineering' for June 4th and 11th, 1909, and also in the 1910 edition of his book. His treatment of the effect of earth-surface conductivity seems very thorough, but as regards the effect of aerial conductivity our knowledge is still slight.

The reason of the observed obstructive influence of sunshine is not yet clearly known; but if the opacity of ordinary air due to observed ionization is calculated from recognized data, it appears to be by no means sufficient to account for the observed effect by simple obstruction: though the surprisingly high conductivity of rarefied air in the absence of electrodes must not be forgotten.

On the whole it seems probable that the difficulty of transmission by day must be due to something happening in the upper conducting layer of the atmosphere. I assume that grazing reflexion from this layer must usually assist transmission. If the transition of density is sudden, the layer will

constitute a better reflector than if it were gradual ; and if it were not sudden enough, either greater power or longer wave-length would help to overcome the difficulty. If, however, under the influence of rising sunlight or heat the reflecting layer should become puckered, so as to offer something nearer normal incidence to approaching waves,—thereby letting them escape into space,—no increase of power alone will do very much towards remedying the evil ; and increased wave-length may become a necessity.

To examine this whole question further :—

An absorbed plane wave equation is

$$\frac{d^2F}{dr^2} = \mu K \frac{d^2F}{dt^2} + \frac{4\pi\mu}{\sigma} \frac{dF}{dt};$$

and for a solution there are two extreme cases according to whether a critical number

$$\frac{4\pi}{\sigma p K} \quad \text{or} \quad \frac{4\pi v^2 \mu T}{2\pi \sigma} \quad \text{or} \quad \frac{2v\lambda}{\sigma/\mu}$$

is small or large. (See for instance Lodge “ On Opacity ” in *Phil. Mag.* for April, 1899.)

Now the ionization of sun-lighted air under some conditions has been estimated as 10^{-12} of the total number of molecules present : if so it will have a specific resistivity

$$\sigma = 2 \times 10^{20} \mu \text{ sq. centimetres per second.}$$

In that case the critical number will be small, being of the order 10^{-5} for a wave comparable with a kilometre in length.

The form of solution applicable in that case is

$$F = F_0 e^{-\frac{2\pi\mu v}{\sigma} r} \cos(mr - pt).$$

So the distance required to reduce the amplitude of these true waves to $1/eth$ would then be independent of the frequency, *i. e.* would be the same for waves of any length, and its value is

$$r_1 = \frac{\sigma}{2\pi\mu v}.$$

Inserting the above estimate of σ for ionized air, this comes out

$$\begin{aligned} r_1 &= \frac{1.8 \times 10^{20}}{18 \times 10^{10}} = 10^9 \text{ centimetres} \\ &= 10,000 \text{ kilometres.} \end{aligned}$$

The ionization and conductivity of air encountered by the waves must therefore manifestly be greater than that—*i. e.* the resistivity must be smaller than 10^{20} c.g.s.—if the atmosphere is to stop waves by sheer opacity.

But for a conductivity like that of sea-water (which may well be reached and considerably exceeded in the atmosphere, even without special ionization, by mere reduction of density, at the best conducting horizontal level—at least when the electric force surpasses a certain critical intensity below which even rarefied air must insulate unless ionized—),

say $\sigma = 3 \times 10^{10} \mu$ sq. centimetres per second,
the critical number,

$$\frac{2v\lambda}{\sigma/\mu} = \frac{2\lambda}{1 \text{ centimetre}},$$

is certainly big; and in that case the other or diffusion solution applies, namely

$$F = e^{-\sqrt{\left(\frac{2\pi\mu p}{\sigma}\right)r}} \cos \left\{ pt - \sqrt{\left(\frac{2\pi\mu p}{\sigma}\right)r} \right\};$$

and the distance for reduction of amplitude to $1/e$ th of its value would then depend on the frequency, for it is

$$r_1 = \sqrt{\left(\frac{\sigma}{2\pi\mu p}\right)} = \frac{1}{2\pi} \sqrt{\left(\frac{\sigma\lambda}{\mu v}\right)} = \sqrt{\left(\lambda \times \frac{1}{40} \text{ centim.}\right)}.$$

For a 4 kilometre wave this distance is 1 metre; and the absorption constant varies inversely with the square root of the wave-length. Differently sized waves, moreover, would travel at different rates; and accordingly the trouble of *distortion*, so familiar in cables, would be introduced by high atmospheric conductivity. But we have no knowledge of the actual existence of such conductivity except at great elevation, where, if it formed a sharply defined smooth horizontal layer it would be a help, not a hindrance, and would assist in overcoming the curvature of the earth—either for the mirage-like reason suggested by Dr. Eccles or by still more simple reflexion.

A law of absorption dependent on the inverse root of the wave-length has been suggested by observation; and such a law indicates greater effective conductivity in the general atmosphere than is usually considered likely.

Connexion between Ionization and Conductivity.

It may be convenient here to write out the connexion between ionization and conductivity for air, as ordinarily treated electrolytically.

Let n be the number of ions of one sign per c.c. supposed equal, e the charge on each, and u ($=u+v$) their combined velocities.

The intensity of current, $\frac{\text{current}}{\text{area}} = i = neu$.

The dissociation ratio n/N we may call k , N being the

total molecules per c.c. ; and by Professor Townsend's measurements the value of N_e for air at ordinary pressure and temperature is 1.22×10^{10} E.S. units per c.c., or $\cdot 41$ E.M. units. So, since $e = 4.65 \times 10^{-10}$ E.S. units, $N = 2.6 \times 10^{19}$.

The speed of ions in air at ordinary pressure, when urged by a force X , has been measured, and is given by

$$u_1 = \frac{u+v}{X} = 420 + 510 = 930 \text{ centim. per sec. per unit E.S.F.,}$$

$$= 3.1 \text{ centim. per second for a gradient of 1 volt per centim.}$$

It is found that over a considerable range of pressure u_1 varies inversely with the concentration, or Nu_1 is constant. So, from the above data, $Neu_1 = 4.1 \times 3.1 = 13$ amperes per square centimetre when driven by a volt per centimetre. The intensity of current $i = kNeuX$, so the specific conductivity

$$\frac{i}{X} = \frac{1}{\sigma} = kNeu,$$

and
$$\frac{1}{k\sigma} = 13 \frac{\text{amperes}}{\text{sq. centimetre}} \div \frac{1 \text{ volt}}{\text{centimetre}}.$$

Hence
$$\sigma = \frac{1}{13k} \text{ ohm centimetre, or } \frac{10^9}{13k} \text{ c.g.s.}$$

and the number of ions per c.c. is

$$n = kN = \frac{2.6 \times 10^{19} \times 10^9}{13\sigma} = \frac{2}{\sigma} \times 10^{27}$$

when σ is expressed in absolute c.g.s. units.

At really low pressures, comparable with a millimetre of mercury or less, the mobility of ions is much greater than what is here dealt with. Besides, all this refers to atomic or molecular ions, *i.e.* to electrolytic conduction, and does not take into account the far greater mobility of free electrons, even though they be only momentarily or transitionally or potentially free. It seems possible that some writers, in considering the opacity of air, may have been satisfied with the known kinds of ion for which data were available ; and that the presence of free electrons in the upper regions would give a much higher conductivity than has been suspected. It can hardly be doubtful that electrons are directly supplied to the upper air, in the form of β rays from the sun.

Ionization Causes.

With reference to the likely amount of ionization in the upper atmosphere, I doubt if sufficient attention has been paid to the positive charges presumably received from the sun. If the sun is radioactive it probably emits α as well as

β rays ; and though the β rays, being most penetrating, seem to have been most studied, the α particles may be really more important. The β rays will tend to be magnetically deflected towards the poles, presumably returning along upper strata ; the α particles will travel with the beam of light and will be stopped in the upper regions of the atmosphere, where they will tend to accumulate. If any γ rays exist in solar radiation,—and if β rays escape from the solar atmosphere surely γ rays will—they will exert a deep-seated effect on our atmosphere ; and a horizontal beam of them might produce a fairly vertical stratum of ionized air, such as would constitute a fairly effective screen or obstacle to waves which are dependent on reflexion from an upper region for their advance.

Living under a reflecting dome it is natural that there should be occasional local concentration of signals, and that the varying shape and quality of the dome should greatly influence the signals locally received. Earth or sea conductivity has its more uniform effect, and assuredly conveys some part of the signals ; but sea-water conduction is not likely to be the cause of capriciousness in signalling, nor would it contribute to daylight effects, nor to those specifically observed at sunrise and sunset. All those must be due to atmosphere.

As regards practical telegraphy—on which here I am only touching very incidentally—it by no means follows that earth conduction and earth tapping ought not to be more employed for signalling purposes than they are ; perhaps already they are giving more assistance to long-distance signalling than is recognized. It is quite possible that, by the aid of electric vibrations maintained in the earth's crust, aerial or Hertzian waves may ultimately be dispensed with, and something less liable to stray or varying atmospheric influences be employed. The trouble of *distortion*, to which this method would be liable, could be overcome by emitting only a single pure wave. Meanwhile, and so long as Hertzian waves are used, it is safe to say that if by reason of inequalities at sunrise the best conducting layer of the atmosphere becomes corrugated or bent, it is quite likely to divert a good deal of radiant energy which at sufficiently oblique incidence would be reflected : and it would be most deadly to the shorter waves. Also, the effect of a vertical conducting layer, or of corrugations in a horizontal one, would be likely to be felt most when they were moderately near a sending or a receiving station, and would probably be less noticeable when the abnormalities were diffused over the half-way region ; though

an observation of Mr. Marconi in a Royal Institution lecture to the effect that the signals were weakest between Clifden and Glace Bay when the boundary between day and night was half-way across the Atlantic, tends to negative and reverse this idea.

If anything like a vertical reflector existed behind a sending station (as just before sunrise, for instance) it might lead to a temporary intensification of distant response. Furthermore, any kind of opacity which increased with the intensity of radiation,—and we shall proceed in a sequel to consider such kinds,—would be more effective near a sending than near a receiving station. The fact that sunrise or sunset at either station—*i.e.* a horizontal beam—is specially effective, whether as assistance or as obstruction, and the maxima and minima which then occur, are very suggestive. For facts of observation, see first the original discovery by Mr. Marconi of the effect of sunshine, in the course of his fine experiment of sending Hertz waves across the Atlantic and detecting them at different distances and under different conditions all the way across; as described by him in *Proc. Roy. Soc.* June 1902; also his Nobel Prize lecture, December 1909, quoted by Fleming, ‘Wireless Telegraphy,’ p. 826 (1910 edition). On the same subject Mr. Pickard made observations in America, which are quoted by Professor Pierce in his book on *Wireless Telegraphy*, page 135; Dr. Austin, of the U.S. Naval Wireless Department, made important measurements in 1910 which are quoted in Erskine Murray’s book, page 298 of the 1913 edition. In this book indeed there is a general discussion of the whole subject, with a summary of practical experience; and there are doubtless other data now available. Some recent ones by Messrs. Round and Tremellen are recorded in the ‘Marconigraph’ of November 1912, where also a British Association discussion at Dundee is reported. Special attention must be called to the Addresses of Prof. Fleming and Dr. Eccles reported in *Nature*, xc. p. 262, and in *Electrician*, 27 Sept. 1912; also to Dr. Eccles’ paper in *Proc. Roy. Soc.* June 1912.

I see that Professor Zenneck in his important paper in the *Annalen der Physik*, vol. xxiii. p. 862, makes a very low estimate of the conductivity of ordinary air, and doubts if it can effectively obstruct the passage of waves. But the fact which he notes, that mist-laden air is more transparent to long-distance signalling than clear air, speaks powerfully in favour of the hostile influence of ionic conduction, or at least of the adverse influence of free electric charges; since in mist the ions would have moisture condensed round them, and would therefore be loaded so as to destroy the ready

mobility on which conducting power, or any influence which they could exert, must depend. Thus whether ions act by ordinary conductivity, or in some other way such as is considered below, we can at least say that opacity and conductivity are similarly affected, both being reduced by the presence of mist.

Going back to the opacity equation, pp. 776, 7, and its two cases there considered, there is one intermediate possibility; namely that the resistivity of the medium might sometimes have a value such as would make the critical number neither large nor small, but say unity. We may consider what will happen then.

If $4\pi/\sigma pK$ is to be 1, it follows that $\sigma = 2\mu v\lambda$; or, for a kilometre wave, that σ is of the order

$$6 \times 10^{15} \mu \text{ sq. centimetres per second.}$$

This appears a very possible value for rarefied air;—indeed Dr. Schuster has estimated that, at a height of 100 kilometres, atmospheric conductivity is of the order 10^{-13} c.g.s., equivalent to 10,000 ohms per c.c., in order to satisfy the requirements of his theory of magnetic variations;—and in that case we must use the general solution

$$F = F_0 e^{-\alpha r} \cos(pt - \beta r)$$

$$\text{with } \alpha^2 \text{ or } \beta^2 = \frac{1}{2} \mu K p^2 \left\{ \sqrt{1 + \left(\frac{4\pi}{\sigma p K} \right)^2} \mp 1 \right\}.$$

Or calling the critical constant c ,

$$\alpha = \frac{\pi}{\lambda} \left\{ 2\sqrt{1 + c^2} - 2 \right\}^{\frac{1}{2}}$$

$$\text{while } \beta = \frac{\pi}{\lambda} \left\{ 2\sqrt{1 + c^2} + 2 \right\}^{\frac{1}{2}}.$$

These are general values; so, taking c unity, as the special case we are now considering, we get

$$\alpha = \sqrt{(2\sqrt{2} - 2)} \frac{\pi}{\lambda} \doteq .9 \frac{\pi}{\lambda},$$

$$\beta = \sqrt{(2\sqrt{2} + 2)} \frac{\pi}{\lambda} \doteq 2.1 \frac{\pi}{\lambda}.$$

Hence, with the intermediate value for σ , the distance for reduction of amplitude to $1/e$ th is comparable with the wavelength; being, in the special case just written, about $\lambda/3$. The absorption constant begins in this case to be inversely as the root of the wave-length, and there is incipient departure from true wave propagation.

Any local approach to such atmospheric conductivity as belongs to the intermediate case,—for instance by the stirring

up of some highly ionized layer by convection currents,—would amply account for serious obstruction to any but the longest waves.

Other Causes of Atmospheric Opacity.

Apart from what is caused by regular electric conductivity in the ordinary way, there is another possible kind of opacity, due to a curious and unexpected effect of radiation on electrons, discovered mathematically as far as I know by Sir J. J. Thomson in 1902, and contained in his paper "On the Emission of Negatively Electrified Corpuscles by Hot Bodies," in the *Philosophical Magazine* for August 1902 (ser. 6, vol. iv. p. 258). This paper appears to have attracted very little attention, though it is referred to by Professor Fleming in his comprehensive treatise on *Wireless Telegraphy*, 1910 edition, page 824.

The foundation of it is the action of etherial waves in propelling or sweeping up electrified particles in the direction of wave propagation, thereby communicating to them energy which presumably must be taken from the available energy of the waves ; though the author of the theory does not seem to attach importance to this process as an absorber of energy, nor to contemplate it from that point of view. He directs attention to another and more ordinary kind of opacity, due to the scattering of radiation by corpuscles over which the waves are passing. So far as *light* is concerned, this process is indeed likely to be more effective than the other as a disperser of radiant energy, though it leaves the energy in the ether and does not transfer it to particles of matter. The radiation scattered by the particles should be polarized, as all light reflected from small particles is, and Sir J. J. Thomson calculates the coefficient of absorption due to this kind of scattering, as

$$\frac{4\pi\mu^2Ne^4}{3m^2}.$$

This therefore is independent of wave-length, but must always be very small, even when the ions are electrons, because the fourth power of ionic charge occurs in the numerator. The ionization might be great, say a million electrons to the cubic centimetre, and yet the above absorption-coefficient would be only of the order 10^{-20} per centimetre. This is insignificant of course for all terrestrial distances, but in the depths of space it seems likely to have an effect of some importance, not indeed as destroying energy in the ether, but as ultimately converting transparency into translucency.

What the ionization of interstellar space is I have no

idea, but assuming there may be no more than four stray electrons on the average to the cubic centimetre, there would still be a calculable opacity due to this cause; for a distance of 10^{21} kilometres, or a hundred million light-years, would reduce the energy of direct radiation to $1/e^{th}$ of its value.

Professor Barkla has informed me that for X-ray pulses it is not necessary for electrons to be isolated in order to exert a scattering influence, but that electrons associated with atoms of matter appear to be sufficiently free to take part in the process. It may be that thus much ultra-violet light is stopped, for to small enough waves the opacity so caused would be considerable, because of the immense value of N . That which is supposed by the above theory to occur to waves of all kinds, in really ionized space, has thus been already observed in the case of those minute waves to which atom-bound electrons are partially and sufficiently free.

Returning to the consideration of the other phenomenon, the bodily propulsion or sweeping forward of electrons by the wave: at first sight it is not easy to realize physically why electrified particles should be thus propelled; but no flaw appears in the reasoning, and it may be classified as a phenomenon akin to the magnetic deflexion of cathode rays. For (a) The electric force of a wave will obviously tend to move a charged particle in its own direction in the wave-front; (b) directly it moves, it is a current, and is therefore acted on by the magnetic component of the wave; and (c) this action will propel it in a direction at right angles to both, *i. e.* normal to the wave-front.

Taking the plane of the wave as xy , and the electric intensity as X , the force acting on a charge e is Xe in the first instance; though in so far as the particle is propelled along the ray it becomes subject to magnetic force also, and the whole x force is

$$m\ddot{x} = Xe - \mu He \dot{z}.$$

Also

$$m\ddot{y} = 0,$$

and

$$m\ddot{z} = \mu He x.$$

These are the equations; and when they are worked out, as they are on pages 257–8 of the Philosophical Magazine for August 1902, the result is a progression superposed upon an oscillation of twice the wave-frequency, a sort of fore-shortened cycloidal motion, expressed by the equation:—

$$v^2 - \left(v - \frac{dz}{dt}\right)^2 = \frac{e^2 \mu^2 H_0^2 \lambda^2}{8\pi^2 m^2} \left\{ 1 - \cos 2(pt - qz) \right\},$$

the original wave being

$$H = H_0 \cos (pt - qz).$$

Hence, denoting the quantity $\frac{e\mu H_0 \lambda}{m\pi\sqrt{8}}$ by u , and the maximum or ultimate value of $\frac{dz}{dt}$, apart from oscillations, by w , we have the equation

$$v^2 - (v - w)^2 = u^2;$$

or, since u is generally decidedly smaller than v ,

$$w = \frac{u^2}{2v} = \frac{e^2 \mu^2 H_0^2 \lambda^2}{16\pi^2 m^2 v}.$$

The particle will be joggled forward with twice this speed every time a ventral segment reaches it, and will be reduced to momentary rest in the suck-back of the nodes.

On showing this to Professor Poynting he stated his belief that a resistance term had been omitted from the original equations, a term expressive of the energy consumed in radiation whenever a charge is accelerated. Indeed a moving charge seems likely to be in a curiously unstable condition, for although it encounters no resistance as long as its velocity is uniform, yet directly there is acceleration of any kind, even retardation, it must begin to transfer its energy to the ether in a way which is equivalent to the action of a retarding force; so that an initial retardation would tend to be intensified, and thus apparently an electron could be readily induced to stop dead. If this be the case, then the opacity hereafter treated may depend not merely on the newly born ions, as hereafter supposed, but on the total ionic, or at least electronic, content: and the sweeping up of the ions would itself constantly make a call upon the energy of the propelling waves, unless their motion could be guaranteed absolutely uniform. I do not propose to attempt to develop this important suggestion, and will proceed without further reference to it.

The inverse electrochemical equivalent e/m is $10^7/\sqrt{\mu}$ c.g.s. units, and the wave-energy per c.c. is $\mu H_0^2/8\pi$; (remembering the electric energy as well as the magnetic, and also the fact that H_0 is the maximum, not the average, of H).

$$\text{So} \quad w = \frac{\mu e^2}{m^2} \cdot \frac{\mu H_0^2}{8\pi} \cdot \frac{\lambda^2}{2\pi v};$$

and the velocity imparted to the particles is proportional both to the energy-density and to the square of the wave-length. Short waves, like those of light, cannot be expected to do much in the way of propulsion, except perhaps in the neighbourhood of the sun where they are very intense; but anything like radiation of Hertzian wave-length may be

expected to sweep away the charged corpuscles which it encounters and to leave a clear space.

To get an idea of the magnitude of this influence of a Hertz vibrator, take a straight vertical one of electric moment Ql with a current amplitude in it $C_0 = 2\pi Q/T$. The magnetic field at any distance r (greater than say half a wave-length) is

$$H = \frac{Qlpq}{r} \cos \theta \cdot \sin (qr - pt),$$

where θ is the inclination to the horizon (the latitude, so to speak). So on the "equator" the magnetic amplitude is

$$H_0 = \frac{4\pi^2 Ql}{T\lambda r} = \frac{2\pi C_0 l}{\lambda r}.$$

Hence the velocity acquired by the particles,

$$\begin{aligned} v &= \left(\frac{\mu}{4\pi} \cdot \frac{e}{m} \right)^2 \frac{(\lambda H_0)^2}{v} \\ &= \frac{\mu^2}{4v} \left(\frac{e}{m} \right)^2 \left(\frac{C_0 l}{r} \right)^2. \end{aligned}$$

So the speed generated in an electron by an upright Hertz radiator, at a distance 10 times the height of the aerial along its equator, will be comparable to a kilometre per second if the mean aerial current is 600 amperes. The velocity thus generated naturally falls off with the square of the distance, just as the wave-energy does.

The mere propulsion of a set of particles will not appreciably consume the energy of a wave, provided the particles remain individually the same and continue free, for electrons steadily on the run would not contribute to opacity*. Under the influence of Hertzian waves they would either be driven into the atoms, or else would speedily acquire a terminal velocity and be swept out of the way. The process suggests a curious method of clearing the air of electric charges; and there may be some application of long electric waves for this purpose. Assuming that ions in the atmosphere must have some meteorological influence, it would seem just possible that an indirect ether-wave effect on the weather, such as cranks have anticipated as likely to be due to wireless telegraphy, may not be so absurd as at first sight it appeared.

But passing this for the moment, and returning to the

* See, however, the suggestion of Professor Poynting, referred to on page 784.

question of a possible opacity or obstruction to the passage of waves due to this cause, we must realize that solar radiation consists not of light alone but probably of α , β , and γ rays also. Ultra-violet light, and α rays if they reach us, will be active ionizers in the upper regions of air, but the more penetrating kinds of radiation should ionize much more than a superficial layer, and when the beam of sunshine is horizontal a great deal of atmosphere may be affected.

By some such extra-terrestrial influence, in addition to any effect of emanations from the earth's crust, the ionization of the atmosphere may be preserved and constantly renewed, in spite of the clearing-away tendency of Hertzian waves. And if these waves thus have a continually renewed set of charged particles to deal with, they will be virtually encountering a constantly increasing mass; and some amount of their momentum and energy must be absorbed by transference to the particles.

Now we know, from Maxwell, Poynting, and others, that the energy of radiation per unit volume may be regarded as a momentum carried across unit area per second; in other words, as a pressure or potential pressure in the direction of travel. This pressure P may be expressed either as an energy density, *i. e.* in ergs per c.c.; or as a pressure, in dynes per square centimetre; or as a surface density multiplied by an acceleration; or as a volume density multiplied by the square of a velocity; or merely as the momentum travelling per second through unit area. If no obstacle is encountered, the radiation momentum is merely passed on in the ether undiminished, and the potential pressure is not mechanically exerted; but if matter is present, some of it is transferred to matter, and the etherial power will to that extent diminish, even without any production of heat.

It has long been known that small particles are most readily moved by the pressure of light, but now we see that charged ions of low atomic weight, and especially electrons, are more affected than anything else; especially by long waves.

The momentum transmitted per second to matter will be a certain fraction of Pv , and will equal the material momentum generated in the same time, $Nmvw$; where mw is the momentum attained by each particle, and Nv the number freshly encountered per unit area per second.

We may express it better thus:—

The loss of P per centimetre is dP/dx , and this will be accounted for by the gain of momentum generated per

second in each cubic centimetre, $\frac{d}{dt} (Nmw)$. Ordinarily, in such an expression, speed is the variable; but here w is a terminal velocity, which must ultimately be attained by all the fresh matter encountered, so N is the variable; and dN/dt signifies the number of ions continually produced by extraneous causes in each c.c. per second. Hence our equation is

$$\begin{aligned}\frac{dP}{dz} &= -mw \frac{dN}{dt} \\ &= -\dot{N}m \cdot \frac{\mu e^2}{m^2} \cdot \frac{\lambda^2}{2\pi v} \cdot P = \frac{1}{z_0} P.\end{aligned}$$

Or the wave energy-density remaining, after a journey of length z , is

$$P = P_0 e^{-\frac{z}{z_0}}.$$

It must here be remembered that the relevant variation of P has nothing to do with its natural decrease with distance as a function of r , but represents solely its gradual diminution by absorption in successive layers, in geometrical progression. Hence the distance needed to reduce the wave energy per c.c., or the momentum per second per square centimetre, to $1/eth$ of the value it would otherwise have had at any given place, is z_0 , where

$$z_0 = \frac{2\pi v m}{\dot{N} \mu e^2 \lambda^2}; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

which is of *length* dimension, as it ought to be. We see that it will be shorter for electrons than for any other kind of ions, and that the absorption will vary with the square of the wave-length.

To get an idea of its value we can remember

that $\mu e^2/m^2$ is of the order 10^{14} c.g.s., for electrons,

that $v = 3 \times 10^{10}$ centimetres per second,

that m is of the order 10^{-27} grammes,

and that in practice λ may be anything from 100 metres to 10 kilometres.

Taking these two extreme cases as typical; and assuming, as a moderate estimate, that 10,000 electrons are liberated by sunshine or other agency, per c.c. per second, all along the effective path of the wave; the distance required for etherial-wave-energy to fall to $1/eth$ of the value it would otherwise have

had is $z_0 = \frac{6\pi \times 10^{23}}{\dot{N} \lambda^2}$ centimetres, or $20 \times 10^{19}/\lambda^2$.

This distance, therefore, for a 100 metre wave is very great, and for a 10 kilometre wave is 2000 kilometres.

The case of interstellar space.

As to an infinitesimal opacity of interstellar space due to this cause, assuming that any ionization goes on there at all, it is only a question of how long it will be before even light-waves are absorbed; though long waves are much more readily dealt with. Let there be only half an electron produced per c.c. per second, and take the wave-length as 6×10^{-5} centimetre, the absorption-distance in such a case is 10^{33} centimetres, which corresponds to a light journey of 10^{15} years.

The other or scattering kind of absorption above spoken of is therefore likely to be of much greater proportional influence, so far as the short waves of light are concerned; and in the immediate neighbourhood of the sun Sir J. J. Thomson thinks it likely that it may partially account for the Corona.

But in any solar system region of space, where electrons are plentifully produced, long Hertzian waves will be liable to become absorbed and to exhibit their energy in the form merely of streams of corpuscles.

SUMMARY.

Part I. of this paper gives the theory of the Goldschmidt Dynamo, for any number of circuits, up to a magnifying ratio of 10.

Part II. deals with obstacles to electric wave transmission due to various kinds of opacity, or virtual opacity, in the atmosphere; and emphasises the important influence which the highly conducting layer necessarily existing at a certain height must play, with fluctuations according to whether it is uniformly spherical or irregular in shape, and with reference also to the distribution and amount of its ionization. It is suggested that sunshine interferes with this layer; either by altering its shape through heat, or by making its transition more gradual through general supply of β particles. It is also suggested that under the action of solar radiation of all kinds electrons may be momentarily set free enough to promote several newly-expected kinds of atmospheric opacity. Incidentally a useful practical expression for radiation from an aerial is given in equation (5).

In the same way the differential equation for y can be obtained; it only differs in having $+nn'b$ substituted for $-n'bs$.

Therefore x and y are both functions of s .

Hence we may assume that they can be expanded in powers of $\sin \theta$; an expansion which readily takes the form

$$x = a_0 + a_1 \sin \theta + a_2 \cos 2\theta + a_3 \sin 3\theta + \dots \quad (\text{iii.})$$

$$y = b_0 + b_1 \sin \theta + b_2 \cos 2\theta + b_3 \sin 3\theta + \dots \quad (\text{iv.})$$

Substituting in the original equations, (i.) and (ii.), we get two equations like

$$n(a_0 + a_1 \sin \theta + a_2 \cos 2\theta + a_3 \sin 3\theta + \dots)$$

$$\equiv -(b_0 + \frac{1}{2}b_2) \sin \theta + (b_1 + b_3) \cos 2\theta - \frac{3}{2}(b_2 + b_4) \sin 3\theta + \dots$$

Equating coefficients in this pair of identities, we find

$$a_0 = 0, \quad (1)$$

$$b_0 = b, \quad (2)$$

$$na_1 = -(b_0 + \frac{1}{2}b_2), \quad (3)$$

$$n'b_1 = -(a_0 + \frac{1}{2}a_2), \quad (4)$$

$$na_2 = b_1 + b_3, \quad (5)$$

$$n'b_2 = a_1 + a_3, \quad (6)$$

$$\dots \dots \dots$$

$$\dots \dots \dots$$

$$na_{2r} = r(b_{2r-1} + b_{2r+1}),$$

$$n'b_{2r} = r(a_{2r-1} + a_{2r+1}),$$

$$na_{2r+1} = -\frac{1}{2}(2r+1)(b_{2r} + b_{2r+2}), \quad n'b_{2r+1} = -\frac{1}{2}(2r+1)(a_{2r} + a_{2r+2}).$$

Taking a_1, b_1 , as the arbitrary constants, and using these equations in numerical order, we find in succession $b_2, a_2, b_3, a_3, \dots$ in terms of a_1, b_1 and the known constants n, n', b . This is the General Solution.

With $b_1 = 0$ as the special case, we find successively all the even a 's and odd b 's zero.

Hence (iii.) and (iv.) reduce to

$$x = a_1 \sin \theta + a_3 \sin 3\theta + a_5 \sin 5\theta + \dots \quad (\text{iii'.})$$

$$y = b_0 + b_2 \cos 2\theta + b_4 \cos 4\theta + \dots \quad (\text{iv'.})$$

where

$$na_1 = -(b_0 + \frac{1}{2}b_2),$$

$$b_0 = b,$$

$$na_3 = -\frac{3}{2}(b_2 + b_4),$$

$$n'b_2 = a_1 + a_3,$$

$$na_5 = -\frac{5}{2}(b_4 + b_6),$$

$$n'b_4 = 2(a_3 + a_5),$$

$$\dots \dots \dots$$

$$\dots \dots \dots$$

$$na_{2r+1} = -\frac{1}{2}(2r+1)(b_{2r} + b_{2r+2}),$$

$$n'b_{2r} = r(a_{2r-1} + a_{2r+1}).$$

This solution is excellent, given the legitimacy of a Fourier expansion; but my brother distrusts this as manifestly divergent, and considers that, apart from physical considerations and electrical devices, the strict solution is an exponential one. His own treatment is as follows:—

$$\text{Given} \quad nx = \frac{d}{d\theta}(y \cos \theta) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$n'(y-b) = \frac{d}{d\theta}(x \cos \theta), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\therefore nn'(y-b) = \frac{d}{d\theta} \left\{ \cos \theta \frac{d}{d\theta}(y \cos \theta) \right\} \quad . \quad . \quad (3)$$

Let $y \cos \theta = z$, $\tan \theta = \sinh u$; and call $nn' = N^2$.

Whence $\sec \theta = \cosh u = du/d\theta$;

$$\text{also } \frac{dz}{du} = \cos \theta \frac{d}{d\theta}(y \cos \theta); \text{ and } \frac{d}{d\theta} \cdot \frac{dz}{du} = \sec \theta \frac{d^2z}{du^2}.$$

Therefore the differential equation becomes

$$\frac{d^2z}{du^2} = N^2(y-b) \cos \theta; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\begin{aligned} \text{i. e.,} \quad \frac{d^2z}{du^2} - N^2z &= -N^2b \operatorname{sech} u = -N^2b \cdot \frac{2e^{-u}}{1+e^{-2u}} \\ &= -2N^2b(e^{-u} - e^{-3u} + e^{-5u} + \dots). \end{aligned}$$

$$\therefore z = A \cosh Nu + B \sinh Nu + \frac{2N^2b}{N^2 - d^2/du^2} \{e^{-u} - e^{-3u} + e^{-5u} - + \dots\}. \quad (5)$$

$$\text{Now} \quad \frac{1}{N^2 - D^2} e^{ku} = \frac{e^{ku}}{N^2 - k^2};$$

$$y \cos \theta = z = A \cosh Nu + B \sinh Nu + 2N^2b \left\{ \frac{e^{-u}}{N^2 - 1^2} - \frac{e^{-3u}}{N^2 - 3^2} + \frac{e^{-5u}}{N^2 - 5^2} \dots \right\}$$

$$nx \cos \theta = \frac{dz}{du} = N(A \sinh Nu + B \cosh Nu) - 2N^2b \left\{ \frac{e^{-u}}{N^2 - 1^2} - \frac{3e^{-3u}}{N^2 - 3^2} \dots \right\},$$

where $\cosh u = \sec \theta = \sec pt$, and $N^2 = RR'/p^2M^2$, as stated above.

That this solution satisfies the equations (1) and (2) can be verified; but the series of circular functions is more practically useful, since the higher frequencies which go to build up the above total result are barred by the conditions of the actual problem,

LXXXIII. *Some Experiments on Polarized Röntgen Radiation.* By J. CROSBY CHAPMAN, B.Sc., Tutor in Mathematics, King's College, London; late Research Student of Gonville and Caius College, Cambridge*.

Introduction.

ALL the experimental evidence obtained within the last few years indicates the fundamental identity of X-rays and light: this evidence includes experiments on the properties of the scattered, fluorescent, and corpuscular radiations, as well as on the polarization, interference, reflexion, and the velocity of X-rays. These seem to establish the theory that X-rays are merely light-waves of exceptionally short wave-length. Previous to the recent experiments on interference, one of the most significant properties which Röntgen rays had been shown to possess was that of polarization. Barkla†, as early as 1906, showed that it was possible to produce a secondary beam of X-rays which shows fairly complete polarization.

Up to the present all experiments on the rotation of the plane of polarization have been made using light of a wave-length of the order of that found in the visible spectrum. The results indicate that the magnitude of the rotation in quartz and other active substances varies *inversely* as some power of the wave-length. This power over a considerable portion of the spectrum examined is the square, but it does not hold over a wider range.

On the assumption that Röntgen radiation is merely light of exceptionally short wave-length, it seemed possible that a great rotation of the plane of polarization of X-rays might be obtained under suitable conditions.

The object of this present research, suggested by Professor Barkla, was to test directly whether anything corresponding to a rotation of the plane of polarization could be obtained with X-rays.

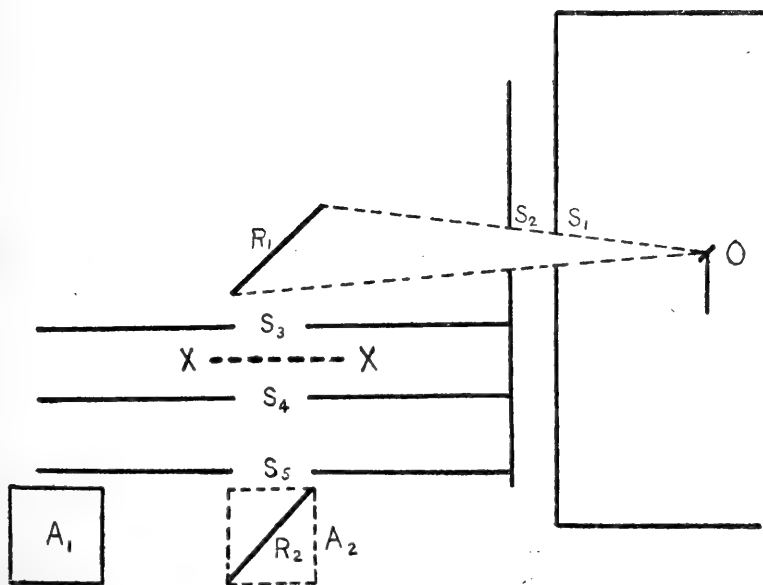
Apparatus.

The apparatus was essentially similar to that used in previous experiments on X-ray polarization. X-rays from the anticathode O of an X-ray tube passed through the slits S_1 and S_2 in lead screens on to the first radiator R_1 ; a portion of the rays scattered from this radiator passed through the slits S_3 , S_4 , and S_5 in further lead screens, on to the radiator R_2 . At equal horizontal and vertical distances of

* Communicated by Prof. C. G. Barkla, F.R.S. The expenses of this research have been partly covered by a grant from the Royal Society.

† Barkla, Proc. Roy. Soc. Series A, vol. lxxvii. pp. 247-255 (1906).

about 12 cm. from the radiator R_2 , two similar electroscopes, A_1 horizontal, and A_2 vertical, were placed so as to subtend the same solid angle at the plate R_2 , the face of which was equally inclined to vertical and horizontal lines drawn from the centre of the radiator to the electroscopes A_1 and A_2 .



A_2 (Dotted lines) vertically above R_2

The substance which was being tested as regards its power of rotating the plane of polarization was placed at XX, so that the secondary partially polarized beam of rays from R_1 passed directly through it before striking R_2 . A full account of this apparatus and the conditions which it must satisfy is given in the original paper *, where it is demonstrated that while there is but little polarization in the primary beam, yet in the secondary beam there is a considerable amount of polarization. This follows from elementary considerations of the usual theory of scattering.

In the present experiment, the primary and secondary beams were horizontal. When this was the case, and both the radiators at R_1 and R_2 consisted merely of a scattering agent such as carbon, it was found that the horizontal tertiary beam passing into A_1 was of much greater intensity than the vertical tertiary beam passing into A_2 . When, however, the carbon plate at R_2 was replaced by a plate capable of giving a preponderating characteristic radiation, which has been shown to be distributed equally in all directions †, the intensities of the radiation reaching the

* Barkla, Proc. Roy. Soc. Series A, vol. lxxvii. pp. 247-255.

† Barkla and Ayres, Phil. Mag. Feb. 1911, pp. 271-278.

electroscopes became approximately equal, showing that the solid angle subtended by each electroscope at R_2 was the same.

General Method.

The ratio :—

$$\frac{\text{intensity of horizontal tertiary radiation}}{\text{intensity of vertical tertiary radiation}},$$

when carbon is used as a tertiary as well as a secondary radiator, can be taken as a measure of the polarization of the beam. When this ratio is unity, there is no polarization, and the greater this ratio becomes, the larger is the polarization in the beam. It was this ratio, determining the polarization, which was measured in the experiments.

Suppose that in a particular case this ratio has been determined when the secondary beam has passed directly from R_1 to R_2 . If, now, at XX there is placed a substance which is capable of rotating the plane of polarization of X-rays, after transmission through this substance, we should expect each portion of the beam to be rotated through an angle which is a function of its wave-length and the distance traversed in the substance. If Röntgen radiation is light of an exceptionally short wave-length, then, while there would be considerable polarization in the incident secondary beam, after transmission the polarization of the beam would be destroyed, for something amounting to a random rotation of the various constituents would have taken place. If, however, as seemed possible, only a few of the electrons of the rotating agent were effective, then a much smaller change in the state of polarization might be expected.

With the idea of investigating this possibility of there being a considerable rotation, the following experiments were made. Three substances were examined :—

- (a) Iron in a magnetic field.
- (b) Quartz.
- (c) Sugar solution.

Experiments on Iron in a Magnetic Field.

The magnetic field was produced by means of a coil of wire consisting of 200 turns, through which currents up to 4 amperes could be passed. In the centre of the magnetic field so produced and perpendicular to it was placed the thin sheet of iron, the power of rotation of which it was required to investigate. The pure iron, specially rolled by Messrs. Johnson and Matthey, was of thickness .008 cm., which enabled a considerable portion of the X-ray beam used in the experiment to be transmitted. The iron mounted

in the coil was placed at XX, directly opposite the slit S_4 in the lead screen, and its diameter was slightly greater than that of the slit.

In the first part of the experiment the iron was unmagnetized, and the ratio of the intensities of the tertiary radiations reaching the electroscopes A_1 and A_2 from R_2 was determined. This involved two measurements:—(1) the intensities when the radiator R_2 is present; (2) the intensities when the radiator R_2 is absent. By subtracting these two readings the required ratio was determined. The iron was then magnetized, and this ratio again measured. It should be stated that the deflexion in the electroscopes when the radiator R_2 is absent is due largely to natural ionization and the electrostatic leak across the ebonite which supported the gold leaf, only a negligible fraction being due to that scattered from the slit at S_5 and from the air. This was shown by removing R_2 and measuring the leak in the two electroscopes, firstly when R_1 was present, and secondly when R_1 was absent. There was next to no difference in the two deflexions, showing that the scattering effect is negligible when R_2 is absent.

In the Tables I. and II. a complete set of observations is given, and in Table III. the final results obtained in a similar manner are summarized. The time of observation varied from ten to fifteen minutes.

TABLE I.

Iron in a magnetic field.—Intensity of field = 320 gauss.

Conditions of experiment.	Deflexion of electroscope receiving hori- zontal tertiary beam.	Deflexion of electroscope receiving vertical tertiary beam.
Carbon radiators $R_1 + R_2$ present. } Iron unmagnetized	14.4	6.3
Carbon radiators $R_1 + R_2$ present. } Iron magnetized	14.4	6.4
Carbon radiator R_1 present, R_2 } absent..... } Iron present	8.3	4.8
Carbon radiator R_1 present. } At R_2 an arsenic plate	7.8	4.4
Carbon radiator R_1 present. } R_2 absent	6.2	2.8

Whence by subtraction :—

TABLE II.

Conditions of experiment.	State of iron.	Intensity of tertiary radiation reaching horizontal electroscope.	Intensity of tertiary radiation reaching vertical electroscope.
Carbon radiators $R_1 + R_2 \dots$	unmagnetized	6·1	1·5
Carbon radiators $R_1 + R_2 \dots$	magnetized	6·1	1·6
Carbon radiators $R_1 \dots \dots$ Arsenic radiator at $R_2 \dots$	present	1·6	1·6

Whence :—

$$\left. \begin{array}{l} \text{Polarization of beam when transmitted} \\ \text{through unmagnetized iron} \dots \dots \dots \end{array} \right\} = \frac{6\cdot1}{1\cdot5} = 4\cdot1.$$

$$\left. \begin{array}{l} \text{Polarization of beam when transmitted} \\ \text{through magnetized iron} \dots \dots \dots \end{array} \right\} = \frac{6\cdot1}{1\cdot6} = 3\cdot8$$

$$\left. \begin{array}{l} \text{Polarization of beam radiated from} \\ \text{arsenic plate at } R_2 \dots \dots \dots \end{array} \right\} = \frac{1\cdot6}{1\cdot6} = 1\cdot0.$$

Combining this result with others deduced in a similar manner :—

TABLE III.

Polarization of beam when transmitted through unmagnetized iron.	Polarization of beam when transmitted through magnetized iron.
4·1	3·8
3·2	3·0
3·0	3·2
Mean value <u>3·4</u>	<u>3·3</u>

These results show that the ratio which determines the polarization of the secondary beam does not alter when the iron through which the beam is transmitted is magnetized. Had there been present anything of the nature of a rotation of the plane of polarization, it can be seen at once that there

would have been a decrease in the intensity of the horizontal tertiary beam and a consequent increase in the intensity of the vertical tertiary beam, resulting therefore in a considerable decrease in the ratio which determines the polarization. The fact that this ratio does not alter proves that no appreciable rotation of the plane of polarization takes place.

Experiments on Quartz.

The crystal used had to satisfy two conditions: firstly, it had to be approximately of the area of the slit in the lead screen at S_4 , and it had also to be thin enough to transmit rays of the hardness used in the experiment. The quartz, a right-handed crystal cut perpendicular to the optic axis, was 6.5 cm. in diameter, and of thickness 4 mm.

The method of investigating its rotatory power for a beam of polarized X-rays was very similar to that described in the case of iron. In the first part of the experiment, the ratio of the intensities of the tertiary beam reaching the electroscopes A_1 and A_2 was determined when the quartz was absent. The quartz was then placed at XX, in the path of the secondary beam, and the ratio which standardized the polarization again determined. In the experiment the quartz transmitted from 70 to 30 per cent., according to the hardness of the bulb.

The full results are given in tabular form.

Quartz.
TABLE IV.

Condition of experiment.	Deflexion of electroscope receiving hori- zontal tertiary beam.	Deflexion of electroscope receiving vertical tertiary beam.
Direct secondary beam. $\left\{ \begin{array}{l} \text{(i) Carbon radiators} \\ \quad R_1 + R_2 \text{ present.} \\ \text{(ii) Carbon radiator} \\ \quad R_1 \text{ present} \\ \quad R_2 \text{ absent} \end{array} \right\}$	12.8 7.5	4.9 3.6
Secondary beam transmitted through quartz. $\left\{ \begin{array}{l} \text{(i) Carbon radiators} \\ \quad R_1 + R_2 \text{ present.} \\ \text{(ii) Carbon radiator} \\ \quad R_1 \text{ present} \\ \quad R_2 \text{ absent} \end{array} \right\}$	11.8 8.4	4.5 3.7

TABLE V.

Condition of experiment.	Intensity of tertiary radiation reaching horizontal electroscope.	Intensity of tertiary radiation reaching vertical electroscope.
Direct secondary beam	5·3	1·3
Secondary beam transmitted through quartz	3·4	0·8

Whence:—

$$\text{Polarization of direct secondary beam ...} = \frac{5\cdot3}{1\cdot3} = 4\cdot1.$$

$$\left. \begin{array}{l} \text{Polarization of secondary beam after} \\ \text{transmission through quartz,} \end{array} \right\} = \frac{3\cdot4}{0\cdot8} = 4\cdot2.$$

Combining this with other results deduced in the same way:—

TABLE VI.

Polarization of direct secondary beam.	Polarization of secondary beam after transmission through quartz.
4·1	4·2
3·9	3·8
3·4	3·2
3·4	3·2
4·2	3·8
Mean value. <u>3·6</u>	<u>3·5</u>

Again it will be seen that the polarization present in the secondary beam is the same before and after transmission through the quartz. That is, quartz which is active for ordinary light has no power of rotating the plane of polarization of X-rays.

Experiments on Sugar Solution.

A solution of active sugar exerts a powerful rotation on the plane of polarization of light. A similar experiment has been made, using a beam of plane-polarized X-rays in the place of the beam of ordinary light.

A concentrated solution in water of centrifugal sugar was made, and a thin film of this solution was placed in a cell 8 cm. \times 8 cm. \times 2 mm., the walls of the cell being of thin mica. In this way a film 2 mm. thick of the active sugar solution was obtained, through which a considerable part of the polarized beam of X-rays could be transmitted.

The method of the experiment was precisely similar to that used in the case of the quartz.

The results are given below.

Sugar solution.

TABLE VII.

Condition of experiment.	Deflexion of electroscope receiving hori- zontal tertiary beam.	Deflexion of electroscope receiving vertical tertiary beam.
Direct secondary beam.		
{ (i) Carbon radiators $R_1 + R_2$ present. }	12.5	5.3
{ (ii) Carbon radiator R_1 present R_2 absent }	5.1	3.2
Secondary beam transmitted through quartz.		
{ (i) Carbon radiators $R_1 + R_2$ present. }	9.7	4.5
{ (ii) Carbon radiator R_1 present R_2 absent }	4.9	3.1

TABLE VIII.

Condition of experiment.	Intensity of tertiary radiation reaching horizontal electroscope.	Intensity of tertiary radiation reaching vertical electroscope.
Direct secondary beam	7.4	2.1
Secondary beam transmitted through sugar solution ...	4.8	1.4

That is :—

$$\text{Polarization of direct secondary beam ...} = \frac{7.4}{2.1} = 3.5.$$

$$\left. \begin{array}{l} \text{Polarization of secondary beam after} \\ \text{transmission through sugar solution..} \end{array} \right\} = \frac{4.8}{1.4} = 3.5.$$

Combining this result with others obtained :—

TABLE IX.

Polarization of direct secondary beam.	Polarization of secondary beam after transmission through sugar solution.
3·5	3·5
3·6	3·7
3·4	3·3
3·4	3·4
3·4	3·6
Mean value . <u>3·5</u>	<u>3·5</u>

These results clearly prove that no measurable rotation of the plane of polarization of X-rays is produced by a sugar solution which is active for light in the visible spectrum.

The interpretation of these results is not that a fundamental difference exists between X-rays and light, but the experiments rather indicate that the usual formulæ which determine the relation between rotation and wave-length for light in the visible spectrum are quite inadequate when light of exceptionally short wave-length is concerned.

Absorption of polarized X-rays by Iron in Magnetized State.

It is legitimate to assume that the absorption of X-rays by an atom of any given substance must depend to a certain extent on two factors :—(1) the period of the X-radiation absorbed ; (2) the natural period of vibration of the electrons within the atom.

In order to explain double refraction and other phenomena peculiar to crystalline substances, it is necessary to suppose that the period of vibration of the electrons is dependent on the direction of vibration with respect to the atomic system.

Now in a polarized beam of X-rays, the electrical vibrations are largely in one direction. Consider now such a beam being transmitted through iron in which, since it is unmagnetized, there is no regular orientation of the orbits of the electron in the system. If, now, the iron is magnetized, the orientation becomes more regular, and if absorption of X-radiation is dependent on the direction of its own electrical vibration relatively to that of rotation of the electron in the

absorbing substance, it might be expected that there would be a considerable alteration in the absorption of the material. With such an idea in mind, the following experiment was tried.

A polarized beam of X-rays was passed through iron when unmagnetized, and later when magnetized. The absorption of the polarized beam was determined in each case. In the first experiment, the field produced was perpendicular to the sheet of iron absorbing and parallel to the direction of the X-rays absorbed. In the second part the field was perpendicular to the direction of the X-rays absorbed and parallel to the sheet of iron absorbing. The field was produced in the first instance by a coil of wire, and in the second case by a powerful horseshoe electromagnet. In each case a standardizing electroscope was employed to allow for changes in the primary beam.

The results are given in tabular form.

Magnetic field perpendicular to X-rays and
parallel to iron sheet.

$H = 30,000$ gauss.

Absorption by iron unmagnetized.	Absorption by iron magnetized.
68.0 per cent.	68.0 per cent.
67.2 ,,	67.0 ,,
20.1 ,,	20.3 ,,
20.5 ,,	20.1 ,,

Magnetic field parallel to X-rays and perpendicular
to iron sheet.

$H = 320$ gauss.

Absorption by iron unmagnetized.	Absorption by iron magnetized.
53.0 per cent.	53.1 per cent.
31.7 ,,	31.0 ,,
31.7 ,,	32.4 ,,
31.8 ,,	31.9 ,,

Thus the absorption of a polarized beam of X-rays by iron is not appreciably dependent upon whether it is magnetized or unmagnetized; that is, absorption of X-rays is independent of the orientation of the electronic orbits inside the atom, so far as they are affected by the magnetic state.

Absorption of polarized X-rays by Tourmaline.

For light in the visible spectrum, tourmaline is a double refracting crystal in which the ordinary ray is absorbed if the crystal is thicker than 1 or 2 mm., while the extraordinary ray is transmitted without loss of intensity.

The absorption of a tourmaline crystal cut parallel to the optic axis was determined when:—(1) the optic axis was parallel to the plane of polarization; (2) the optic axis was perpendicular to the plane of polarization. If X-rays behave in a similar manner to light, the absorption in the two cases should show great dissimilarity.

The results are shown.

Absorption by tourmaline crystal cut parallel
to optic axis.

Absorption when axis of crystal was parallel to plane of polarization of X-rays.	Absorption when axis of crystal was perpendicular to plane of polarization of X-rays.
54.9 per cent.	54.1 per cent.
58.9 "	59.9 "
58.5 "	59.1 "
57.2 "	59.8 "
58.5 "	58.5 "

These results show that the absorption of a plane-polarized beam of X-rays by tourmaline crystal cut parallel to the optic axis is independent of the orientation of this axis with reference to the plane of polarization of the X-ray beam.

Summary.

The three substances, iron in a magnetized state, quartz, and active sugar solution have been examined to see whether they have any power of rotating the plane of polarization of X-rays. The X-rays themselves are assumed to be essentially similar to light only of exceptionally short wave-length. In all cases a negative result was obtained, indicating the limited range of wave-length over which the usual rotation formulæ hold.

Iron has been shown to absorb a polarized beam of X-rays to the same extent whether magnetized or unmagnetized. The absorption of a plane-polarized beam of X-rays by tourmaline cut parallel to the optic axis has also been found independent of the orientation of its axis with reference to the plane of polarization of the X-rays.

It is with great pleasure that I thank Professor Barkla for suggesting this research, and also for his encouragement during its progress.

LXXXIV. *Ionization by Charged Particles.*By NORMAN CAMPBELL, *Sc.D.**

1. **T**HE following numbers denote papers which will be frequently quoted:—

- (1) Lenard, *Ann. d. Phys.* v. p. 149 (1902).
- (2) " " " xii. p. 449 (1903).
- (3) Füchtbauer, *Phys. Zeit.* vii. p. 748 (1906).
- (4) v. Baeyer, " " x. p. 176 (1909).
- (5) Gehrts, *Ann. d. Phys.* xxxvi. p. 995 (1911).
- (6) Kossel, " " xxxvii. p. 393 (1912).
- (7) Bloch, " " xxxviii. p. 559 (1912).
- (8) Bumstead, *Phil. Mag.* xxii. p. 907 (1911).
- (9) " and McGougan, *Phil. Mag.* xxiv. p. 462 (1912).
- (10) Campbell, *Phil. Mag.* xxii. p. 276 (1911).
- (11) " " " xxiv. p. 527 (1912).
- (12) " " " xxiv. p. 783 (1912).
- (13) J. J. Thomson, *Phil. Mag.* xxiii. p. 449 (1912).
- (14) Bohr, *Phil. Mag.* xxv. p. 10 (1913).
- (15) Ramsauer, *Jahrb. d. Radioakt.* ix. p. 515 (1912).

2. When α rays, positive rays, or β rays fall on a metal plate they cause the emission of electrons moving with speeds of less than 30 volts. These electrons have been termed δ rays when they have been produced by α rays, and secondary cathode rays when they have been produced by positive or β rays; in this paper they will always be termed δ rays. It is generally believed that similar secondary rays are emitted from the molecules of a gas acted on by the same primary rays, and that the mechanism of the liberation of the delta rays is precisely the same as that of the ionization of a gas. The evidence for this belief is based on the experiments of (1), (2), (4), (5), (6), (7), (8), (9), which show that the power of α and β rays to excite δ rays varies in the same way as their power to cause ionization in a gas.

Bumstead and McGougan (9) have produced evidence to show that the α rays excite also a secondary β radiation with velocities from 40 to 2000 volts or more, and suggest that the δ rays are liberated by the action of these secondary rays and not by the α rays themselves. The matter will be discussed further in § 11, but most of the considerations here presented are independent of the correctness of this view.

3. The experiments of Füchtbauer have shown that the velocity with which the δ rays are emitted is the same, whether they are excited by positive rays or by cathode rays, and whatever is the speed of those rays, at least if that speed

* Communicated by the Author,

is greater than 4000 volts. My own experiments (10, 11, 12) have shown that there is a similar independence of the velocity of the δ rays on the nature of the primary, when the primary rays are α rays or β rays excited by X rays. The same observations and those of (4) and (5) also show that the velocity of the δ rays is independent (or nearly independent) of the metal on which the primary rays act.

Absolute measurements of the velocity with which the δ rays leave a metal plate have been made by many observers under very different conditions, and have given very various results. Much of the apparent disagreement can be attributed to differences in the form of the apparatus. However, almost all observers agree that the greater part of the δ rays leave a metal plate with velocities less than 10 volts, while some small proportion of them have a velocity as great as 30 volts. The only experiments which cannot be reconciled immediately with this statement are those of (3), which led to the conclusion that the majority of the rays had velocities between 27 and 30 volts; I think it would be agreed that the method of these experiments is not so reliable as that of the others. Lenard states (2) that the velocity of the secondary rays is not greater than 11 volts, but an examination of the observations on which that statement is based shows that they support it only if it is made concerning the greater portion of the rays and not concerning all of them.

4. When the velocity of the primary rays is so small that it is comparable with that of the δ rays, a change in the nature of the latter is to be expected. The experiments (4) and (5) on the rays liberated by such very slow β rays have led to the following conclusions:—

β rays of which the velocity is less than 11 volts liberate no δ rays. Electrons may leave the surface of a metal on which such rays fall, but they are to be regarded as a “reflected” primary rather than as a secondary radiation.

The number of δ rays liberated by a given number of primary rays is a maximum when the speed of the latter is about 250 volts.

The velocity of the δ rays is independent of the metal from which they are liberated and approximately independent of the velocity of the primary, so long as this velocity is not less than 80 volts. It appears, however, from Gehrts’ results that there is some variation of the velocities of the δ rays with that of the primary, even when the latter is greater than 80 volts. Table I. gives, for various values of V_1 and V_2 , the proportion of δ rays leaving the plate

with a velocity greater than V_2 when the velocity of the primary is V_1 ; the figures are the means of those obtained by Gehrts with several different metals. The column $V_1 = \infty$ gives the corresponding figures obtained in the experiments (10) for δ rays liberated by β rays under conditions which seem to make them comparable with those of Gehrts.

TABLE I.

$V_1 =$	80	260	500	∞
$V_2 = 0$	1.000	1.000	1.000	1.000
2	0.506	0.445	0.433	0.400
4	0.267	0.220	0.208	0.198
6	0.167	0.129	0.120	0.112
8	0.113	0.084	0.079	0.064
10	0.083	0.060	0.053
12	0.064	0.043	0.036
14	0.046	0.032	0.027
16	0.038	0.026	0.021
20	0.023	0.014	0.008	0.004

When the speed of the primary rays lies between 11 and 80 volts, the δ rays are mixed with reflected rays and no precise measurements of their velocities have been obtained. In the reflected rays the proportion of electrons having a given velocity increases as that velocity approaches that of the primary rays, while in the δ rays it increases as that velocity approaches zero.

5. Some further experiments have been made on the δ rays liberated by slow β rays in the hope of throwing fresh light on the mechanism of ionization. Most of these were made with an apparatus essentially similar to that employed by Gehrts (5); the results of them need not be described in detail, because they resemble so closely those obtained by Gehrts. Attention was especially directed to three questions:—

(1) Is it certain that no true δ rays are liberated by primary rays of a velocity less than 11 volts?

Evidence for the existence of ionization, as distinct from reflexion, would be obtained if the number of electrons leaving the plate were greater than the number of the primary rays falling on it. The velocity of the primary rays for which these numbers are equal gives a maximum estimate of the least velocity required for ionization. The

smallest value obtained by v. Baeyer and Gehrts for this velocity is 25 volts; by no modification of the apparatus was it found possible to obtain a smaller value. Similar evidence would be obtained if positively charged particles were found leaving the plate on which the primary rays fell; such particles were found to be present when the velocity of the primary rays exceeded 30 volts, but never when it was smaller than that value. (It is almost impossible to tell whether the ionization giving rise to these positive particles takes place at the surface of the metal plate or at a layer of gas adhering to it, or in the trace of gas left when the vessel is evacuated to the highest possible degree.)

Thus no evidence could be obtained which threw doubt on the conclusion, based on other experiments, that primary rays of a velocity less than 11 volts do not cause ionization or liberate δ rays.

(2) If primary rays of any speed greater than 11 volts can liberate δ rays and the δ rays produced by fast primary rays have speeds as great as 30 volts, and if these speeds are independent of that of the primary, it is possible that primary rays with speeds between 11 and 30 volts might liberate δ rays faster than themselves. Can any evidence be found of such rays?

Several times in the course of the investigation it was thought that the presence of δ rays faster than the primary had been detected, but the evidence always disappeared on further investigation. (See § 7.) It appears to me quite certain that the δ or reflected rays never have a speed greater than that of the primary.

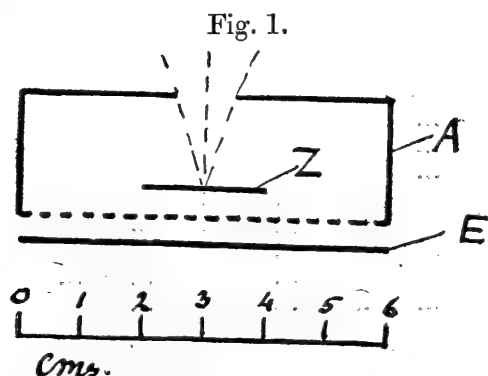
(3) Can any evidence be found of reflected electrons when the speed of the primary is considerably greater than that required to produce δ rays?

A search was made for δ rays having a speed between 30 volts and that of the primary rays when the speed of the latter exceeded 40 volts. The presence of the positively charged particles made it very difficult to be sure that there were no such rays, but no evidence whatever of their existence could be detected*. The observations which have been made on the scattering of very fast rays suggest that there must be some electrons returned from the plate with velocities near to that of the primary, but the proportion of such rays scattered must be very small compared with that

* It may be noted that, if there are no such rays, the explanation given on p. 533 of (11) of a curious phenomenon noted by Pound and myself is inadequate; the phenomenon is sufficiently explained by Bumstead's secondary β radiation excited by α rays.

reflected when the velocity of the primary rays is less than 11 volts. Reflexion of the rays, as distinct from scattering, and ionization by them seem almost mutually exclusive alternatives ; Lenard has already put forward this view, and explains the fact on the ground that ionization or reflexion occurs according as the primary ray does or does not enter the atom which it strikes.

6. It appeared that a further determination was desirable of the distribution of the velocities of the electrons returned from a plate struck by primary rays with velocities between 10 and 80 volts ; such rays were not investigated by Gehrts. But after this determination had been made by his method, doubts were thrown upon the results by the discovery that the primary rays were not nearly homogeneous. Gehrts' figures show that his rays were very nearly homogeneous when their maximum speed was 10.4 volts, but he appears not to have investigated the homogeneity of the faster rays he used. The heterogeneity of the primary rays in my arrangement arose doubtless from the fact that the rays in their passage from the place where they were produced (a zinc plate acted on by ultra-violet light or a Wehnelt cathode), struck the metal diaphragm limiting the accelerating field and caused the emission from it of δ rays which became mingled with the primary rays. In order to avoid this source of error a rather different form of apparatus was employed (fig. 1). Ultra-violet light passes through the



quartz window in the brass box A and falls on the zinc plate Z, which is supported by a rod insulated from A. A potential difference V_1 is established between A and Z. It appeared that the current between A and Z was zero when V_1 was less than -2 (V_1 is counted positive when A is positive to Z), and saturated when V_1 was greater than $+2$; consequently all the electrons liberated from Z must fall on A with a velocity which is very nearly V_1 . The rays liberated

from A emerge from the box (probably in some cases after striking the walls of A again) through the wire gauze at the bottom and fall on the electrode E, which is covered with soot to prevent reflexion. Between E and A a potential difference V_2 can be established, which is counted positive when A is positive. The potential of a lead accumulator is taken as 2 volts. The current flowing to E was measured by a compensation method, so as to make the results independent of the intensity of the light falling on Z. It was found that a small negative current flowed from E, even when V_1 was less than -2 and no electrons left Z; this current was independent of the value of V_1 , so long as V_1 was less than -2 . It doubtless represents the photoelectric action of scattered light on the parts of the apparatus outside A; the values of the current given are in all cases those obtained by subtracting the value obtained when $V_1 = -2$ from that obtained when V_1 has the value under consideration. Table II. gives the values of the negative current flowing to E for various values of V_1 and V_2 . The number of electrons received by E was never greater than 6 per cent. of those liberated from Z.

TABLE II.

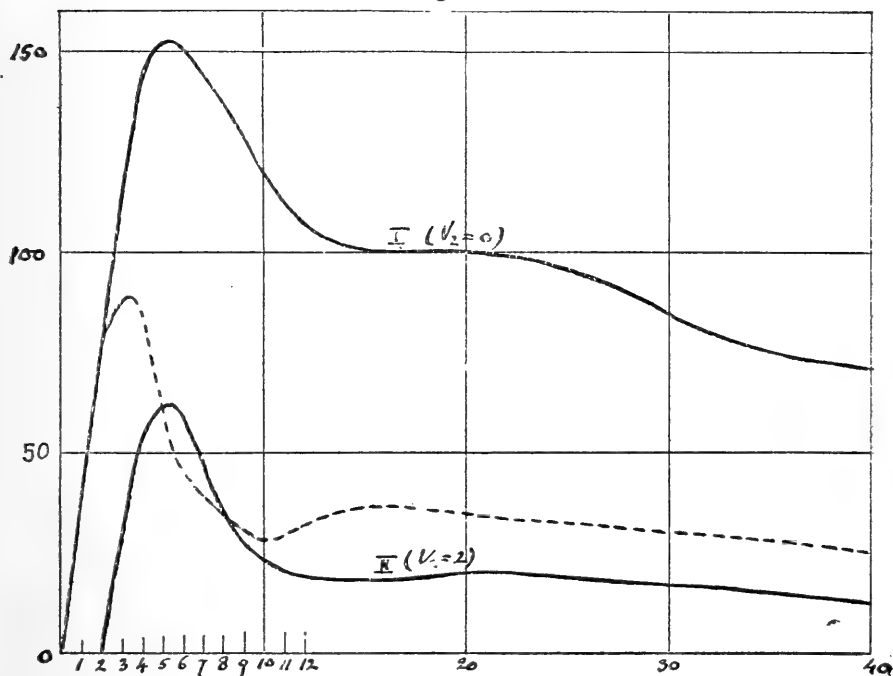
$V_1 =$	2	4	6	8	10	12	16	20	30	40
$V_2=0$	0.76	1.42	1.50	1.37	1.19	1.06	1.00	1.00	0.84	0.72
1	1.09	1.28	1.18	1.05	0.86	0.76	0.76	0.64	0.54
2	0.56	1.05	1.00	0.91	0.74	0.64	0.66	0.55	0.47
3	0.30	0.78	0.82
4	0.04	0.47	0.65	0.68	0.55	0.46	0.46	0.39	0.34
6	0.03	0.29	0.47	0.41	0.34	0.34	0.28	0.24
8	0.02	0.21	0.28	0.26	0.25	0.21	0.18
10	0.02	0.13	0.18	0.18	0.17	0.16
12	0.02	...	0.13
14	0.06	...	0.13	0.13
16	0.06
20	0.07	0.06
30	0.02	0.01

The results obtained with this apparatus are not nearly so easy to interpret as those obtained with that used by Gehrts or v. Baeyer, for the δ and reflected rays in their passage from A to the electrode pass through the electric field between A and Z; the proportion of rays of a given speed which emerge from A is probably not that of the rays liberated with that speed from A; it would seem probable that a large proportion of the slower rays would be driven by the field back into A and would fail to emerge. Or, again, some of

the rays liberated from A may strike A again and either suffer a loss of energy or liberate new δ rays. Nevertheless, the results of the experiments are sufficiently interesting and suggestive to be worthy of record.

7. Fig. 2 gives the results of the measurements when V_2

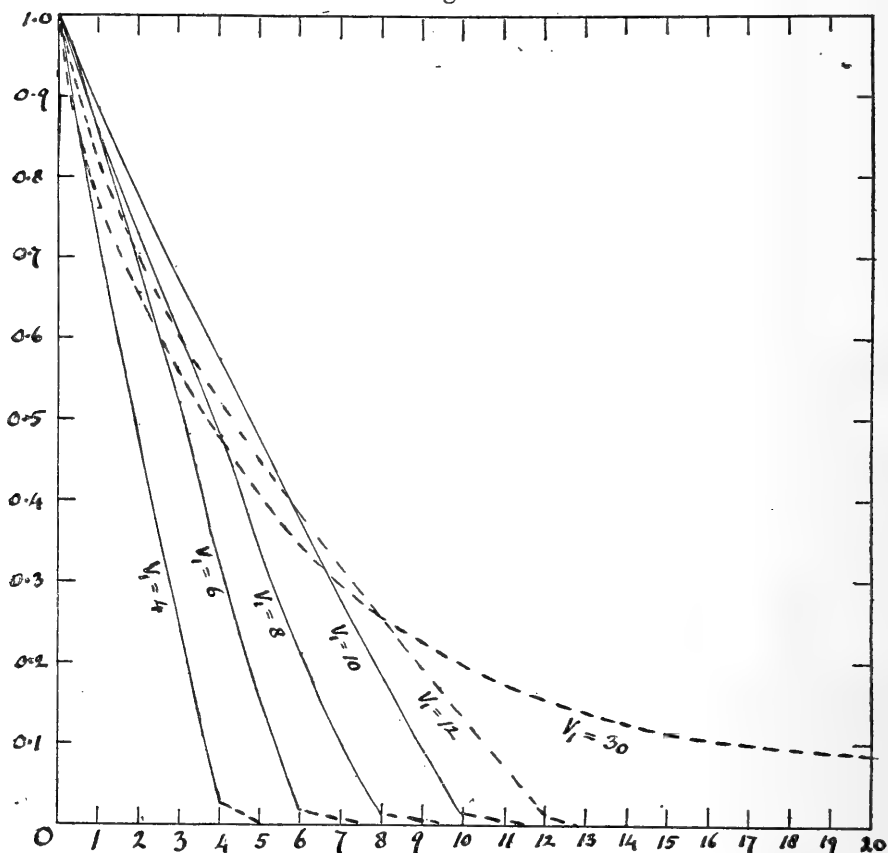
Fig. 2.



is constant and V_1 is variable. Any ordinate gives the number of electrons having a velocity greater than V_2 which emerge from A when the electrons from Z striking A have a velocity denoted by the corresponding abscissa V_1 . It will be observed that, for all values of V_2 , the number of rays emerging from A decreases as V_1 increases for all values of V_1 greater than 6 volts. The absence of the second rapid increase in the number of δ rays with increase in V_1 , noted by Gehrts and v. Baeyer, when V_1 exceeded 11 volts, is doubtless due to the action of the field between A and Z, which tends to retain the electrons within A and to prevent them from emerging. However, in the dotted curve (obtained by subtracting the curve for $V_2=2$ from that for $V_2=0$), which gives the number of rays emerging with a velocity less than 2 volts, there is distinct evidence of the minimum at about 11 volts, followed by the second increase which was noted by Gehrts. It appears, then, that among the rays due to ionization there is a much larger proportion of very slow rays than among those due to reflexion.

Fig. 3 gives the results of the measurements when V_1 is constant and V_2 variable, the value of the current when $V_2=0$ being in all cases put equal to 1. Any ordinate of a curve gives the fraction of the rays emerging from the box

Fig. 3.



with a velocity not less than that given by the corresponding abscissa. It will be seen that so long as the value of V_1 (*i. e.* the velocity with which the electrons liberated from Z strike A) is not greater than 10 volts, the curves are nearly straight lines and the velocities of the rays emerging from A are very nearly equally distributed over the range 0 to V_1 . On the other hand, when V_1 is not less than 12, the curves have a completely different form; the greater proportion of the rays emerging from A have low speeds; the proportion of rays having a speed less than 2 volts increases with V_1 until it reaches a definite limit (0.35), when $V_1=20$. When V_1 is greater than 30 the distribution of the velocities of the rays emerging from A appears to be independent of V_1 , the maximum speed of the rays being about 30 volts. Experiments were made with values of V_1 greater than 40, but they were not very accurate; but no indication of a change in the

form of the curve was found. As before, no evidence could be found of the presence of rays emerging from A with a velocity greater than about 30 volts, whatever the value of V_1 . When both V_1 and V_2 were greater than 30 volts, a small positive current flowed to E, indicating the presence of a few positively charged particles liberated within A ; but the magnitude of this positive current was so small that no variations of its amount could have been detected.

In the earlier experiments it was found that the current flowing to E was dependent on V_1 , even when V_2 was greater than V_1 ; it was thought that evidence had been obtained of the emission of δ rays faster than the primary. After much inquiry this effect was traced to a reflexion (or emission of δ rays) from the underside of Z, due to the impact of electrons from E which had been dragged through the meshes of the gauze. When all parts of Z other than that on which the direct light fell were covered with sealing-wax and so rendered insulating, the current flowing to E was entirely independent of V_1 , so long as V_2 was greater than V_1 . There is, again, no evidence that the δ rays can be faster than the primary.

8. Similar experiments were made when the interior of A was covered with soot. v. Baeyer and Gehrts found that such a covering diminished very greatly the reflexion of electrons, but did not diminish to the same extent the emission of δ rays. An accurate comparison of the results with those obtained when there was no soot was difficult, but it appeared that the maximum number of electrons emerging from A was not decreased very greatly by the presence of the soot. This observation is not necessarily inconsistent with that of v. Baeyer and Gehrts, for even when the interior of A is polished a very small proportion of the electrons leaving Z emerge from A ; the proportion emerging must be determined by the geometrical form of A and by the field between A and Z rather than by the reflecting power of the walls of A.

It appeared that the maximum number of electrons emerged from the sooted box when V_1 is only 2 in place of 6 for the polished box. On the other hand, the average velocity of the rays emerging from A for a given value of V_1 was certainly greater if A is sooted ; in fact, when $V_1=40$ no rays could be found emerging with a velocity less than 2 volts.

9. The only theory of ionization which has been put forward in so definite a form that it can be made a basis for the discussion of these results is that of J. J. Thomson (13). Ionization is supposed to represent another aspect of the

scattering and absorption of the charged particles in the primary rays which arises from their interaction with the electrons of the atoms through which they pass. The electrons of the atoms take up energy from the rays; if this energy is sufficient they break free from the atom and appear as δ rays. On the assumption that the forces holding the electron to the atom may be neglected in calculating the action between the electron and the rays, the following relations are deduced between T , the kinetic energy of a β ray, e its charge, a the distance of the undisturbed electron from the asymptote of the path of the ray, Q the energy given by the ray to the electron, and 2θ the angle through which the ray is deflected:—

$$Q = \frac{T}{1 + \frac{a^2}{e^4} T^2} \quad . \quad . \quad (1), \quad \sin^2 \theta = \frac{1}{1 + \frac{a^2}{e^2} T^2} \quad . \quad . \quad (2)$$

If the ray is an α ray, supposed to act as a point charge $2e$, then it can be shown that, so far as communication of energy to the electrons is concerned, it behaves in exactly the same manner as a β ray travelling with a speed twice that of the α ray.

Ionization is supposed to occur if $Q > W_0$, when W_0 is the energy necessary to ionize an atom. If it be assumed that, while the ray passes through unit thickness, the number of collisions in which a has a value lying between a and $a + da$ is $2\pi n a da$, where n is the number of electrons in unit volume of the substance, formulæ can be deduced for the scattering of the rays and the amount of ionization caused by them which agree with experiment when very fast β rays are considered.

From (1) together with this assumption it can be proved readily that the ratio of the number of electrons acquiring at a single collision an energy greater than $W + W_0$ to the number so acquiring an energy greater than W_0 , is

$$R = \frac{T - W - W_0}{T - W_0} \cdot \frac{W_0}{W + W_0} \quad . \quad . \quad . \quad (3)$$

The latter number is the whole number of δ rays, the former may be plausibly identified with the number of δ rays originally liberated with an energy greater than W . Hence, if T is very great compared with W (and it is only in this case that the theory is likely to be valid), the proportion of the δ rays liberated with an energy greater than W is $\frac{W_0}{W + W_0}$, a quantity which is independent of T . Hence the theory is in

agreement with experiment in predicting that, for fast rays, the forms of the curves of figs. 3 and 5 or the numbers in Table I. should be independent of the nature of the primary rays. Different substances differ probably in the forces binding the electrons to the atoms; since the agreement of Thomson's theory with experiment in the matter of the number of ions formed shows that these forces may be neglected if the primary rays are fast enough, the theory is also in agreement with experiment in predicting that the properties of the δ rays should be independent of the material on which the primary rays fall.

10. But the predicted proportion of δ rays having an energy greater than W does not agree in absolute magnitude with experiment. If $W_0 = 11$ volts, then half the rays should emerge with energies greater than 11 volts, whereas not more than 0.1 of the rays have so great an energy. Two hypotheses may be introduced to explain the discrepancy.

In the first place, it may be supposed that the velocities with which the δ rays emerge from a solid body are not those with which they are liberated from the atoms. If the rays which emerge have undergone collisions with other atoms since their liberation, the average velocity of the rays will be decreased; the proportion of rays having velocities greater than W_0 will undergo the greatest diminution, for these rays will produce fresh ionization. After an infinite number of collisions the velocities of all the rays would be reduced to zero, but there might be an intermediate stage in which the proportion of rays of any velocity existing in the beam is roughly inversely proportional to the power of those rays to produce ionization; it may be that the distribution of velocities which is observed among the emergent δ rays is really that corresponding to this state.

Some support for this view might be found in the absence of any difference between the velocities of the emergence and incidence δ rays (see (10)); if the δ rays emerged with the velocities with which they were liberated from the atoms, the emergence rays should certainly be faster on the average than the incidence. Again the result, obtained in the experiments described in § 7, that the distribution of velocities among the δ rays is independent of the potential V_1 (when V_1 is greater than 30 volts), provides some evidence for the same view. For in those experiments the field between A and Z undoubtedly diminished very greatly the number of rays emerging from A, and yet it diminished the number of rays of all speeds in nearly the same ratio; if the distribution observed represented a state of equilibrium arising from the

collisions of the rays originally liberated with other atoms, the independence of this state of the field through which the rays pass after liberation might possibly be explained. And again, the occurrence of collisions between the liberation of the rays and their emergence would explain the remarkable absence of rays emerging with speeds much greater than that required for ionization. On the other hand, there is no evidence that the δ rays which emerge come from a layer of finite thickness; the layer from which they come is certainly thinner than the thinnest material films obtainable, but then these layers are not less than 100 molecules thick.

A second explanation of the discrepancy might be obtained by supposing that the 11 volts, which is the minimum speed of the primary rays necessary for ionization, is not the least energy which must be communicated by those rays to an electron in order to cause it to appear as a δ ray. According to Lenard, 11 volts is the energy necessary to enable the primary rays to penetrate within the atom at all and to act upon the electrons within it; the energy which they would have to give to an electron in order to liberate it when they act on it may be quite different.

If W were much smaller, (3) might be made to agree much more nearly with experiment, and the predictions of the theory as to the ionizing power of fast β rays might still be in accordance with observation if the estimate of the number of electrons per atom were proportionally reduced; it is to be noted that the estimate given by Thomson as a result of this theory (2 or 3 times the atomic weight) is considerably greater than that based on considerations of the scattering of α and β rays. On the other hand, if the primary rays have to penetrate through an opposing field in order to enter the atom, the δ rays would have to emerge through the same field, and the velocity with which they emerged would not be that which they received directly from the primary rays.

11. When the primary rays are not very fast and T is comparable with W , (3) indicates that the proportion of δ rays having very small velocities ought to increase relatively to those having higher velocities. On the other hand, the figures in Table I. seem to show that the contrary proposition is true, and that the slower primary rays excite the smaller proportion of very slow β rays. But when T is small, there is no doubt that the forces holding the electrons to the atoms have to be taken into account. Ramsauer (13) has pointed out that Thomson's theory does not agree with

experiment in respect of the ionizing power of very slow β rays, unless allowance is made for the smaller power of such rays to penetrate within the atom. It is very doubtful whether any precise physical significance can be attributed to the conception of "penetration within the atom"; the influence exerted by the forces determining atomic structure is probably represented better in the work of Bohr (14), who considers that the electrons are restrained by elastic forces and capable of vibrations of definite frequency. Bohr's analysis is inapplicable to cases where the disturbance caused by the primary rays is so great as to give rise to ionization, and it appears impossible to predict anything definite concerning the velocities with which such electrons would be liberated by rays so slow that the elastic forces are of importance. But Bohr's view, as well as Lenard's, might explain the existence of a very powerful "reflexion" of rays too slow to ionize, for the elastic forces restraining the electrons would cause them to behave towards such slow rays as if they were held rigidly; at an encounter with such rigid electrons a primary ray would be powerfully deflected, but would suffer little loss of energy. It is only when the electron is free that the deflexion of a ray with which it reacts increases with the energy which it takes from that ray, as shown by (1) and (2).

These two equations also show that a primary ray will not be deflected through a right angle, and so appear as a "reflected electron" in consequence of a reaction with a free electron, unless it gives to that electron half its energy. By this consideration we might explain the absence of electrons leaving the incidence side of a plate struck by primary rays with a velocity of 80 volts, and having a velocity between 80 and 30 volts. However, the absence of δ rays with velocities greater than 30 volts, whatever the velocity of the primary, is more probably to be attributed to the fact that such rays can produce further ionization, and so tend to lose energy rapidly before they emerge. There may be some δ rays faster than 30 volts, but they may be difficult to detect because they cause the emission of fresh δ rays from the electrode at which they are received. Indeed, Bumstead's secondary β rays excited by α rays are probably such very fast δ rays liberated by the direct action of the α rays on the electrons of the atoms through which they pass. Since an α ray with a velocity of 2×10^9 cm./sec. behaves, according to Thomson's theory, like a β ray with twice that speed, (1) shows that such an α ray could liberate δ rays with an energy of 4500 volts, a value higher than that attributed by

Bumstead to his secondary β rays. If this be the true nature of Bumstead's secondary β rays, a large proportion of, but certainly not all, the δ rays ultimately emerging may be due to their action.

Some interesting considerations are suggested by estimates of the energy which rays of various kinds spend in making an ion, obtained by dividing the total energy lost by the ray by the number of ions made. For α rays this energy turns out to be a little less than 40 volts; for β rays the figures given for the absorption and ionizing power by Kossel (6) lead to values between 300 volts for the rays of 200-volt velocity to 800 volts for the β rays of RaC. It is clear that this energy must be greater than that necessary to make an ion (for some of the δ rays are liberated with a finite energy), and that it is less than the average energy which the ray communicates to those electrons which it liberates as δ rays (for some of the δ rays liberated collide with atoms and so liberate fresh δ rays). It is not surprising, therefore, that, though the least energy required to make an ion and the velocities of the δ rays are the same on whatever material the rays act, the average energy spent in making an ion is not the same; for this average energy depends in some measure on the frequency with which an electron, liberated directly by the primary rays as a δ ray, subsequently makes ions by collisions with other atoms. The remarkable fact noted by Bragg that, whereas the stopping power of materials for α rays is an additive atomic property, the molecular ionization depends on the state of chemical combination, may find some explanation in this direction.

The fact that the average energy spent by an α ray in producing an ion is less than that spent by any β ray, shows that the theory which leads to the conclusion that α rays should behave in respect of ionization exactly like β rays of twice their speed cannot be wholly correct. But it is not surprising that conclusions based on the hypothesis that an α ray is a simple point charge should not agree in all respects with experiment.

12. This discussion has been vague and tentative. The conclusion which is intended to be drawn is that, while Thomson's theory of ionization does not provide a complete explanation of all the facts, and cannot do so until the intra-atomic forces are further taken into account, there is nothing resulting from experiments on δ rays which is necessarily inconsistent with that theory. The most remarkable of these results which formerly seemed to me inconsistent with any simple theory of ionization, namely, that the velocities

of the δ rays are almost independent of the nature of the primary rays and the material on which they act, appears to be a direct consequence of Thomson's theory and Lenard's proof that the least energy necessary for ionization is approximately the same for all gases. The quantitative discrepancy between the theory and experiment is probably to be attributed to secondary action by the δ rays after they are liberated from the atoms.

It does not appear to me likely that any further light will be thrown on the mechanism of ionization by direct measurements of the velocity of δ rays emitted under various conditions.

SUMMARY.

The existing information as to the emission of δ rays is reviewed.

Some new experiments on the δ rays excited by very slow β rays are described. They are in complete accordance with the work of v. Baeyer and Gehrts and provide little new information.

An attempt is made to discuss the experimental results on the basis of the theory of ionization by moving charged particles, put forward by Sir J. J. Thomson. It is concluded that, while that theory cannot at present provide a complete explanation of the facts, it is qualitatively in agreement with them and in no way obviously inconsistent with them.

Leeds, April 1913.

LXXXV. *On Rotational Optical Activity of Solutions.* By G. H. LIVENS, M.A., *Fellow of Jesus College, Cambridge* *.

1. *Introduction.*

THE most satisfactory theoretical treatment of the phenomena of intrinsic optical activity of rotational type is that given by Drude in his 'Optics.' The actual phenomenon has, however, been found to be much more complicated than Drude's theory would lead one to expect. This is especially the case with solutions of active substances in active or inactive liquids, wherein the rotativity depends on the nature of the substances and the concentration of the solution. The discrepancies between theory and practice have been the subject of a large amount of experimental

* Communicated by the Author.

investigation, but so far no good theoretical explanation has been obtained.

From the enormous amount of experimental data collected together by Landolt in his book * on this subject, it appears that in most cases very simple empirical relations can be constructed which represent the variability of the rotativity of a dissolved substance. For solutions of active substances in simple inactive solvents these relations usually assume one of the three forms

$$(i.) [\omega] = A + Bc,$$

$$(ii.) [\omega] = A + Bc + Cc^2,$$

$$(iii.) [\omega] = A + \frac{Bc}{C + c},$$

where $[\omega]$ is the specific rotation calculated in a manner hereinafter described, and c the concentration of the solution; A , B , C are constants depending on the nature of the substances involved.

In a few cases mentioned by Landolt and also in several cases recently investigated by Patterson †, it appears that the behaviour cannot be correctly represented by an empirical relation of either of the above forms, and no other form has as yet been suggested. The variability of $[\omega]$ with c for these cases is usually exhibited on a graph. From a careful study of the curves thus obtained, however, one realizes that there is a great deal of similarity between them and that certain typical forms can be picked out. The four curves given in fig. 1, which represent the relation for ethyl tartrate dissolved in (i.) ethylidene chloride, (ii.) α -bromonaphthalene, (iii.) benzaldoxime, (iv.) methyl iodide, are taken from papers by Patterson and are typical ones which show the general behaviour in the more complicated cases.

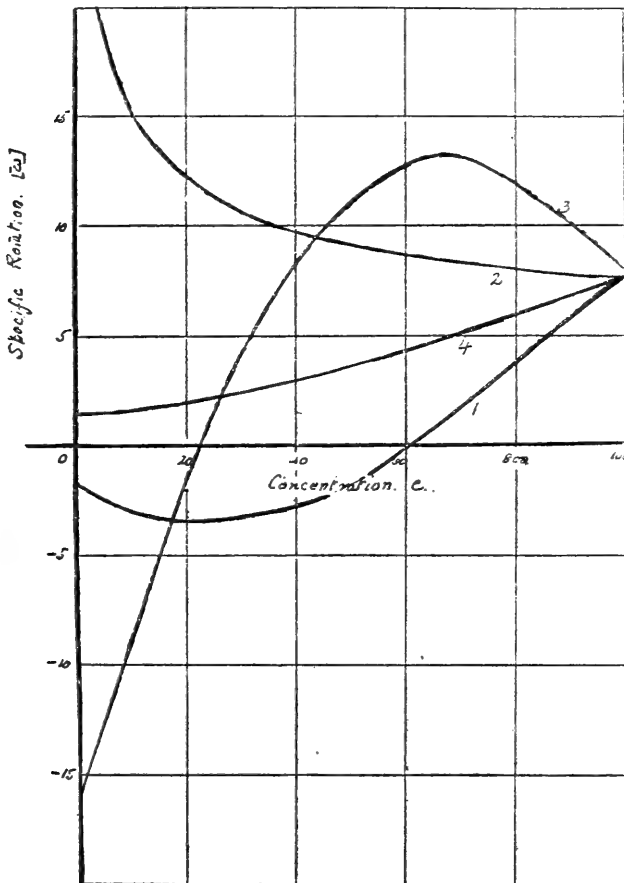
This short description may be claimed to represent the general conclusions which have been drawn from the experimental data in as far as it represents by far the largest majority of known cases. There are of course a few exceptional cases not included, and as they are not in accord with the subsequent theoretical discussion they will be reserved for future consideration.

* *Das optische Drehungsvermögen* (Brunswick, 1898).

† *Journal of Chemical Society (Transactions)*, 1908.

The object of the present communication is to show how a simple modification of Drude's theory, based on almost unassailable theoretical considerations, provides a very good

Fig. 1.



explanation of all of the above-mentioned experimental results. A general formula is obtained which includes formulæ (i.) (ii.) and (iii.) as approximations, and also provides us with the equation of the more general form of curve given in the graph.

2. General Theory.

In the modern electromagnetic theory of optics we have always to deal with the electric and magnetic force and the electric and magnetic flux, such that each flux is derived from the other force by the universally valid circuital relations. If we denote the electric and magnetic force

vectors by \mathbf{E} and \mathbf{H} respectively, and the corresponding fluxes by \mathbf{D} and \mathbf{B} , these relations are expressed by the following vector equations:

$$-\frac{1}{c}\dot{\mathbf{H}} = \text{Curl } \mathbf{E}, \quad \frac{1}{c}\dot{\mathbf{D}} = \text{Curl } \mathbf{H}.$$

The Herz-Heaviside units are adopted.

The influence of the molecules of the medium expresses itself only on the form of the relations, depending on the constitution of the medium, connecting each flux with the corresponding force. Since in light phenomena we can always assume $\mathbf{B} = \mathbf{H}$, we need only to investigate further the relation between \mathbf{D} and \mathbf{E} . This is obtained in Drude's theory by a statistical analysis of the motions of the contained electrons, to which the electric flux due to the presence of the medium is directly reducible. These electrons are supposed to be connected to the molecules of the medium by quasi-elastic forces, and are resisted in their motion by frictional forces proportional to the velocity. In the present discussion we shall neglect these frictional forces, so that the equations of motion of the electrons are of a type

$$m(\ddot{x} + n_0^2 x) = eE_x,$$

wherein (x, y, z) are the components of the displacement of the electron from its position of rest; m its mass and e the charge on it; mn_0^2 is the parameter of the quasi-elastic force.

Lorentz has, however, shown* that the force on a contained electron due to the electric field is not completely represented by $e\mathbf{E}$. We must, in fact, add a term $e\mathbf{f}(\mathbf{P})$, where $\mathbf{f}(\mathbf{P})$ denotes an undetermined vector function of the polarization \mathbf{P} of the medium. To a first approximation it is shown that $\mathbf{f}(\mathbf{P}) = a\mathbf{P}$, where a is very nearly equal to $\frac{1}{3}$; but in second order effects of the kind under discussion other terms may occur. In order to explain the broad general facts of the phenomenon at present under review, it is, in fact, necessary to assume, after Lorentz, that

$$\mathbf{f}(\mathbf{P}) = a\mathbf{P} + b \text{Curl } \mathbf{P}.$$

The constant b being another physical constant of the medium. This second order term $b \text{Curl } \mathbf{P}$, which has its origin in an intrinsic chiral structure of the molecule or

* *Versuch einer Theorie der elekt., u. opt., Erscheinungen &c.* (Leipzig, 1906) pp. 78-81.

molecular group, is, however, only appreciable in the neighbourhood of the optically active molecules: for simplicity it will be assumed to act only on the electrons actually contained within these molecules.

The typical equation of motion of a contained electron thus assumes the more general form

$$m(\ddot{x} + n_0^2 x) = e(E_x + \alpha P_x) + eb \text{Curl}_x P.$$

If plane homogeneous waves of light of frequency n are propagated through the medium, we find in the usual manner that the above equations lead to a general relation connecting the electric force E with the electric polarization intensity P of the form

$$P = \left(\sum \frac{e^2/m}{n_0^2 - n^2} \right) (E + \alpha P) + \left(\sum' \frac{be^2/m}{n_0^2 - n^2} \right) \text{Curl } P;$$

wherein Σ denotes a sum taken over all the electrons, but Σ' only over those contained in the optically active molecules.

Lorentz writes this relation in the form

$$E = \alpha P + \beta \text{Curl } P,$$

without giving any account of the constants α and β .

Starting from this relation, it can be easily verified that the velocities of the two kinds of circularly polarized waves are respectively the roots of the two cubic equations in μ :

$$(\mu^2 - 1)(\alpha \pm \beta n \mu) = 1.$$

The combination of these two oppositely circularly polarized beams leads as usual to a pencil of linearly polarized light whose plane of polarization is being rotated at a rate per unit length

$$\omega = \frac{1}{2}(\mu_+ - \mu_-)n.$$

In any case we know that the coefficient β is so small that we can approximate to the values of μ by expanding in powers of β . This gives

$$\mu_{\pm} = \mu_0 \pm \frac{1}{2} \frac{\beta n}{\alpha^2} + A\beta^2 + \dots$$

so that very approximately

$$\omega = \frac{1}{2} \frac{n^2 \beta}{\alpha^2},$$

or inserting the values of α and β we deduce that

$$\frac{2\omega}{n^2} = \frac{\left(\sum' \frac{be^2/m}{n_0^2 - n^2}\right) \left(\sum \frac{e^2/m}{n_0^2 - n^2}\right)}{\left(1 - \sum \frac{ae^2/m}{n_0^2 - n^2}\right)^2}.$$

We now assume that $\sum' \frac{e^2/m}{n_0^2 - n^2}$ taken per unit volume for any definite set of electrons is proportional to the partial density of the substance with whose molecules they are associated. Thus, if active substances are present in a mixture at partial densities ρ_1, ρ_2, \dots with inactive substances at partial densities $\sigma_1, \sigma_2, \dots$ we shall have

$$\frac{2\omega}{n^2} = (r_1'\rho_1 + r_2'\rho_2 + \dots) \frac{r_1\rho_1 + r_2\rho_2 + \dots + s_1\sigma_1 + s_2\sigma_2 + \dots}{[1 - a(r_1\rho_1 + r_2\rho_2 + \dots + s_1\sigma_1 + \dots)]^2},$$

wherein $r_1', r_2', \dots; r_1, r_2, \dots; s_1, s_2, \dots$ are all physical constants of the respective substances to which they refer, depending on the nature of these substances and the frequency of the light used. Regarding the magnitude of the undashed letters, we know that if μ is the index of refraction for the solution, then

$$\frac{\mu^2 - 1}{a(\mu^2 - 1) + 1} = \sum r_1\rho_1 + \sum s_1\sigma_1.$$

We thus see that the rotative power of the mixture depends to a large extent on the presence of the inactive substances, and is not merely proportional to the partial density of the active substances, as the elementary form of Drude's theory would lead one to expect. An examination of this formula in a less general case will throw more light on the exact nature of this dependence of the rotativity on the constitution of the mixture.

3. *Application to a special case : a simple solution.*

We shall now discuss the above formula in as far as it applies to the experimental case, viz. that where a simple active substance is dissolved in an inactive liquid. The results for these cases are usually exhibited as a function of the concentration c of the solution, *i. e.* the number of grams of active substance per cubic centimetre of solution. If d

is the density of the solution we shall have $(d-c)$ grams of inactive solvent per unit volume so that

$$\rho_1 = c, \quad \sigma_1 = d - c, \quad \rho_2 = \sigma_2 = \dots = 0.$$

Thus in this case

$$\frac{2\omega}{n^2} = r'c \frac{rc + s(d-c)}{[1 - \alpha(rc + s\overline{d-c})]^2}.$$

Although there is no actual theoretical reason for the assumption, yet a sufficiently good approximation is obtained if we put

$$d = d_0 + d_1c,$$

d_0 and d_1 being constants of the substances involved.

Thus we have

$$\frac{2\omega}{n^2} = r'c \frac{c(r + s\overline{d_1-1}) + sd_0}{[1 - \alpha sd_0 - \alpha c(r + s\overline{d_1-1})]^2}.$$

The quantity usually determined is the specific rotation of the solution, *i. e.* the rotation produced by a solution containing 1 gram of active substance per c.c. of solution, and this is always defined as $\frac{\omega}{c}$. If we denote it by $[\omega]$ we have

$$[\omega] = \frac{\omega}{c} = r' \frac{c(r + s\overline{d_1-1}) + sd_0}{[1 - \alpha sd_0 - \alpha c(r + s\overline{d_1-1})]^2},$$

a formula which expresses the specific rotativity of the solution as a function of the concentration: the constants in it are dependent essentially on the nature of the solvent and active solute. This is the general formula, but if the terms in c are small as is usually the case, various approximations may be made by expanding it in different ways. Direct expansions in powers of c would give a result

$$[\omega] = A + Bc + Cc^2 + \dots, \quad \dots \dots \dots (i.)$$

or expansion of numerator and denominator separately would give

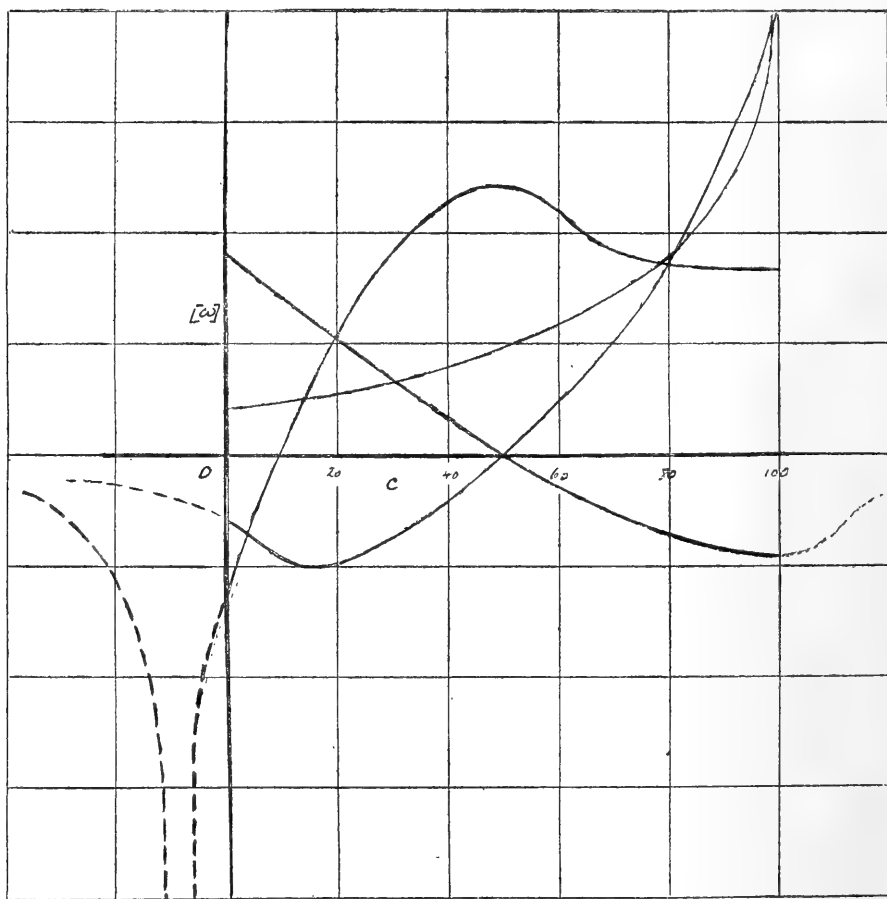
$$[\omega] = \frac{(A' + B')c + A'C'}{C' + c} = A' + \frac{B'c}{C' + c}, \quad \dots (ii.)$$

so that each of the empirical relations quoted may be regarded as approximations to the more general formula, which we can write in the form

$$[\omega] = \frac{A'' + B''c}{(C'' + c)^2} \cdot \dots \dots \dots (iii.)$$

Moreover, this general formula would appear to include most of the results which have not yet been expressed by an empirical relation. This is perhaps best seen by plotting a graph of the function and comparing it with that given as fig. 1. As, however, the curve may have various dispositions with regard to the axes and only a portion of it in each case corresponds to a real experimental region, I have drawn four possible cases, in one of them only completing the curve beyond the experimentally attainable region by a dotted line.

Fig. 2.



It would thus appear that the more correct form of equation representing the empirical relation between the quantities involved is the formula (iii.) which results from our theoretical investigation.

Such a discussion, short as it is, provides almost convincing proof of the appropriateness of our theory; but there are certain facts which detract from its completeness. There are a few substances whose behaviour is quite contradictory to

the present exposition. Of course, in a subject of such complexity it is hardly likely that any such simple theory can give a complete account of the whole matter ; but it is nevertheless interesting to notice one or two points where the present theory fails.

Firstly, according to our formula the specific rotation has a minimum value

$$[\omega] = -\frac{r'n^2}{8a},$$

corresponding to the concentration

$$c = \frac{1 - asd_0}{a(r - s1 - d_1)},$$

which may conceivably be experimentally attainable. The minimum value of the rotation would thus on this theory appear to be entirely independent of the particular solvent, unless indeed the constant a involves some account of that substance. Although approximately verified in one or two instances, this relation does not seem to be generally true for most of the substances for which the minimum is attainable.

Again, with some few substances in particular solvents it is found that the rotation decreases with increasing concentration, but that the minimum value occurs before a change of sign takes place. This could not happen according to our formula.

4. Conclusion.

In spite of these few discrepancies the experimental results may be said to be satisfactorily verified by the theoretical formula deduced. The apparent anomalous behaviour of the few substances which do not conform to the general rules above laid down will form the subject of further investigation, as it probably has its origin in some additional (probably chemical) actions involved in the phenomena ; actions which are consistent with but not necessarily dependent on those discussed. In the meantime, however, direct experimental evidence of an additional and independent nature may be obtained for the present theory, or against it. The most general method of investigating its appropriateness is by a detailed analysis of the other optical properties of such solutions ; for it appears on this theory that the variation in the rotativity of a dissolved substance is not due to any direct modification of the rotatory power

of a molecule, but to the modified electrodynamic constitution of the medium, through which the light travels, causing a variation of the velocity of transmission. The variations here discussed will therefore be closely associated with the variation with the concentration of the ordinary index of refraction ϵ of the solution for the particular light used. In fact, for the case above discussed in detail

$$\frac{\epsilon^2 - 1}{a(\epsilon^2 - 1) + 1} = rc + s(d - c),$$

so that

$$[\omega] = \frac{r'n^2a}{2} (\epsilon^2 - 1) \left(\epsilon^2 - 1 + \frac{1}{a} \right),$$

which gives a relation between $[\omega]$ and ϵ . Unfortunately, I have not sufficient information to hand to tell whether the variation of the function $(\epsilon^2 - 1) \left(\epsilon^2 - 1 + \frac{1}{a} \right)$ with the concentration of the solution is at all similar to the variations of $[\omega]$, especially in the more complicated cases. I hope, however, that some one will take up the question experimentally at this point so as to provide the necessary data for a comparison.

LXXXVI. *The Origin of the Bands in the Spectrum of Active Nitrogen.* By E. PERCIVAL LEWIS, *Professor of Physics, University of California*.*.

[Plate X.]

IN 1899 the writer observed a new form of afterglow in nitrogen, excited only by a condensed discharge with spark-gap, and having a characteristic band-spectrum †. Further results were published in 1904 ‡. The approximate wave-lengths of the bands were determined, and the remarkable fact emphasized that the vapours of mercury from the pump and from aluminium, zinc, and platinum electrodes participated in the afterglow some time after the discharge had ceased, their principal spectral lines appearing as long as the glow lasted. Experiments on a larger scale were made by Strutt §, who showed that other substances were also excited to luminosity by the glowing gas, to which he gave the name "active nitrogen." Strutt and Fowler published the details of the spectrum of the active nitrogen || with greater dispersion than had been available to me.

* Communicated by the Author.

† *Astrophys. Journ.* xii. p. 8 (1900); *Ann. der Phys.* ii. p. 249 (1900).

‡ *Astrophys. Journ.* xx. p. 49 (1904).

§ 'Bakerian Lecture,' *Proc. Roy. Soc.* lxxxv. p. 219 (1911).

|| *Proc. Roy. Soc.* lxxxv. p. 777 (1911).

In discussing the phenomenon, I was inclined to the opinion that the afterglow might be the result of the presence of infinitesimal traces of oxygen or of nitric oxide, partly because, in spite of the utmost precautions, it seemed unlikely that the nitrogen used by me was entirely free from these impurities, but more particularly because of the usual presence in the spectrum of the third group of "nitrogen" bands, attributed by Deslandres and others, apparently with good reason, to nitric oxide. The nitrogen was prepared by heating a solution of sodium nitrite and ammonium sulphate, and was then passed through pyrogallie acid solution and drying-tubes. When the gas was first admitted to the tube while a feeble discharge was passing, the glass fluoresced brilliantly for several seconds, but this effect soon died out, apparently as the result of some chemical reaction. The spectrum taken during the fluorescent stage showed the third group of bands of remarkable intensity, and this ultra-violet radiation produced the fluorescence. These bands were also usually present in the spectrum of the afterglow.

Strutt and Fowler are of the opinion that the afterglow occurs only in nitrogen entirely free from oxygen, and that both the third group and the new bands are due to nitrogen. Recently, however, Comte* has made some experiments from which he has concluded that the afterglow is not found in pure nitrogen, but only when minute quantities of oxygen are present.

In my photographs, reproduced in the 'Astrophysical Journal' for July, 1904, it may be seen that in some cases the new ultra-violet bands appear, in others there is no trace of them, the only features of this region being the mercury lines and some bands apparently due to cyanogen. The visual bands in the green, yellow, and red were invariably observed. At the time the cause of these differences was not apparent. More recent attempts to reproduce the original results invariably failed, the cyanogen bands and visual bands always appeared, but there was no trace of the ultra-violet bands. It may be noted that in the later experiments nitrogen was used which had for some time been standing in the storage system, which consisted of bottles of pyrogallie acid and caustic potash solutions and drying-tubes containing caustic potash and phosphorus pentoxide.

Recently, while studying the spectra of mixtures of nitrogen and oxygen, the explanation has been found. With no kind of discharge, strong or weak, could the spectrum of the third group be obtained when approximately pure nitrogen was used; but when a small quantity

* *Phys. Zeit.* xv. p. 74 (1913).

of oxygen was added they invariably appeared when the discharge was weak, and also with the condensed discharge in a large vacuum-tube. In addition, feeble traces of the new group of bands observed by me, and called the β group by Strutt and Fowler, were found whenever the third group was seen.

The study of the afterglow was then resumed. The spectra were obtained with the large quartz spectrograph secured with the aid of a grant from the Carnegie Institution of Washington*. A large end-on tube was used, with a quartz window, and a real image of the cross-section of the tube was thrown on the spectrograph slit. In this way the spectrum of the active nitrogen was superimposed on that of the discharge, and extended a little way beyond it. At the first trial the tube leaked slightly, but the afterglow could be maintained by repeatedly pumping out and refilling. The spectrum showed every band recorded by Strutt and Fowler and by me, and also the "fourth positive group" first observed by Strutt and Fowler. As remarked by them, these bands are found only in the spectrum of the discharge which produces the afterglow, but not in the spectrum of the afterglow itself.

A fresh supply of nitrogen was prepared as before. Kreusler† states that nitric oxide is present in nitrogen prepared from sodium nitrite and ammonium sulphate. Such appeared to be now the case; with a feeble discharge the fluorescence of the glass was strong when the gas was first admitted, and the spectrum of the third group was intense. In the afterglow spectrum the other ultra-violet bands (except the "fourth positive") also appeared. The smell of nitrogen peroxide in the gas escaping from the pump left no doubt as to the original presence of nitric oxide. After twenty-four hours the fluorescence could barely be produced; after seventy-two hours none was to be seen, and in the spectrum of the active nitrogen the third group and β bands were barely perceptible, while cyanogen bands appeared. The nitric oxide had evidently been absorbed by the pyrogallic acid or by the drying materials.

When oxygen was admitted, so long as it was thoroughly mixed with the nitrogen in advance, there was no afterglow until the proportion of oxygen was reduced to something below one per cent. At less than one-half per cent. the glow was fairly strong, and was very bright when at least one-tenth per cent. was certainly present. The discharge

* *Astrophys. Journ.* xxiii. p. 390 (1906).

† *Ann. der Phys.* vi. p. 419 (1901).

was greatly affected by traces of oxygen ; with one-half per cent. present, the condensed discharge would not pass at a pressure above 2.5 cm. ; when the nitrogen reached the limit of purity, the discharge passed at a pressure over 4 cm. One of the most remarkable facts noted was that after the glow had been once established, oxygen could be admitted to the pump until the pressure was raised 20 per cent. without destroying it. The discharge-tube was connected with the pump by a tube about 4 mm. in diameter and 250 cm. long, and as the oxygen slowly diffused over into the tube the active nitrogen seemed able to dispose of it in some way—possibly by converting it into nitrogen peroxide. Under these conditions the afterglow would last several hours, only slowly diminishing in intensity. If a little nitrogen was admitted, however, it drove the oxygen into the tube *en masse*, and the glow was immediately destroyed. If several minutes elapsed after admitting the oxygen before the discharge was set up, the afterglow was weak or absent. It was also noted that nitrogen which at first contained a sufficient amount of oxygen to barely produce the third group of bands, would cease to do so after the discharge had passed for some time. (Compare fig. *f* in the ultraviolet of Plate X. with *e* and *d*. These were made with the same filling of gas, *f* being taken first.) Possibly all the oxygen or nitric oxide had been converted into peroxide by the discharge.

Photographs of the pure afterglow spectrum, after the discharge had ceased, were obtained by the use of a sectorized occulting disk which rotated in front of the slit and broke the circuit at regular intervals before the exposure was made. A number of photographs were taken with the nitrogen as pure as possible, and also with various proportions of oxygen. Some of these photographs are reproduced in Plate X. and are described below. The comparison spectrum is that of the iron spark.

a. The true afterglow spectrum of nitrogen containing a small proportion of oxygen initially. After the afterglow was established, enough oxygen was admitted to the pump to raise the pressure 15 per cent. Nevertheless, the glow lasted during a three-hour exposure. The third and β groups are strong ; the second positive group do not appear.

b. The condensed discharge in the same gas (taken before *a*). It is to be noted that the “fourth” group of bands do not appear.

c. The uncondensed discharge in nitrogen containing a

small trace of oxygen. The β group are clearly seen on the original negative, but are not relatively so strong as in *a* and *b*.

d. The true afterglow spectrum with a minimum of oxygen present. The third group and β group are absolutely lacking (compare with *a*), although the former are faintly visible in *f*' and *e*, taken previously with the same gas. The cyanogen bands, which are lacking in the other photographs, are now strong. In structure they are exactly like the bands described by Strutt and Fowler*, and attributed by them to cyanogen. They probably arise from stop-cock grease.

e. The condensed discharge in the same gas, accompanied by the afterglow. Some bands of the third group are faintly visible.

f. The spectrum of the uncondensed discharge in the same gas.

Other photographs taken after the nitrogen had been for a longer time in storage showed absolutely no trace of the third and β groups under any conditions.

The visual bands in the green, yellow, and red were strong in all these cases. Without doubt Strutt and Fowler are correct in stating that they are the survivals of certain bands in the first positive group. It may be mentioned that these bands, first observed by me, were also seen by Schniederjost in an apparently imperfectly developed afterglow†.

In addition to the bands heretofore described, three pairs of faint bands were found, of approximate wave-lengths 4390, 4410, 4488, 4505, and 4596. The first pair appears to belong to Strutt and Fowler's β_1 group, the others to the β_2 group, as shown by their series relations.

A number of observations were also made with nitrogen prepared by passing air over phosphorus. The afterglow was strongly developed, but the third and β groups of bands were not found in the spectrum. The cyanogen bands were strong.

The spectrum of nitrous oxide continuously admitted to the tube and pumped out contained all the bands found in the afterglow spectrum, but nothing additional. It did not destroy the afterglow when admitted, but produced merely a slight change in colour, which passed away in a few moments. When nitric oxide was admitted to the glowing gas, the green flame mentioned by Strutt was seen. The spectrum obtained by adding oxygen, nitrous oxide, and nitric oxide

* Proc. Roy. Soc. lxxxvi. p. 105 (1912).

† Zeit. für Wiss. Bot. ii. p. 277 (1904).

to nitrogen appears to be the same, both for the uncondensed discharge and the afterglow. There is strong fluorescence of the glass at first when either nitrous or nitric oxide is admitted to the uncondensed discharge, accompanied by a strong flaring-up of the third group. There is no strong fluorescence when oxygen is admitted, although there is enough to be observed.

These results show that the third positive group of bands always appear when very small traces of oxygen are present, and are absent when the nitrogen is freed from oxygen as far as possible. The β group of bands always appear with the third group, but have a greater relative intensity in the spectrum of the afterglow. Both appear with the condensed discharge in a large tube, but not in a small one, where the current density is greater. No characteristic difference can be observed between the effects of adding small quantities of oxygen, nitrous oxide, or nitric oxide, but the inference is inevitable that these bands are in some way dependent upon oxygen.

It appears that the only invariably characteristic part of the afterglow spectrum are the bands with heads at 6322, 5854, 5442, and 5053, belonging to the first positive group. In my experiments the afterglow continuously increased in intensity as the proportion of oxygen was reduced; but I doubt whether in any case the nitrogen was completely freed from oxygen or nitric oxide. The origin of the afterglow seems, therefore, an open question; it may be an attribute of pure nitrogen, or it may be caused by traces of oxygen or other impurity. When so much oxygen is mixed with the nitrogen that there is no trace of afterglow with a moderate discharge, it may be set up brightly by an intense discharge; and it seems possible that with a sufficiently strong discharge it might be produced with large quantities of oxygen present.

I have so far failed to determine the conditions under which Strutt and Fowler's "fourth group of positive bands" appear. They were first obtained by me in the spectrum of the condensed discharge in nitrogen in which the afterglow could be maintained only with difficulty on account of leakage of air, and since I have been able to obtain them with clearness only when air was introduced. There are faint indications of their presence on films taken with a slight admixture of oxygen, but no trace of them on photographs of the spectrum of nitrogen free as far as possible from oxygen. There were some indications that they are due to enhancement of certain lines of the third group of bands, but this is

not certain. Their structure is so unlike that of other nitrogen bands that, in spite of the series relationships indicated by the results of Strutt and Fowler, it is hard to believe that they are due to nitrogen alone.

It seems clear from these experiments and the photographs previously published in the 'Astrophysical Journal,' that the second group of bands belong exclusively to the discharge, not to the afterglow; while the third and β groups are relatively more intense in the afterglow. The former are associated with the period of dissociation, the latter with the period of recombination. Of course these effects are superimposed in the uninterrupted discharge.

In closing this paper my attention has been called to an article by König and Elöd in the *Physikalische Zeitschrift* for February 15, 1913. They are of the opinion that the afterglow is a property of pure nitrogen. This may well be the case, but I doubt whether it has been proven. It seems certain that the nitrogen used by me and by Strutt was not free from oxygen, and I am not convinced that anyone has ever worked with nitrogen free from oxygen.

Berkeley, Cal.,
March 11, 1913.

LXXXVII. *Ionization in Gases and Gaseous Mixtures by Röntgen and Corpuscular (Electronic) Radiations.* By C. G. BARKLA, F.R.S., Wheatstone Professor of Physics, and A. J. PHILPOT, B.Sc., Layton Research Scholar, King's College, London*.

A STUDY of the ionization produced in gases and in mixtures of gases and vapours by corpuscular radiations and by Röntgen radiations furnishes valuable information regarding the processes taking place during the transmission of these rays through matter. The investigations on this subject described in the following paper will be considered under several headings.

Total Ionization by Corpuscular (Electronic) Radiation in Gases.

The relative ionizations produced in several gases by the complete absorption of corpuscular radiations set up by Röntgen radiation were investigated by Kleeman†, and important conclusions were drawn from the results obtained.

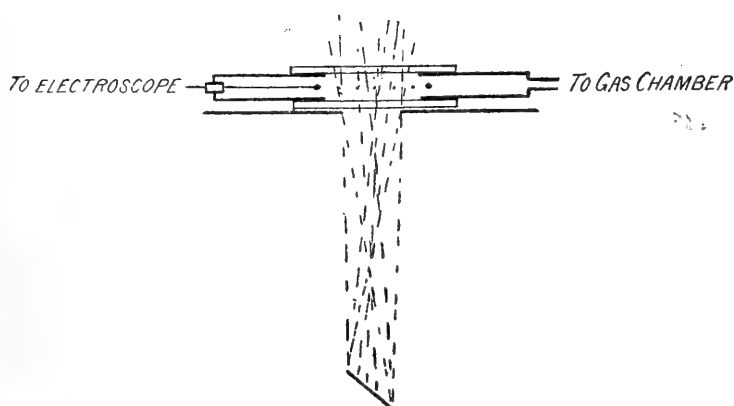
* Communicated by the Authors.

† Proc. Roy. Soc. A. lxxxiv. pp. 16-24 (1910).

The corpuscular radiations were, however, of the variable and uncertain type set up by heterogeneous beams of Röntgen rays and the gases and vapours ionized were not the most suitable for our purpose, as the following considerations will show. In our experiments the corpuscular radiation studied was that emitted by thin sheets of gold traversed by homogeneous beams of X-rays. As is well known, the velocity of the ejected corpuscles depends not on the element emitting them *, or on the intensity of the Röntgen radiation causing their ejection, but simply on the absorbability—(or wavelength)—of this Röntgen radiation. In these respects as in many others the properties of Röntgen radiation are identical with those of ultra-violet light.

The ionization-chamber used in these experiments consisted of a shallow metal box 1 centimetre in depth, with square ends of about 10 centimetres edge (see fig. 1). Large square

Fig. 1.



apertures were cut in these metal ends, and carbon plates about 2 mm. thick were placed on the flat ends over these apertures, and the whole chamber made air-tight by means of wax poured on the outside of the plate, and round the edges. The carbon plates could be easily detached and refixed in the same position. A square electrode of aluminium wire crossed by meshes of extremely fine aluminium thread was placed in a plane midway between the two end faces. This electrode was connected through an insulating ebonite plug to the gold-leaf system of an electroscope. When the homogeneous X-radiation from a secondary radiator was allowed to fall on one face of the ionization-chamber, the beam which traversed the carbon window passed within the outer

* It is possible that the velocity depends to a slight extent on the element, as it appears to do when ultra-violet light causes the ejection. No such dependence has been established in the case of X-rays.

boundary of the square terminal, and left through the opposite carbon plate. The only portion of the terminal exposed to the radiation was the meshwork of threads,—too fine to produce an appreciable secondary radiation. The corpuscular radiation emerging from the carbon plates into the gas was then small, less in fact than the corpuscular radiation leaving the gas and entering the carbon except when hydrogen was the ionized gas, or in some cases when the pressure of the gas was low.

The ionization produced in the gas by the beam of Röntgen radiation was observed first when the carbon plates were uncovered inside, and afterwards when they were both covered inside with three gold leaves about 10^{-5} cm. in thickness. (A second electroscope was used to standardize the intensity of the homogeneous Röntgen radiation.) The difference between the two ionizations observed in the ionization-chamber described was due to the much greater intensity of corpuscular radiation entering the contained gas from the gold than from the carbon. It may be readily shown from the observations of Barkla and Sadler on secondary X-radiation, that the X-radiations from the gold produced a negligible ionization in a chamber so short as that used. This has also been shown by direct experiment by Kleeman* for a longer ionization-chamber. The loss of secondary radiations of all types from the gas into the walls of the chamber was of course the same in each case, and for our present purpose need not be considered. The return of tertiary X-radiations excited by these secondaries in the carbon or gold walls of the chamber may also be neglected because tertiary radiation of the X-type from either carbon or gold was certainly far too weak to be appreciable. We have, however, to consider the possibility of different amounts of energy of corpuscular radiation being returned by the gases into the ends and by the ends into the gases when the ionizations in two gases were compared. Though accurate data giving the amounts returned thus are not available, examination of the different possibilities shows that the error would be small in the cases investigated, and a close examination of the results themselves supports this. We hope by using ends of very different reflecting power to be able to reduce the possible error, if this is at all appreciable.

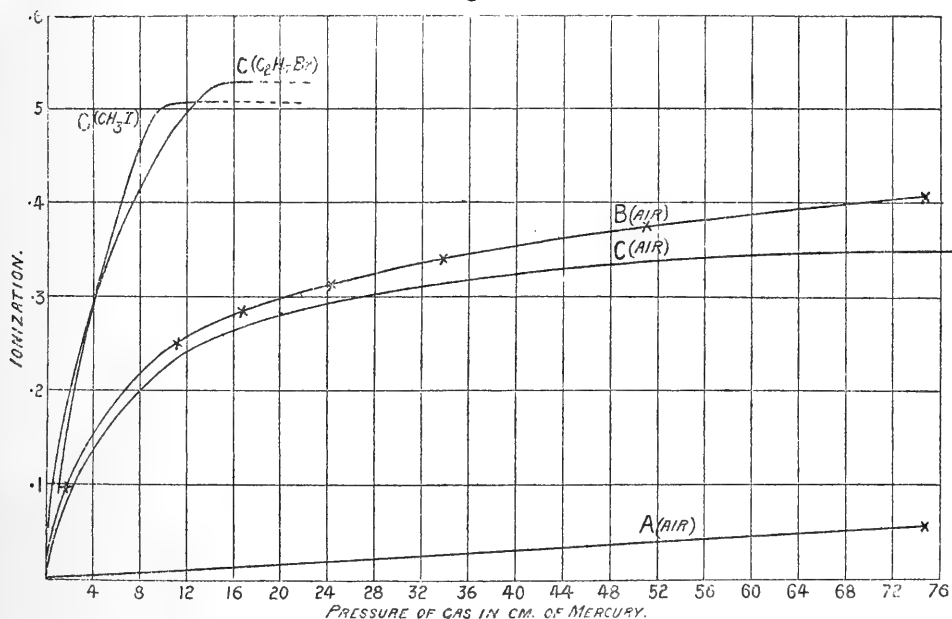
The difference between the two ionizations when a particular primary X-radiation was used was thus due to the excess of corpuscular radiation escaping from gold over that from carbon, when these were traversed by that primary

* *Loc. cit.*

radiation. That the corpuscular radiation was totally absorbed by the gas inside the ionization-chamber was shown by finding the relation between ionization and pressure of the gas in the manner of Beatty*.

In fig. 2, line A shows the ionization produced by Sn X-radiation (series K) in air at different pressures, when the

Fig. 2.



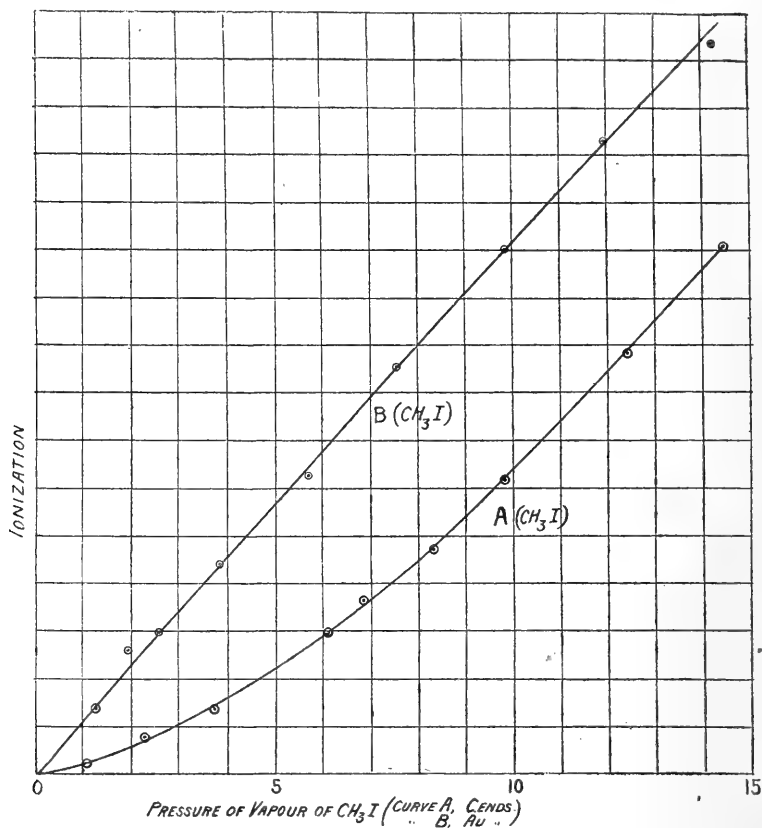
ends of the ionization-chamber were of carbon, assuming the ionization to be proportional to the pressure. Such a relation would of course hold only if the ends were of air; with carbon ends the curve is actually concave upwards, but the ionization is so small in comparison with that due to the corpuscular radiation, that the error in assuming proportionality is negligible. In the apparatus we used, the deviation was too small to be readily measured. Curve B shows the relationship between ionization and pressure when the ends were of gold. Subtracting the ordinates of curve A from the corresponding ordinates of curve B gives the ordinates of curve C, which thus represents the relation between the ionization produced by a corpuscular radiation in the air and the pressure of the air,—the corpuscular radiation being the difference between the corpuscular radiations from gold and carbon, excited by the X-radiation of series K characteristic of tin.

Similar experiments were performed with ethyl bromide and methyl iodide vapours in the ionization-chamber. The

* Proc. Roy. Soc. A, lxxxv. p. 358 (1911).

corresponding final curves are shown in fig. 2. In the experiments with ethyl bromide and methyl iodide, the full ionization-pressure curve was obtained experimentally when the ends of the ionization-chamber were of carbon as well as when of gold. Fig. 3, for instance, shows the corresponding

Fig. 3.



A and B curves for methyl iodide. They are specially interesting because of their particular form. The curve A is concave upwards because there is a net loss of radiation by the methyl iodide at the ends when these are of carbon. Curve B is only slightly convex upwards because there is only a slight gain of radiation at the ends from the gold.

It is evident from these curves then that at atmospheric pressure, air and all heavier gases completely absorbed the corpuscular radiation from the two end faces; and that ethyl bromide and methyl iodide produced complete absorption of the end corpuscular radiation at much lower pressures. The critical pressures for air, C₂H₅Br, and CH₃I—that is, the pressures at which no corpuscular radiation was able to get across a chamber 1 centimetre in thickness—were 66, 16, and 12 centimetres of mercury respectively. If we multiply

these by the molecular weights of the gases, we get numbers proportional to 190, 174, and 170, which are the relative masses of these gases required to produce complete absorption of the corpuscular radiation. The agreement between the products for ethyl bromide and methyl iodide is very close, while the difference between this and that for air amounts to about 10 per cent. of the whole. These results show that the maximum distance traversed by a corpuscle through these gases is approximately inversely proportional to the density of the gas.

It will be observed that there were large differences between the ionizations produced in the two vapours and in air by the complete absorption of the corpuscular radiation, the relative values being 1·0, 1·50, and 1·48 in air, ethyl bromide, and methyl iodide respectively.

It was evidently unnecessary to determine a series of ionizations at various pressures for all gases, for beyond the pressure just sufficient to completely absorb the corpuscular radiation, the measured ionization was seen to be constant. (See curves C, fig. 2.) Various gases were therefore introduced into the ionization-chamber, two ionizations—those obtained with carbon and with gold ends to the ionization-chamber—were measured, and the difference was found. As an example showing the order of agreement between the results of different experiments, the following details of observations are given.

TABLE I.

Giving results of experiments on the relative total ionizations produced by corpuscular radiation (that excited by Sn X-rays, series K) in air and sulphur dioxide.

Gas.	Ionization in chamber with carbon ends.	Ionization in chamber with gold ends.	Corrected ionization due to corpuscular radiation.	Total ionization in SO ₂ by corp. radiation.
				Total ionization in air by corp. radiation.
Air	1·0	9·77	8·80	·97
SO ₂	7·46	15·90	8·66	
Air	1·0	9·73	8·76	·95
SO ₂	7·46	15·51	8·27	
Air	1·0	10·79	9·82	·96
SO ₂	7·82	17·00	9·42	

This table requires little explanation. Column 4 gives the difference between the value in column 3 corrected for
Phil. Mag. S. 6, Vol. 25, No. 150, June 1913. 3 L

the absorption by the gold leaves and that in column 2. Column 5 gives the ratio of ionization in SO_2 to ionization in air due to the complete absorption of a corpuscular radiation.

The actual order of experiments was the determination first of ionizations in a number of gases occupying the ionization-chamber in turn when this was faced with carbon, and afterwards of the ionizations in the same gases when the two ends were faced with gold. This ensured more exactly the same experimental conditions for the various gases.

The range in the velocity of the corpuscles obtainable by means of the homogeneous Röntgen radiations is certainly not very wide, though the absorbabilities may vary enormously. The extreme radiations with which accurate results could be obtained were those excited by Se and by Sn X-radiations of series K. According to Whiddington the range of velocity of the most rapidly moving corpuscle in each case is from $\cdot 8$ to $1\cdot 2 \times 10^{10}$ cm. per second. Using Sn X-radiation (series K) to excite the corpuscular radiation, the ratio of total ionizations in SH_2 and SO_2 was $1\cdot 40$; using Se radiation it was $1\cdot 43$, which was within the possible error of experiment in agreement with the other. It was evident that within the range of velocity here experimented upon the relative ionizations were independent of the velocity.

The corpuscular radiations subsequently employed in these experiments were those excited in gold by Ag, Sn, and Ba X-radiations (series K).

The relative total ionizations produced in nine gases and vapours by the complete absorption of identical corpuscular radiations are given in the following Table.

TABLE II.

Showing relative numbers of ions produced by corpuscular radiation (set up by a homogeneous X-radiation) when completely absorbed in various gases.

Gas ionized.	Relative total ionization by corpuscular radiation.	Relative energy of corpuscular radiation absorbed per pair of ions produced.
Air	100	1·00
H_2	102	·98
N_2	93	1·07
O_2	110	·91
CO_2	102	·98
SH_2	133	·75
SO_2	96	1·04
$\text{C}_2\text{H}_5\text{Br}$	150	·67
CH_3I	148	·68

The relative total ionizations due to corpuscular radiation resemble the relative ionizations found by Bragg for the complete absorption of the α rays, though there are marked differences. For α rays, for instance, some of the relative ionizations are air 100, O_2 109, CO_2 108, CH_3I 133.

Kleeman concluded from his experiments on other vapours that the relative ionization by these two types of rays were almost exactly the same. There is certainly similarity between them, but perfect agreement cannot be said to have been established.

If we divide the values found by Kleeman for the ionization per centimetre path of a β particle by the density of the absorbing substance, then on the assumption that the diminution of energy of a corpuscle per centimetre of path is proportional to the density of the substance traversed (the range of velocity being the same), we get the following relative values of the total ionization: Air 100, O_2 106, CO_2 105, SO_2 101, C_2H_5Br 116, CH_3I 112. Comparison of these results with those given in Table II. suggests either a complete change in the relative ionizations with the velocity of the corpuscles, which other experiments do not support, or that the absorption of energy is not according to the density law. Kleeman's suggestion that the absorption of β particles follows the same law as that for α particles, that is, that the relative distances travelled by α and β particles in different gases for equal losses of energy are probably the same, does not appear to be in harmony with our previous experiments on the maximum distances traversed in different gases by corpuscles.

One interesting feature of the results given in Table II. is the marked difference between the energy spent in producing a pair of ions in SH_2 and in SO_2 .

Total Ionization produced by Corpuscular Radiation in Gaseous Mixtures.

As the ionization produced by corpuscular radiation depends on the particular gas absorbing the radiation, accurate experiments on the ionization produced in gaseous mixtures by corpuscular radiation show us at once on the simplest assumptions what portion of the ionization takes place in each gas. Thus the total ionization in ethyl bromide is 1.5 times that in air. If the total ionization in a mixture of air and ethyl bromide is x times that in air, then

$$x = f(1.5) + (1 - f),$$

where f is the fraction of energy absorbed in ethyl bromide.

Knowing x we determine f .

The results of experiments similar to those on the simple gases and vapours are given in Table III.

TABLE III.

Showing relative total ionizations by corpuscular radiation in gaseous mixtures.

Gas ionized.	Total ionization due to corpuscular radiation.
Air	100
H ₂	102
C ₂ H ₅ Br	1.50
Air (59.4) + C ₂ H ₅ Br (16.6)	1.26
H ₂ (59.4) + C ₂ H ₅ Br (16.6)	1.48

Column 1 gives the gas or gaseous mixture ionized by corpuscular radiation, and the partial pressures of the constituents of a gaseous mixture; column 2 gives the relative total ionizations produced in these gases by the complete absorption of the corpuscular radiations set up by homogeneous beams of X-rays.

From the above values of the ionization in the mixture of C₂H₅Br and air, we find that 52 per cent. of the radiation was absorbed in C₂H₅Br and 48 per cent. in air. The masses were about 51 per cent. and 49 per cent. of the whole respectively. Thus as nearly as such experiments are capable of showing, in a mixture of C₂H₅Br and air the absorption of energy of corpuscular radiation by the two constituent gases is proportional to the relative masses. There is no evidence of appreciable selection. In the mixture of about 94 per cent. C₂H₅Br and 6 per cent. H₂, the calculated relative absorptions of energy by the two constituents were about 96 per cent. and 4 per cent. respectively. This result shows a large excess of energy absorption by the C₂H₅Br, though as the above was based on a single observation and as the absorption by hydrogen is very small, the possible error is too great to allow us to form a conclusion as to the deviation of the absorption by hydrogen from the density law.

Ionization in Gases and Vapours by Röntgen Radiation.

The ionization produced in gases and vapours by homogeneous beams of Röntgen radiation was first studied by one of us several years since. The results of experiments on

only two, CO_2 and $\text{C}_2\text{H}_5\text{Br}$, were published at the time, as these two were typical of all the others. The relation between the ionization of a gas and its characteristic spectrum was then shown, and a considerable portion of the ionization in ethyl bromide was seen to be due to the secondary corpuscular radiation from bromine. The results of experiments by Sadler were made use of in estimating the ionization due to the corpuscular radiation. From later work by Beatty and Bragg it appears that some of these results of Sadler's were somewhat small. Accepting Beatty's experimental results instead, the calculated percentage of ionization in $\text{C}_2\text{H}_5\text{Br}$ and air due to corpuscular radiation becomes about 80 per cent. Beatty made a careful investigation of the ionization in seleniuretted hydrogen, and concluded that in some cases at least much the greater part of the ionization was due to the secondary corpuscular radiation. By the application of the results already given in this paper to the results of Beatty's experiments, we can show that there is probably very close agreement between the ionization due to secondary corpuscular radiation and the total X-ray ionization. In the absence of more definite information, however, Beatty assumed that the corpuscles ejected from Se in SeH_2 produced the same number of ions in SeH_2 as they would in air. As Se has an atomic weight very close to that of Br, and as H_2 in SeH_2 takes the place of C_2H_5 in $\text{C}_2\text{H}_5\text{Br}$, we should estimate the number of ions that would be produced in SeH_2 to be about 1.6 times the number in air. If, then, we multiply Beatty's calculated value of the ionization produced by the corpuscular radiation by 1.6, we find in the various cases considered that 120, 87, 84, 86, and 103 per cent. of the ionization was due to the secondary corpuscular radiation. The average of these is 96 per cent.

Bragg, however, was the first to insist on the interpretation that the whole ionization was due to the secondary action of the ejected corpuscles. All experiments on ionization, however, did no more than merely indicate the possibility of this. The first convincing proof was given by C. T. R. Wilson, who showed by his condensation experiments that all the ions formed in air were to be found along the trails of the secondary corpuscles.

Turning now to the accurate determination of the relative ionizations produced in various gases and vapours by Röntgen radiation, only the results of experiments on one or two gases have been published. In addition to the work to which reference has been made, E. A. Owen * has recently made careful measurements of the ionizations in CO_2 and SO_2

* *Proc. Roy. Soc. A.* lxxxvi. pp. 426-439 (1912).

when traversed by homogeneous beams of X-rays. We give below the results of experiments which have been made at various times within the last four years on the ionizations in a number of gases and vapours produced by homogeneous radiations.

When a beam of Röntgen radiation traverses a gas, ionization is produced by secondary radiations of three types from the window and walls of the containing-chamber, exposed to the primary radiation, in addition to secondary radiations of three types from the atoms of the gas itself; consequently the total ionization depends to a large extent upon the particular conditions of the experiment governing the extent to which the gas absorbs these secondary radiations. In large ionization-chambers practically all the secondary radiations may be absorbed, while much may escape through the gas contained in small chambers. Without closely reproducing the experimental conditions, it is almost impossible from different experiments to get numerical results which show close agreement. It is essential then that in giving the results of investigations it should be precisely stated what the ionization is produced by, that is what radiation is really absorbed in the gas.

In these experiments homogeneous beams of Röntgen radiation were used as the ionizing agents, and ionization-chambers of various lengths were employed. One of these was a brass cylindrical vessel 12 cm. long and 7 cm. in diameter. This was lined with aluminium in some cases and paper in others. A very thin aluminium wire terminal was placed axially in the cylinder, and was connected through a side tube with an electroscope of the ordinary Wilson pattern. The chamber was provided with inlet and outlet tubes for the admission of gases and vapours. This ionization-vessel and a standardizing ionization-vessel were placed in position so that each received a portion of the fluorescent radiation from a particular element which was subject to the primary X-radiation from an X-ray tube. The usual precautions were taken to screen the ionization-chambers from other radiations.

The ionization in the ionization-chamber when it contained a particular gas was compared with the ionization in the same when it contained air, the radiation being unchanged and the intensity of the radiation being constant, as shown by a constant ionization in a second chamber which contained air. These observations were repeated with many radiators. As the radiation traversing the various gases is absorbed to various extents, the intensity of radiation

to which the deeper layers are exposed varies with the gas. We wish, however, to compare the ionizations produced in different gases by beams of the same intensity. If i be the ionization produced by a beam of unit intensity and unit cross-sectional area per unit length of gas traversed when all or a definite fraction of the secondary radiation is absorbed, we may write the ionization produced by a beam of intensity I and cross-sectional area A in a layer of thickness dx as $iAI dx$, and in a length l of the gas as

$$iA \int_0^l I dx,$$

provided the same fraction of secondary radiation is absorbed. We will call i the coefficient of ionization of that particular radiation in that particular gas. As the experimentally determined ionization may or may not include the ionization due to all the secondary radiations from the gas itself, the values obtained for the ionization coefficients must depend on the particular circumstances of the experiment. The particular secondary radiations which are absorbed or which escape must be stated along with the ionization coefficient.

The total ionization in a length l of gas

$$\begin{aligned} &= iA \int_0^l I_0 e^{-\lambda x} dx \\ &= iAI_0 \left(\frac{1 - e^{-\lambda l}}{\lambda} \right), \end{aligned}$$

where λ , the coefficient of absorption, has the usual meaning.

Thus, owing to the screening of the deeper layers of the gas, the ionization produced in the chamber is that which would be produced in one of length $\frac{1 - e^{-\lambda l}}{\lambda}$, if all the gas were exposed to a radiation of the intensity of the beam as it is at incidence. Calling this the effective length of the ionization-chamber, the relative coefficients of ionization are obtained by comparing the total ionizations of the gases in chambers of equal effective lengths.

It is necessary, also, to eliminate the effects of the secondary radiations from the ends of the ionization-chamber. There is, however, not only an increase of ionization due to secondary radiations from the solid ends into the gas experimented upon, but a loss of ionization owing to radiation

from the gas leaving through the ends of the chamber. The net result may be either a gain or a loss. By selection of the material forming the ends of the chamber, it is possible to make these effects calculable from observations which have already been made on secondary radiations of the three types. Aluminium ends were used, as Sadler had made a fairly exhaustive study of the corpuscular radiation from aluminium under the action of various homogeneous radiations.

When the gases nitrogen, oxygen, carbonic acid, nitrous oxide, coal-gas were used, the net gain of corpuscles from the ends was, within a small error, equal to that when air was used as the gas being ionized. When sulphuretted hydrogen and sulphur dioxide were ionized, the gain or loss became inappreciable, first because the total ionization was very great and the end effect proportionately smaller; secondly, because the corpuscular radiation from sulphur, an element of atomic weight near to that of aluminium, being lost by the gas, would tend to neutralize the gain from aluminium. When combined with hydrogen the balance would be fairly good; when combined with oxygen in sulphur dioxide there would probably be a net gain from aluminium, for the oxygen would intercept and prevent about half of the corpuscles from sulphur which would otherwise escape from getting away, while the oxygen would contribute little to the corpuscular radiation.

When heavier vapours were ionized and the incident radiation was sufficiently penetrating to produce comparatively large corpuscular radiations from the aluminium ends, the net result would be a loss of ionization due to the ends. This loss, however, was small compared with the total ionization, for the thickness of the layer from which they emerged was small compared with the total length of the ionization-chamber. In these, then, the end effect was negligible.

The end effect due to gain or loss of corpuscular radiation was thus corrected in the calculation of the ionization in some gases, and was negligible in others.

From a knowledge also of the penetrating powers of the fluorescent and scattered X-radiations from the elements constituting the gas, it may readily be shown which of these was absorbed in the gas itself in the particular experiment the results of which are given. When an appreciable fraction of the primary radiation absorbed was re-emitted as scattered radiation, this was of so penetrating a type that it produced a negligible ionization compared with that

produced by the direct primary beam. We may therefore neglect further consideration of this. The fluorescent radiations from the ionized gas can only be dealt with individually as we consider each gas.

The radiation scattered from aluminium being of the same penetrating power as the primary would produce relative ionizations similar to those due to the primary, so that except for a different correction for absorption due to divergence of the scattered radiation, the ionization may be included with that of the primary. The error introduced by neglecting this is negligible.

The very soft fluorescent X-radiation from aluminium contains only a very small portion of the energy of the primary radiation absorbed in the thin layer from which it can emerge. It is also negligible in its ionizing action; if it had not been so it would have been included in the ionizing effect of the soft corpuscular radiation studied by Sadler, and would have been corrected with the corpuscular radiation. After correction for absorption, and where necessary for the corpuscular radiation from the window and walls of the ionization-chamber, the following results (Table IV.) were obtained for the coefficients of ionization in a number of gases compared with the coefficients of ionization for the corresponding radiations in air *. Beatty's values for the ionization in H_2 and SeH_2 have been added †.

Perhaps the simplest way of stating the conditions of the experiments is that the ionization coefficients obtained for air, coal-gas, H_2 , N_2 , O_2 , CO_2 , N_2O , SH_2 , SO_2 were those got by complete absorption of all secondary radiations except the scattered X-radiations. Only in the case of SeH_2 , C_2H_5Br , and CH_3I did the greater part of the characteristic radiation (series K) from Se, Br, or I escape—when it was excited; and only in the case of the former two when ionized by Sr and Mo characteristic radiations would the complete absorption of the fluorescent radiations have made any great difference to the ionization coefficient. Of course, in many cases the absorption of the scattered X-radiation or of the fluorescent X-radiation produces no appreciable increase in the total ionization; so that we may say either that the results include or do not include the scattered radiation ionization. In the case of the ionization of light gases by penetrating radiations, however, nearly all scattered radiation

* E. A. Owen obtained values for CO_2 about 10 per cent. greater than those given in Table IV., and for SO_2 values, within 1 or 2 per cent. of our values in this table.

† Phil. Mag. Aug. 1910; Proc. Roy. Soc. A. lxxxv. p. 578 (1911).

escaped, and if it had been absorbed it would have added considerably to the ionization. Thus the most simple and accurate generalization with regard to the scattered radiation is contained in the statement made above, that the ionization coefficients of Table IV. do not include ionization due to the scattered radiation.

The principal features to be observed in the above results are these :—

The ionization coefficient in a given gas relative to that in air remains practically constant, or changes only slowly with the wave-length or penetrating power of the ionizing X-radiation, except when the wave-length is near and is also shorter than that of a radiation characteristic of an element of the ionized gas. Thus the relative ionization coefficients in coal-gas, N_2 , O_2 , CO_2 , N_2O change little, if at all, through the range of wave-lengths used in these experiments; those in SH_2 and SO_2 rise slightly with decreased wave-length; those in SeH_2 and C_2H_5Br remain practically constant* when the wave-length of the ionizing radiation is longer than that of the X-radiation of series K, characteristic of Se and Br respectively; in CH_3I the ionization coefficient rises more rapidly—as does also the absorption coefficient relative to that in air. When the wave-length becomes shorter than that characteristic of a constituent element of the ionized gas, the ionization coefficient changes in the manner described in a previous paper, rising slowly, then rapidly and finally approximating to a constant relative to that in air as the wave-length becomes shorter. This is seen in the ionization coefficients in SeH_2 , C_2H_5Br , and CH_3I for radiations more penetrating—of shorter wave-length—than those characteristic of Se, Br, and I respectively. A similar variation has also been found in the ionizations in Se_2Cl_2 and $SnCl_2$ for radiations more penetrating than those of Se and Sn, though only the order of magnitude of the ionizations has been observed in these gases.

It may be seen, however, that in H_2 the ionization coefficients as determined by Beatty are constant only as far as the radiation characteristic of arsenic, and that the increase shown for Sn is of the order of magnitude that would be expected if H_2 had a characteristic radiation of a series J not hitherto observed, a series of radiations more penetrating than those of the K series from corresponding

* The range of wave-length over which the ionization coefficient appears constant is, however, shorter in these cases.

elements. Such a result would, however, be produced by the presence of a small quantity of arseniuretted hydrogen in the hydrogen. The ionization in hydrogen is worth further investigation, for, if the results obtained are actually those for hydrogen, they are important in indicating a characteristic radiation of a hitherto undiscovered third series. If, on the other hand, the deviation from proportionality be due to an impurity in the hydrogen, this shows that hydrogen has a remarkably low ionization coefficient for the softer radiations—possibly of the order of $\frac{1}{1000}$ or even a smaller fraction of the corresponding coefficients of ionization in air.

There is a general similarity between the relative ionizations in the gases and vapours, and the relative absorptions of the ionizing radiations in these gases and vapours. The light gases which absorb comparatively little of the primary radiation are ionized to a small extent. There is not, however, exact proportionality between ionization and absorption*. This is clearly seen from the ionizations produced in SH_2 and SO_2 , the ionization in SH_2 being greater than that in SO_2 , whereas the absorptions of the ionizing radiations are in the reverse order. This difference was shown by Barkla and Simons† to be a true case of different energy consumption for equal numbers of ions produced in these two gases.

If we compare the amount of energy truly absorbed in the gases (by subtracting from the absorption coefficient that part due to scattering) with the ionizations produced, we find that the relative energy spent per ion produced varies to a certain extent with the gas. This is shown in relative values of $\frac{\lambda - s}{i}$, that is

$$\frac{\text{coefficient of absorption} - \text{coefficient of scattering}}{\text{relative coefficient of ionization}},$$

for a particular radiation in a particular gas, which are given below. In the cases here dealt with, the scattered radiation was the only secondary radiation to escape.

* Absorption of homogeneous X-rays by gases and vapours was investigated by Barkla and Collier (*Phil. Mag.* June 1912, p. 987). Absorption by elements had been previously studied by Barkla and Sadler (*Phil. Mag.* May 1909, p. 739).

† *Phil. Mag.* Feb. 1912, pp. 317-333.

TABLE V.

Showing relative numbers of ions produced in gases by the complete absorption of Röntgen radiation and all the secondary rays.

Gas.	Relative ionization for equal energy absorptions of X-radiation.	Relative energy of X-radiation absorbed for equal numbers of ions produced.
Air	100	1.0
SH ₂	127	.79
SO ₂	90	1.11
C ₂ H ₅ Br	160	.62
CH ₃ I	140 (approx.)	.72

If we compare these values with the corresponding values of the relative ionizations produced for equal absorptions of corpuscular radiation energy, we see there is a very close similarity,—that is, the relative numbers of ions produced in various gases when a Röntgen radiation is completely absorbed in these gases, are approximately the same as those produced by the complete absorption of a corpuscular radiation.

Accepting as proved that all X-ray ionization is by means of the ejected corpuscles, the above approximate equality of the relative total ionizations in various gases by X-rays and by corpuscular (electronic) rays, shows that the number of corpuscles set free in a gas by a Röntgen radiation which is completely absorbed depends little if at all upon the nature of the gas.

Ionization in Gaseous Mixtures by Röntgen Radiation.

As the number of ions produced by a corpuscular radiation depends to a certain extent upon the gas absorbing that radiation, the total ionization produced by an X-radiation in a mixture of gases should differ from the sum of the ionizations produced in the separate gases, for when a simple gas is ionized it absorbs its own corpuscular radiation, while in a mixture the corpuscles from each gas are partially absorbed by the other gas, and the absorptions of corpuscular radiations by the two gases are by no means proportional to the numbers of corpuscles which they emit. As Barkla and

Simons * pointed out, if all ionization by X-rays be due to secondary corpuscular radiation, the difference between the ionization in a mixture and the sum of the separate ionizations ought to be well marked. Preliminary experiments did not indicate a difference outside the possible errors of experiment. The differences to be expected from these experiments were, however, only small, though apparently outside the limits of experimental error. We have therefore continued these experiments under conditions more favourable to the detection of any difference that might exist. This has been done by two different methods. In one the additional ionizations due to the admixture of a small quantity of vapour of ethyl bromide with two different gases were compared; in the other the sum of the ionizations in two separate gases was compared with the ionization produced in the mixture of the two gases at the same partial pressures as separately.

(a) *Ionization due to mixture of C_2H_5Br with air and with SH_2 .*

It has been seen that when a corpuscular radiation is completely absorbed in sulphuretted hydrogen the number of ions produced is about 33 per cent. greater than when the same corpuscular radiation is absorbed in air. If, then, all ionization by X-rays is due to the secondary corpuscular radiation, we are led to expect that when a very small quantity of ethyl bromide say is added to sulphuretted hydrogen, the additional ionization produced is 33 per cent. greater than when it is added to air and ionized under the same conditions, for in each case the corpuscles from the ethyl bromide are absorbed by the gas with which it is mixed.

When the quantity of ethyl bromide is made so small that the proportion of corpuscles which it absorbs is negligible, the errors of experiment, however, become too large for accurate work. In our experiments we mixed ethyl bromide at pressures of 2, 4, 6, and 10 cm. of mercury with air and with sulphuretted hydrogen, bringing the total pressure in each case to one atmosphere.

The ionization-chamber was cylindrical in shape, 12 centimetres long and 7 centimetres in diameter, while the windows and lining were of aluminium. The ionizing radiation was the Ag X-radiation (series K). The results given in Table VI. are the average of several determinations with each quantity of ethyl bromide.

* Phil. Mag. Feb. 1912, pp. 317-333.

TABLE VI.

Showing that when X-rays are absorbed in a given vapour, the ionization depends on the surrounding gas absorbing the corpuscles from that vapour.

Partial pressure of C_2H_5Br in cm. of mercury.	Ionization due to C_2H_5Br when with air.	Ionization due to C_2H_5Br when with SH_2 .	Ratio of column 3 to column 2.
2 cm.	3.92	4.78	1.22 ?
4 cm.	8.16	9.52	1.17 (irregular)
6 cm.	12.06	14.46	1.20
10 cm.	19.4	22.9	1.18

The numbers in column 4 show the ratio of the ionization due to mixing C_2H_5Br with SH_2 to that due to mixing with air. In each case the former is the greater of the two, as might be foretold from the results of experiments on the ionizing effect of corpuscular radiations, given in Table II. The results for 4 cm. of C_2H_5Br were somewhat irregular, and for 2 cm. of C_2H_5Br much more so; consequently in the latter case, although the percentage error cannot be great, we cannot attach much significance to the exact results of calculations of relative absorptions based on the numerical result given.

Now assuming all X-ray ionization to be due to secondary corpuscular radiation and that energy absorption of such a radiation is proportional merely to the density of the absorbing gas or vapour, we should have expected the ratio of the values given in columns 3 and 2 to be somewhat higher than that actually found. Thus if m_1 and m_2 be the masses of C_2H_5Br and air in a mixture, and if c and a be the ionizations in C_2H_5Br and in air when alone, and f the fraction of the ionization in either gas due to its corpuscular radiation, then the additional ionization due to mixing C_2H_5Br with air is

$$(1-f)c + fc \frac{m_1}{m_1 + m_2} + fc \frac{m_2}{m_1 + m_2} \times \frac{1}{1.5} + fa \frac{m_1}{m_1 + m_2} (1.5 - 1).$$

The four terms in the above expression represent (1) direct ionization in C_2H_5Br ; (2) ionization in C_2H_5Br due to corpuscular radiation from C_2H_5Br ; (3) ionization in air due to corpuscular radiation from C_2H_5Br ; (4) increase in

ionization in the mixture due to corpuscles from air being absorbed in $\text{C}_2\text{H}_5\text{Br}$ instead of in air itself.

The corresponding increase in ionization in SH_2 due to mixing a mass m_1 of $\text{C}_2\text{H}_5\text{Br}$ with m_2' of SH_2 is

$$(1-f)c + fc \frac{m_1}{m_1 + m_2'} + fc \frac{m_2'}{m_1 + m_2'} \frac{1.33}{1.5} + fs \frac{m_1}{m_1 + m_2'} \left(\frac{1.5 - 1.33}{1.33} \right)$$

s being the ionization in SH_2 alone.

The ratio of the two expressions above may be equated to the ratio given in column 4, for a particular pressure of $\text{C}_2\text{H}_5\text{Br}$. Assuming f to be unity, that is all the ionization to be due to the corpuscular radiation, the values 1.35, 1.29, 1.25, and 1.20 would be expected in column 4. We have, however, taken no consideration of the fluorescent X-radiation of series K which is emitted by the bromine when exposed to such a primary X-radiation,—Ag X-radiation of series K. This Br radiation is of course more completely absorbed by the SH_2 than by the air, and consequently tends to raise the ionizations due to mixing with SH_2 . The energy re-emitted by $\text{C}_2\text{H}_5\text{Br}$ as fluorescent X-radiation is, however, only about 7 per cent. of the energy absorbed, and of this only about $\frac{1}{4}$ was absorbed in SH_2 in these experiments, so that the calculated values should be raised by about 2 per cent., making them 1.37, 1.31, 1.27, 1.22 respectively. The experimentally determined values 1.22, 1.17, 1.20, 1.18 are all somewhat lower, but the first, 1.22, is very unreliable and ought perhaps not to be taken as giving more than the order of magnitude.

If we used these experiments to determine the fraction of ionization f due to corpuscular radiation, we should obtain the values .53, .73, .85 for the last three—the more accurate determinations. Thus, the most reliable experimental results would lead to the conclusion that something of the order of 75 or 80 per cent. of the ionization in $\text{C}_2\text{H}_5\text{Br}$ by Ag X-radiation of series K is due to the corpuscular radiation.

(b) *Ionization in $\text{C}_2\text{H}_5\text{Br}$, in air, and in mixture of $\text{C}_2\text{H}_5\text{Br}$ and air.*

In the second series of experiments on gaseous mixtures we determined the ionizations in (1) a small quantity of ethyl bromide when alone, (2) in air at a much higher pressure, and (3) in the mixture of these two gases at the same partial pressures as when separate. After correction for the absorption of the primary X-radiation in these gases, it was found that the sum of the two first ionizations was

considerably greater than the third; and the ionization in the mixture, however, does not agree closely with that calculated on the assumptions that all ionization by Röntgen radiation is the result of the secondary corpuscular radiation and a density law of energy absorption.

In these experiments a cylindrical ionization-chamber 12 centimetres long and about 7 centimetres in diameter was used. In order to obviate the difficulties and uncertainties of the loss or gain of corpuscular radiation at the two ends of the chamber, the soft homogeneous radiation characteristic of copper (series K) was used as the ionizing radiation. In such a case, the gain or loss of ionization owing to the material of the ends differing from that of the ionized gas was almost infinitesimal, the corpuscular radiation penetrating only a small fraction of a millimetre of air under normal atmospheric conditions for instance. It was found that the ionization produced by the radiation in air and also in ethyl bromide did not differ appreciably from proportionality with the pressure, showing that neither corpuscular radiation lost or gained at the ends nor fluorescent X-radiation from the ends produced an appreciable portion of the observed ionization.

After a small correction for the absorption in the separate gases and in the mixture, results were obtained of which the following is typical. The ionizations are expressed in arbitrary units.

Ionization in C_2H_5Br at 2.6 cm. of mercury pressure = .728					} sum = 1.101
„	air at 61.1 cm.	„	„	= .373	
„	mixture of the above			= .989.	

If f is the fraction of ionization in any gas due to corpuscular radiation, then assuming the absorption of energy of corpuscular radiation proportional simply to the density of the gas and independent of its quality, we may write the direct ionization in C_2H_5Br + that due to its corpuscular radiation

$$(1-f) \cdot 728 + \frac{63}{73} f \times 728 \times \frac{1}{1.5} + \frac{10}{73} f \times 728,$$

i. e., direct ionization + ionization in air due to corpuscles from C_2H_5Br + ionization in C_2H_5Br due to its own corpuscles :—

[the relative densities of C_2H_5Br and air being 10 : 63 and the ratio of ionizations in C_2H_5Br and air due to equal absorption of energy of corpuscular radiation being 1.5 : 1].

Similarly, the direct ionization in air + the ionization due to its corpuscles is

$$(1-f) \cdot 373 + \frac{63}{73} f \times 373 + \frac{10}{73} f \times 373 \times 1.5,$$

when mixed with air.

Summing these two and equating to the observed ionization .989, we find

$$f = .63.$$

Similar experiments with $\text{C}_2\text{H}_5\text{Br}$ at pressures 3.8, 4.7, 5.15 cm. of mercury were made, and the results were all of the same order of magnitude, the average value of f being .60. Thus again, though these experiments on the ionization in gaseous mixtures all indicate that a large proportion of the ionization is due to corpuscular radiation, they would not of themselves lead us to conclude that all the ionization is attributable to this secondary radiation. It is true that a small error in some of our experimental determinations would considerably alter the result of the calculation. But these calculations have all agreed in indicating a departure in the same direction from what might have been expected, on assumptions which have, under slightly different conditions, been justified with a certain degree of accuracy. It must be admitted that but for the experiments of C. T. R. Wilson and perhaps those of Beatty to which we have referred, we should regard these results as strong evidence in favour of a considerable direct ionization by X-rays in addition to that due to the swiftly moving corpuscles ejected from the atoms of the gas traversed. They, however, lead us to examine the assumptions and the data upon which the calculations are based. We have assumed that (1) the energies of the corpuscular radiation absorbed by the constituents of a gaseous mixture are proportional to their densities; (2) the number of corpuscles ejected by a constituent gas for a given energy of X-radiation absorbed, and the ionization produced in a constituent gas for a given energy of corpuscular radiation absorbed, are precisely the same as when the gas is alone; (3) the relative ionizations produced in air, SH_2 , and $\text{C}_2\text{H}_5\text{Br}$ by the complete absorption of a corpuscular radiation are as indicated in Table II. Our results would, however, require a large deviation from the density law of absorption of corpuscular energy to afford an explanation. Yet we know of no evidence of such a deviation; indeed, there is much evidence that there is little deviation even for comparatively slowly moving electrons. We have

given evidence in this paper which strongly supports assumptions (1) and (2) in the particular case tested. There seems no reason to doubt the validity of the assumption (2). Again, we see no reason to suspect an inaccuracy of the necessary order in the determination of the relative ionizations produced in C_2H_5Br and in air by the complete absorption of a corpuscular radiation. (Many experiments were performed showing that the value 1.5 given in Table II. for C_2H_5Br is correct within two or three per cent.) Nor, as we have seen, is there reason to doubt the applicability of the ratio to the somewhat slower corpuscles excited by Cu X-radiation (series K). We must therefore leave this result for further investigation.

These experiments, however, show that the deviation of the ionization in a mixture of gases from the sum of the ionizations in the separate constituents is of the kind and of the order of magnitude that would be expected if most of the X-ray ionization were due to the secondary corpuscular radiation. For some reason which we have not isolated, our experiments have not, on the assumptions made, indicated the entire absence of direct X-ray ionization.

Summary.

The relative ionizations produced in various gases and vapours by the complete absorption of corpuscular radiations set free by homogeneous X-radiations have been determined.

No change of relative ionization with velocity of the ionizing corpuscles has been observed.

The relative ionizations due to complete absorption of corpuscular radiation have been found to agree closely with the relative ionizations due to complete absorption of a Röntgen radiation and all its secondary radiations. The results indicate that the complete absorption of a given X-radiation by different gases results in the emission of the same number of corpuscles. [The case in which there is a large transformation of energy of primary X-radiation into fluorescent X-radiation has not yet been fully investigated.]

The ionization coefficients for homogeneous X-radiations in a number of gases and vapours have been determined, and the generality of the laws given by one of us further verified.

The ionizations in gaseous mixtures due to the complete absorption of corpuscular radiation have been determined. On the most obvious and most probable interpretation of the

results these indicate the relative numbers of ions produced in the two constituent gases of a gaseous mixture. In C_2H_5Br and air, the relative absorptions of energy were found very closely in agreement with the relative masses of C_2H_5Br and air.

The ionization by X-rays of gaseous mixtures has been shown to differ considerably from the sum of the ionizations in the two individual gases. The difference shows the effect of corpuscles from one gas being absorbed by the other, the nature of the deviation being what could be foretold from our experiments on ionization by corpuscular radiation. The magnitude of the effect, however, is not so great as we should expect on the simplest theory of ionization by ejected corpuscles alone. The possible causes have been discussed.

I wish to express my thanks to the Solvay International Institute for a grant in aid of these researches.—C. G. B.

LXXXVIII. *The Temperature of Sublimation.*

*By J. JOLY, F.R.S.**

IN a recent number of the Philosophical Magazine (Feb. 1913) I described a simple apparatus (which I have called the Apophorometer) by means of which the chemical analysis of many volatile bodies may be effected by so regulating the temperature of the finely powdered substance as to volatilize one by one its several constituents in the order of their volatility. The successive sublimates are caught and removed in watch-glasses and weighed; the residue also being weighed when desired. I cited some examples of more or less complex mineral bodies quantitatively analysed by fractional sublimation.

I was at the time surprised at the apparent sameness of temperature at which certain very different mineral species decomposed, but contented myself with pointing out the probable importance of temperature measurements and with indicating a method of effecting such measurements. This method—that of determining the temperature in terms of the current which heats the hob upon which the substance reposes—has proved very satisfactory and easily applied; the current and temperature maintaining a rectilinear relation at least so high as $1200^{\circ}C$.

* Communicated by the Author.

Since the writing of my first paper I have been able to observe the temperatures of sublimation of a certain number of typical minerals, and although more observations are desirable, the approximate agreement among the results obtained, as well as the delay which must attend the acquisition of fresh material, induce me to give a brief account of what I have observed. I shall in the present paper refer to four volatile constituents only—antimony, arsenic, sulphur, and tellurium.

The temperature of sublimation is not a fixed and definite point. Substances such as arsenic, sulphur, &c., are more or less volatile even at ordinary temperatures, and the rate of volatilization increases as the temperature rises. When the free element is being dealt with in presence of oxygen, we have to do with this range of increasing vapour-pressure as well as with the complication arising from the interaction of the element with oxygen. In this case the temperature of sublimation is not in general that of the oxide formed, but seems dependent mainly on the vapour-pressure of the volatile element at the particular temperature. In the case of compounds the stability of the compound in presence of oxygen must be the primary factor controlling sublimation at a rising temperature. How far the vapour-pressure of the volatile element in the compound affects the temperature of decomposition cannot be predicted, but, save in the case of deflagration or similar phenomena, the decomposition temperature does not present itself in the experiments as a definite and sharply defined one, and the observation resolves itself into finding the temperature at which the liberated volatilized body, whether oxidized or unoxidized, first appears as a visible sublimate on the watch-glasses; most often on the upper glass. We are here presented with much the same problem as that of determining the melting-point of a body having a certain range of viscosity. A time element enters into the observation. Accordingly I have allowed a fixed time—three minutes—in each case for the sublimate to collect. At the end of that time the hob is cooled and the upper glass removed and examined in a good light. The sublimate as first revealed may be a mere bloom or dullness upon the glass. With a longer allowance of time a somewhat lower temperature would be obtained. The temperatures recorded are, therefore, approximate only, and actually indicate a certain rate of break up of the substance under examination. But they are comparable one with another; and in so far are indicative of the relative stabilities of the

substances examined. I may add that the state of comminution of the powder is not, within limits, important. I have tried the effects of re-grinding a substance already tested but have not obtained any notable alteration of the sublimation temperature.

The sublimation temperature is not arrived at on a single experiment. It is necessary to approximate to it on preliminary experiments made at neighbouring temperatures. As it is approached it is essential to put fresh powder (three or four milligrams) upon the hob for each observation of three minutes' duration. The reason for this is that a powder which has rested on the hob for some time becomes slower in its rate of evolution of sublimate owing to the exhaustion of those lower particles which most perfectly take up the temperature of the ribbon. A deceptively high temperature must be maintained to affect those particles which are out of contact with the platinum. The slower rate of sublimation which arises after a certain time of exposure to a particular temperature also, doubtless, involves the fact that the larger particles are at first only superficially affected, and a higher vapour-pressure is required to maintain the evolution of vapour from their interior.

ANTIMONY.

The observation of the sublimation of antimony is rendered easy by the definite characters presented by its oxides. These are either Sb_4O_6 or Sb_2O_4 . Both are pure white and very well defined sublimate, appearing nearly always in streaks on the upper glass transverse to the length of the ribbon. The commencing sublimate reproduces the distribution of the powder on the hob with a fidelity which shows that there is but little diffusion and suggests electrical repulsion. The streaky deposition is solely due to the vortical air-currents prevailing between the glasses when the hob is heated. Neither of these oxides is volatile, and at no convenient temperature can they be driven off the glasses if these are held over a bunsen flame. The sublimed Sb_4O_6 is instantly soluble in cold HCl ; the sublimate Sb_2O_4 is only soluble in the hot acid. The first faint white streak indicates the commencement of sublimation.

A large number of antimony-bearing minerals carry the antimony in the stibnite or antimonite molecule, Sb_2S_3 . The mineral stibnite sublimes first at about 480° . The following minerals possessing this molecule have been examined :—

TABLE I.

		<i>t</i> °.
1. Stibnite. Sb_2S_3 .	Auvergne	475
2. " "	Transylvania	490
3. " "	Loc. ?	490
4. " "	Iyo, Japan	470
5. Chalcostibite. $\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3$.	Wolfsberg	475
6. Tetrahedrite. $4(\text{Cu}_2\text{S}), \text{Sb}_2\text{S}_3$.	Loc. ?	475
7. Zinkenite. $\text{PbS}, \text{Sb}_2\text{S}_3$.	Wolfsberg	475
8. Jamesonite. $2\text{PbS}, \text{Sb}_2\text{S}_3$.	Cornwall	480
9. Geocronite. $5\text{PbS}, \text{Sb}_2\text{S}_3$.	Sala	450
10. Plagionite. $5\text{PbS}, 4\text{Sb}_2\text{S}_3$.	Wolfsberg	475
11. Boulangerite. $5\text{PbS}, 2\text{Sb}_2\text{S}_3$.	Ober Lahr	495
12. Frieslebenite. $5(\text{Pb}, \text{As})\text{S}, 2\text{Sb}_2\text{S}_3$.	Guanajuato	480
13. Bournonite. $3(\text{Pb}, \text{Cu}_2)\text{S}, \text{Sb}_2\text{S}_3$.	Liskard	490
14. Miargyrite. $\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$.	Brausdorf	500
15. Stephanite. $5\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$.	Schemnitz	490
16. Polybasite. $9\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$.	Loc ?	495
17. " "	Guanajuato	430
18. Berthierite. $\text{FeS}, \text{Sb}_2\text{S}_3$.	Brausdorf	550
19. Cyndrite. $6\text{PbS}, 6\text{SnS}, \text{Sb}_2\text{S}_3$.	Bolivia	600
20. Livingstonite. $\text{HgS}, 2\text{Sb}_2\text{S}_3$.	Huitzucó	440
21. Breithauptite. NiSb .	St. Andreasberg	500
22. Corynite. $\text{Ni}(\text{As}, \text{Sb})\text{S}$.	Siegen	490
23. Dyscrasite. Ag_3Sb .	Baden	520
24. Allemontite. SbAs_3 .	Allemont	400 ?
25. Antimony, native and prepared.	500

The oxide appearing at the temperatures recorded in the table is in general, if not always, the oxide Sb_4O_6 . The oxide Sb_2O_3 appears at a somewhat higher temperature. In many cases there is a definite cessation of sublimation between the appearance of the two oxides as the temperature is raised. The interval may be 60 degrees or more; varying considerably. I have only incompletely examined this phenomenon.

The most interesting feature of the table is the remarkable uniformity of temperature of sublimation of the minerals examined. Nos. 18 and 19 show rather unusually violent deflagration close to the sublimation temperature. This phenomenon seems generally attended by an exceptionally high sublimation temperature. It probably arises from superheating above the normal temperature of decomposition; the deflagration ensuing on a sudden breakdown of equilibrium. The decomposition of the stibnite molecule of No. 20 is preceded by the evolution of a sublimate of mercury. The temperature of subliming of the antimony is,

however, but little affected. This again illustrates how independently the constituent molecules behave under the influence of rising temperature.

From these results we must conclude—contrary to what I think would have been anticipated—that a compound of antimony of the form $n \text{RS}$, $m \text{Sb}_2\text{S}_3$ becomes unstable in presence of oxygen at a temperature which is unaffected by the nature of R or the values of n or m .

It would also appear from the results Nos. 21–25 that other antimony molecules besides the sesquisulphide break up at about this temperature, and that whether sulphur is present or not. The observation of the temperature of sublimation of antimony from allemontite is rendered difficult by the rapid evolution of arsenious oxide which precedes the sublimation of the antimony. I found it, indeed, possible to distill off the whole of the arsenic leaving the antimony almost in entirety on the hob, and in this manner to quantitatively verify the constitution of the specimen.

It is a rather remarkable feature of these observations that the temperature of sublimation of the free element is higher, sensibly, than that observed in the case of some of the compounds examined. This seems to indicate that a certain influence on the temperature of sublimation arises from the presence of a more volatile atom. So far as the few observations go, the temperature of break-up is not appreciably raised when the combined atom is more stable. Thus NiSb breaks up at 500° and Ag_3Sb at 520° . This observation renders the high temperatures of sublimation of Nos. 18 and 19 the more remarkable.

ARSENIC.

The difference between the behaviour of arsenic and antimony as volatile constituents of the molecule is interesting. The break-up of the arsenic-bearing compounds appears to be influenced by the molecular structure, so that these bodies fall into groups defined by very different sublimation temperatures. The number of experiments is small but they stand, so far as my observations go, without exception to the general principles which I have ventured to found upon them. Such exceptions as at first seemed to exist were in every case found explicable either on erroneous identification or were removed by the adoption in one or two cases of alternative and, I believe, more probable formulæ. In some respects the grouping must be regarded as provisional only.

TABLE II.

III. $\text{RAs} : \text{RAsS} : \text{R}_2\text{As}_3 : \text{R}_3\text{As}_4$.

		t°
1. Arsenopyrite. FeAsS .	Cornwall	430
2. " "	Loc. ?	430
3. Cobaltite. CoAsS .	Tunaberg	480
4. " "	Ramsberg	495
5. Gersdorffite. $(\text{NiCoFe})_3(\text{AsS})_4$.	Siegen	500
6. " "	Ems	480
7. Glauco-dot. $(\text{CoFe})\text{AsS}$.	Hakensboda	420
8. " "	"	460
9. Niccolite. NiAs .	Loc. ?	450
10. " "	Gladming	425
11. Leucopyrite. $\text{FeS}, \text{Fe}_2\text{As}_3, \text{Fe}_3\text{As}_4$.	Reichenstein.....	455
12. " var. Fe_3As_4 .	"	520
13. " " "	Breitenbrun	515
14. " " "	"	520
15. Rammelsbergite. Ni_3As_4	510
16. Corynite. $\text{Ni}(\text{AsSb})\text{S}$.	Siegen	500
17. Chloanthite. $\text{As}_2\text{S}_3, 5(\text{Ni}_3\text{As}_4)$.	Val d'Annivier.....	430
18. Smaltite. ?	Cobalt, Ontario	420
19. " ?	Loc. ?	440
20. Domykite. Cu_3As .	Haughton	370
21. Tennantite. $11\text{CuS}, \text{FeS}, 5\text{CuAsS}$.	Carn Brae	500
22. " " "	Herodsfoot mine, Cornwall	430

II. $\text{RS}, \text{As}_2\text{S}_3 : \text{As}_2\text{S}_3 : \text{RAs}_2 : \text{RAs}_3 (?)$.

23. Orpiment. As_2S_3 .	Akchai	220
24. " "	Hungary	190
25. Proustite. $3\text{Ag}_2\text{S}, \text{As}_2\text{S}_3$.	Montezuma	250
26. Pearceite. $9\text{Ag}_2\text{S}, \text{As}_2\text{S}_3$.	Montana	240
27. Dufrenoy'site. $2\text{PbS}, \text{As}_2\text{S}_3$.	Lengenbach	250
28. Sartorite. $\text{PbS}, \text{As}_2\text{S}_3$.	Binn	210
29. Enargite (2). $3\text{Cu}_2\text{S}, \text{As}_2\text{S}_3$.	Butte.....	225
30. Binnite. $3\text{Cu}_2\text{S}, 2\text{As}_2\text{S}_3$.	Lengenbach	250
31 & 18. Smaltite. ?	Cobalt, Ontario	230
32 & 19. " ?	Loc. ?	240
33 & 17. Chloanthite. $2\text{As}_2\text{S}_3, 10(\text{Ni}_3\text{As}_4)$.	Val d'Annivier.....	220
34 & 5. Gersdorffite : same as No. 5.	230

I. $\text{As} : \text{AsS} : \text{loosely attached As}$.

35. Arsenic. Native or prepared.	145
36. Realgar. AsS .	Felsobanya	145
37. " "	Loc. ?	145
38 & 17. Chloanthite (tr. of subl.).	Val d'Annivier.....	135

The chief interest of these results is the support which they give to the view that there exist variations in stability among these compounds which increase *per saltum* and with a certain regularity as measured by the temperature required for decomposition. If this can be sustained a useful method of discriminating in some cases between true and erroneous structural formulæ is to be found in such observations; and, in addition, we seem to obtain information as to the relative stabilities of various interatomic relations. I shall point out some features of the results bearing upon the construction I have placed upon them.

The first question that arises is, of course, how far the suggested subdivisions are actually justified by the observations. In other words, how many and what exceptions and objections to the grouping can be detected? The grouping assumes that a compound begins to sublime at the particular approximate temperature of its group and decomposes at or about this temperature. Now it is often found that a considerable increase of temperature is required if the sublimation or decomposition of the specimen is to be maintained. If the increase is not more than 50 or 100 degrees we may explain this very simply as due to the necessity for heating the upper particles on the hob as well as breaking up the larger grains of the powder. Sometimes, however, an elevation of temperature is required which carries the temperature into the succeeding group. In nearly all cases when this has occurred, if not in all, there is a distinct interval of temperature over which no sublimation is obtained. This interval may be 100 or 200 degrees, and in this interval no trace of sublimate appears, at least during reasonably prolonged periods of observation. When sublimation recommences, the lower limit of the higher group has been entered and sublimation proceeds just as if the substance had commenced its sublimation in this group. In the new group we must again raise the temperature to maintain the sublimation. A deflagration point may be reached, attended, in some cases, by a copious evolution of sublimate, and after this a rapid decline in the rate of expulsion of volatile matter. There may succeed yet another interval of temperature in which no sublimation occurs, and at a temperature which may lie above that defining the highest group—at 800° or higher—a final evolution of sublimate may take place. On account of the occasional occurrence of this phenomenon I have numbered the groups from below upwards, as I think it probable that further observation may show the existence of a higher group.

We can explain these facts in either of two ways. (*a*) As arsenic is expelled from the substance fresh combinations occur within it. Thus if a molecule RAs_2 loses As, the molecule RAs may be formed and this may only break up in the higher group. In this case it should be noticed that either an equal or less amount of arsenic will be liberated in a succeeding stage. If there were a number of stages in which half the arsenic came away each time, of course there would be a geometrical decrease. Other laws of decrease might obtain. I have found, however, that there is often an increase in the amount liberated at a higher stage. If an arsenide in the course of its decomposition passes from group II. to group III., there is often a very marked increase; but if after this the temperature has to be carried very high, into what may be called, provisionally, the fourth group, to complete the liberation of arsenic, the sublimate in the fourth group is smaller than that obtained in the third. The explanation (*a*) cannot, therefore, generally be true, and we must adopt the alternative explanation: (*b*) that the several molecules decomposing at the different group temperatures existed in the substance from the first. There seems no reason to doubt that this is often or generally the case.

It will be seen from this that a substance assigned to a particular group on the strength of a first small sublimate may essentially belong to some higher group. It should appear in more than the one group.

The fact of sublimate being obtained in more than one group is not, I think, an objection to the suggested groups. Rather it is, as I believe, in their support. Many recognized mineral formulæ might involve this passage from group to group; *e. g.*, such as $(CoNi) As + RAs_2$ for certain smaltites. But it would be an objection to the proposed groups if a substance to which we must assign a molecular structure proper to a lower group only, decomposed in a higher. I was at first confronted with what appeared like some difficulties of this kind. I shall now refer to these.

The mineral tennantite was examined on two Cornish specimens. The formula assigned to this mineral in Dana's 'System of Mineralogy' is $4Cu_2S, As_2S_3$. Now three concordant analyses by different observers give approximately the percentages S 27; As 19; Cu 49; Fe 3. These percentages give as the relative numbers of molecules 17 S; 5 As; 16 Cu; 1 Fe. These may be supposed to form 11 CuS, FeS, 5 CuAsS. The formula is, I venture to think, a probable one and would bring the substance into the third group as its temperature of sublimation actually does.

The rammelsbergite examined showed no trace of sublimate till raised to somewhat above 500° . This substance is described as essentially NiAs_2 . An analysis on the apophorometer gave the following percentages As, 58; (Ni, Co), 38. A little sulphur was present which does not enter into the weights found. The residue was mainly nickel. Now the molecule Ni_3As_4 would absorb the arsenic and nearly all the (Ni, Co). A little cobalt sulphide would account for the balance of the residue. I think it reasonable to assume that the mineral in group III. is constituted in this manner. The assumed molecule is similar to that of leucopyrite, which also appears in this group.

Another mineral within group III. was analysed in order to account for its position: the chloanthite of the Val d'Annivier (17). Chloanthite is essentially a diarsenide. This specimen showed a very small sublimate (S_1) in group I. at a temperature of 135° ; which would represent a little loosely combined arsenic if my assumptions are correct. This sublimate ceased to come off after a rise of some 30 degrees. Between 220° and 270° a second sublimate (S_2) is obtained; small, but larger than the first. There is then an interval of about 180 degrees over which no trace of sublimate appears even on prolonged observation. At 455° the evolution of As recommences (S_3) and continues up to about 700° when there is deflagration. After this but little arsenic remains. This is given off at a temperature approaching 1000° . A little S is probably present. Taking 16.7 mgrms. of the powdered mineral, $\text{S}_1 + \text{S}_2$ amounted to 1.4 mgrms.; S_3 to 13.4 mgrms., and this includes the small final sublimate of As_2O_3 . The residue weighed 7.2 mgrms. We have from these quantities 1 mgrm. of As in $\text{S}_1 + \text{S}_2$ and 10.1 mgrm. As in S_3 ; and as the residue appeared to be almost entirely the oxide of nickel, we get 5.7 mgrms. of Ni. The added weights are 16.8 mgrms. The quantities afford as the relative numbers of atoms for $\text{S}_1 + \text{S}_2$, 4 As; for S_3 , 40 As; for the residue, 30 Ni. Of these atoms the molecule 10 (Ni_3As_4) would leave only 4 As as entering into the low temperature sublimate. This arsenic may exist in the form 2 (As_2S_3). The complete formula would be $\text{As}_2\text{S}_3, 5\text{Ni}_3\text{As}_4$. It is worth comparing with this result two analyses of chloanthite cited by Dana (*loc. cit.*) Nos. 14 and 15, approximating to As, 58.7; (Ni, Co), 39 (mainly Ni); S, 2.8. It will be found that these chloanthites are very closely represented by the formula $3\text{Ni}_2\text{S}_3, 20(\text{Ni, Co})_3\text{As}_4$.

Although the results given above seem in every case to show that the molecule RAs_2 is not necessarily present in the substance subliming in the higher group, there is but little

evidence to show that it is contained in group II. beyond the inference that this molecule should be less stable than the molecule RAs. Until more substances are examined the placing of this molecule in group II. must be regarded as provisional only. The two smaltites give a comparatively small sublimate in group II. and the greater part of their arsenic in group III.; somewhat in the manner of the chloanthite just referred to. In order that these substances should be constituted as commonly written, CoAs_2 , there must be rather over 70 per cent. of arsenic present. It is quite certain from rough analyses made of the two smaltites, that this percentage of arsenic does not obtain in these specimens. They probably contain the molecule $(\text{Ni, Co}) \text{As}_2$, but are for the larger part constituted of some molecule containing a lesser percentage of arsenic. The gersdorffite (Nos. 5 and 34), appearing in both the second and third groups, belongs to a species which like the smaltites and chloanthites cannot be considered to be fully understood. The recorded analyses of gersdorffite vary considerably, and Dana suggests various formulæ. This mineral was from Siegen. A good analysis on the apophorometer gave 37 per cent. of As and 47 per cent. of Ni, including some Fe and Co. Sulphur was copiously expelled. By difference it would make 16 per cent. The relation between the numbers of atoms would be As, 5; Ni, 8; and S, 5. Now there is some over-estimation of the Ni, for its amount is obtained on the assumption that the whole of the residue is NiO. The sulphur is therefore probably under estimated and the nickel over estimated. The result points evidently to the molecule $(\text{NiCoFe})_3(\text{AsS})_4$ as forming the greater part of the substance. Dana cites a fairly concordant analysis of the Siegen mineral, *i. e.*, As, 37.52; Ni, 40.97; S, 17.49; Fe, 4.19. This would approximate nearly to the constitution suggested.

While there are doubts about the placing of the diarsenide molecule there are none, as I believe, about the correct placing of the sesquisulphide molecule. For bodies carrying their arsenic in this form all commence sublimation at the low temperature characterizing the second group, and will be found to slowly continue to break up within a range of not more than 100 degrees above this. Suppose we place such a substance as proustite in a thin layer on the hob. It begins subliming at about 250° , and as the lower and hotter particles become exhausted the rate of evolution falls off. But if now we set the temperature to, say, 320° , and continue changing the upper glass every 3 or 4 minutes, an almost steady out-put of arsenious oxide will be observed, till finally

the substance appears to consist of the sulphide of silver. Sometimes a little arsenic may obstinately linger in such cases, but essentially the whole of the arsenic comes away before the temperature of the higher group is attained. All these bodies do not behave precisely as proustite. There seems to be an interesting difference with respect to the evolution of sulphur, a difference which certainly is not accountable on the observations to be presently given relating to the sulphides. In the case of sartorite, for instance, a plentiful liberation of sulphur attends the decomposition of the substance. It is difficult to detect the liberation of this element from the proustite. In this direction some insight may be obtained as to interactions progressing on the hob.

Much remains to be ascertained. From the limited scope of the experiments influences may escape notice which may prove of importance. Thus it happens that the results in group III. are mainly confined to compounds of iron, nickel, and cobalt. We are not, therefore, in a position to examine whether the atomic weight of the stable element or its periodic position exerts an influence. The copper arsenide, domykite, appears exceptional in its temperature of decomposition. Tennantite is, however, normal.

Of the second group we seem justified in stating what has been already said of the similar antimony-bearing bodies; that the nature of the values n , m , and R in the general formula $n R S$, $m As_2S_3$, does not seem to affect the temperature of volatilization.

Throughout the table it does not appear that the presence of sulphur, save when combined as the sesquisulphide molecule, exerts much influence on the sublimation temperature. There is no notable difference between the volatilization temperature of As and AsS ; and, consistently, $NiAs$ and $NiAsS$ show no difference in stability. The sesquisulphide of arsenic shows a stability above that of either of the constituent elements.

It is important in dealing with substances containing both arsenic and sulphur to distinguish between their sublimates upon first appearance. I have found that two characters serve to discriminate between these sublimates and to separate them however faintly developed. The characteristic odour of SO_2 reveals the smallest trace of sulphur when properly sought for. The observation is best made by warming for a moment the watch-glass on the convex side over a low bunsen flame and as the heat soaks through observing the odour while holding the glass in a vertical position. It will also then be found that a separation of the two sublimates may be effected, if

both are present, by properly regulating the temperature ; the sulphur passing off at a considerably lower temperature than what is required to dispel the deposit of arsenious oxide.

SULPHUR.

In contrast with the behaviour of the compounds of arsenic the sulphides show a remarkable sameness in the temperature of sublimation however diverse the nature of the molecule or of the associated elements.

TABLE III.

		<i>t</i> °.
1. Molybdenite. MoS_2 .	Loc. ?.....	450
2. Pyrites. FeS_2 .	Loc. ?	450
3. Marcasite. „	Jasper Co.	440
4. Hauerite. MnS_2 .	Radusa	450
5. Stannite. Cu_2S , FeS , SnS_2 .	St. Agnes, Cornwall.....	460
6. Chalcopyrite. Cu_2S , Fe_2S_3 .	Loc. ?	470
7. Chalcosite. Cu_2S ,	Cornwall	490
8. Linnæite. CoS , Co_2S_3 .	Mussen	480
9. Sphalerite (5). ZnS .	Various.....	610
10. Pentlandite. 2FeS , NiS .	Lillehammer	480
11. Covellite. CuS .	Butte.....	400
12. Galenite. PbS .	Loc. ?	470
13. Bornite. Cu_2S , CuS , FeS .	Audley Mine, Cork.....	430
14. Sternbergite. Ag_2S , Fe_4S_5 .	Königsberg	170
15. Sulphur.	60
16 & 4. Hauerite (trace of free S).	60

Of the several compounds examined above, sternbergite alone (14), departs from the general uniformity of temperature ; possibly because the structure of the molecule Fe_4S_5 may be a loose one. Sphalerite is exceptionally high. All the substances sublime far above the sublimation temperature of the free element. Flowers of sulphur tested under the same conditions gives a sublimate at 60°. It is perhaps open to us to refer such substances as RS , As_2S_3 to the sulphur division and class them as a low-temperature division. But the fact that such analogous compounds as Cu_2S , Fe_2S_3 (6) and CoS , Co_2S_3 (8) maintain a high temperature of sublimation is rather opposed to this procedure and suggests that the instability of the As_2S_3 molecule is more fitly regarded as due to the arsenic. The question is, however, not without obscurities.

TELLURIUM.

Tellurium gives upon the apophorometer two sublimates as stated in my first paper (*loc. cit.*): a black low-temperature sublimate of TeO and a white high-temperature sublimate of TeO_2 . If a little of the black sublimate be scraped from the glass and placed upon the hob, it will be found to melt at about 570° and either to resublime at once as a black sublimate or to again partly solidify on the hob, slowly whiten, melt again at about 850° and, at or near this temperature, volatilize on to the watch-glass as the white sublimate TeO_2 . If a little of the white sublimate is placed directly on the hob and slowly heated from a low temperature it will blacken at a temperature below 500° , reverting to TeO . Rapidly heated it melts as above and sublimes at about 850° . The recognition of these sublimates is easy.

I have examined only 7 tellurides. They appear to indicate that the tellurides will be found divisible into groups according as the molecule is of the structure RTe or RTe_2 . But, of course, the evidence is too slender to justify discussion.

TABLE IV.

RTe .			
			t° .
Altaite. PbTe .	Las Cruces. $\text{TeO}?$	TeO_2	850
Hessite. Ag_2Te .	Altai. $\text{TeO}?$	TeO_2	900

$\text{RTe}_2 : \text{R}_2\text{Te}_3 : \text{Te}$.			
Calaverite. $(\text{AuAg})\text{Te}_2$.		TeO	530
		TeO_2	600
'Petzite'(?). Contains over 60 per cent. of Te .		TeO	460
		TeO_2	900
Tetradymite. Bi_2Te_3 .	Hungary.	TeO	460
		TeO_2	750
Nagyagite. $\text{Au}_2\text{Pb}_{14}\text{Sb}_3\text{Te}_7\text{S}_{17}$.	Nagyag.	TeO	525
		TeO_2	610
Tellurium. Te .	Loc.	TeO	525
		TeO_2	850

It will be noticed that there is a readily observed distinguishing feature in the case of the two indicated groups of tellurides: the presence or absence of the black sublimate. This, of course, is explained by the fact that in the one group the temperature of decomposition is too high for the equilibrium of the molecule TeO .

A few experiments were made to see if different physical or crystallographic conditions affected the sublimation temperature. Sphalerite was tested in the following varieties:— (1) Transparent amber and brown crystal (Santander), 630; (2) Pale olive-green transparent crystal (Cornwall), 600; (3) Small, brilliant opaque crystals (loc.?), 610; (4) Fibrous, dark brown crystals (loc.?), 600; (5) Hepatic blende (Cornwall), 600. Sphalerite shows considerable variations in its specific heat according to its state of aggregation. The above results, depending on the internal stability of the molecule, reveal no definite variation.

Iveagh Geological Laboratory.

LXXXIX. *Notices respecting New Books.*

Les Atomes. By Professor JEAN PERRIN.

Pp. xvi+296. Paris: Félix Alcan, 1913. 3 fr. 50.

THIS volume in the *Nouvelle collection scientifique* is essentially the story of how a phenomenon discovered toward the beginning of the XIXth century by a botanist, and named after him Brownian motion, has in recent years yielded the surest evidence we possess of the validity of the kinetic theory of matter. From the experimental side the advance has been made in the greater part by Professor Perrin himself and his collaborateurs; but he has been helped greatly by the theoretic investigations of Einstein and others. Though the evidence from Brownian motion is the most direct, it is confirmed by several independent lines of evidence based on the blue colour of the sky, the law of radiation from an incandescent body, and on radioactivity. All of these methods give concordant and precise indications of the dimensions and number of the atoms which play the important role in the kinetic theory. The work possesses the attractive feature that it is quite modern, and this little volume constitutes a very suitable introduction to the subject. It is semi-popular in character; any mathematical results are merely summarized. But it is at the same time a very scientific treatise though of an elementary kind.

XC. *Intelligence and Miscellaneous Articles.*

THE PRODUCTION OF FLUORESCENT RÖNTGEN RADIATION.

Wheatstone Laboratory,
King's College.
May 7th, 1913.

To the Editors of the Philosophical Magazine.

GENTLEMEN, —

IN the April number of the *Philosophical Magazine*, Professor Bragg has published a letter dealing with a paper of mine of the previous month entitled "The Production of Fluorescent Röntgen Radiation."

In this letter two objections are made to my conclusion, that the bombardment theory does not explain the production of fluorescent X-rays: these are:—

(1) That the primary X-ray beam used in the experiment was heterogeneous, and therefore its power of producing corpuscles not sufficiently known.

(2) That Lenard's law is assumed to be rigid.

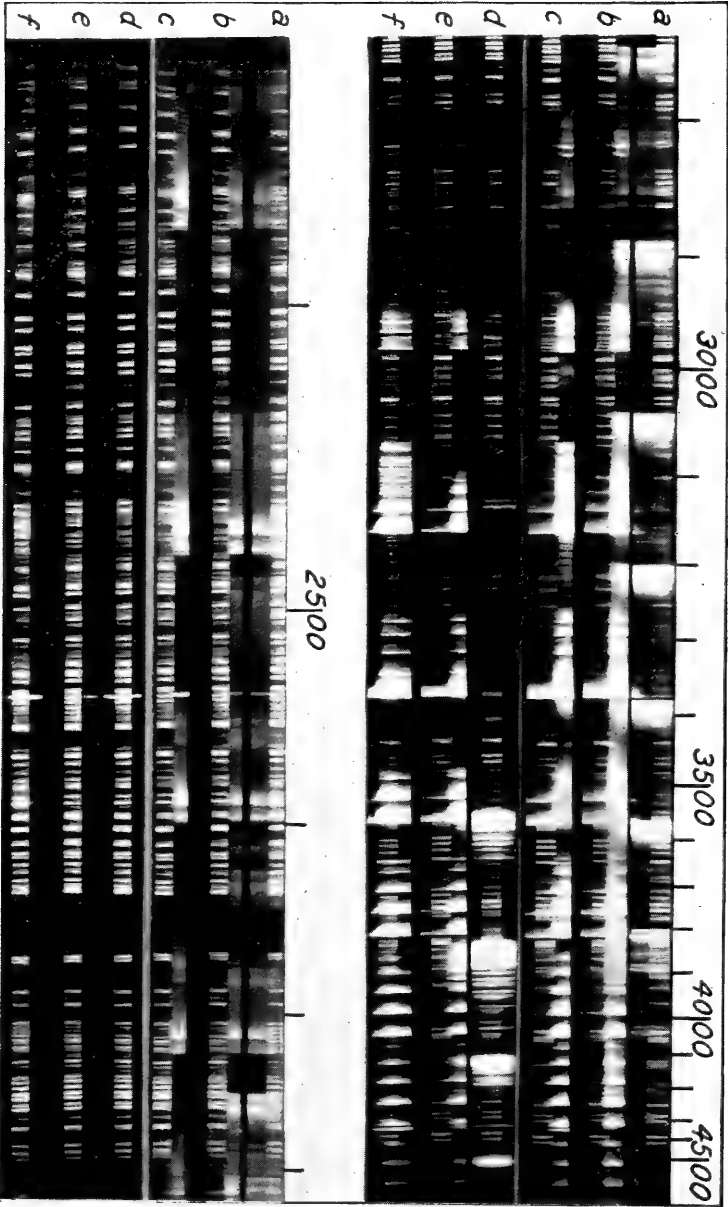
With regard to the first objection, it is necessary to point out a fact which is mentioned in the paper, namely, that in determining the penetrating power of the heterogeneous primary beam, a thin carbon sheet was used as the scattering agent. This carbon sheet, which did not absorb 5 per cent. of the primary radiation, would on this account scatter the softer constituents of the primary beam to a greater extent than the more penetrating rays. So that for this and other reasons, the primary radiation is in reality much harder than the values given in the paper would suggest. But the more penetrating this primary radiation, the greater is the velocity of the expelled corpuscles, and therefore the stronger the case for the theory which the paper supports.

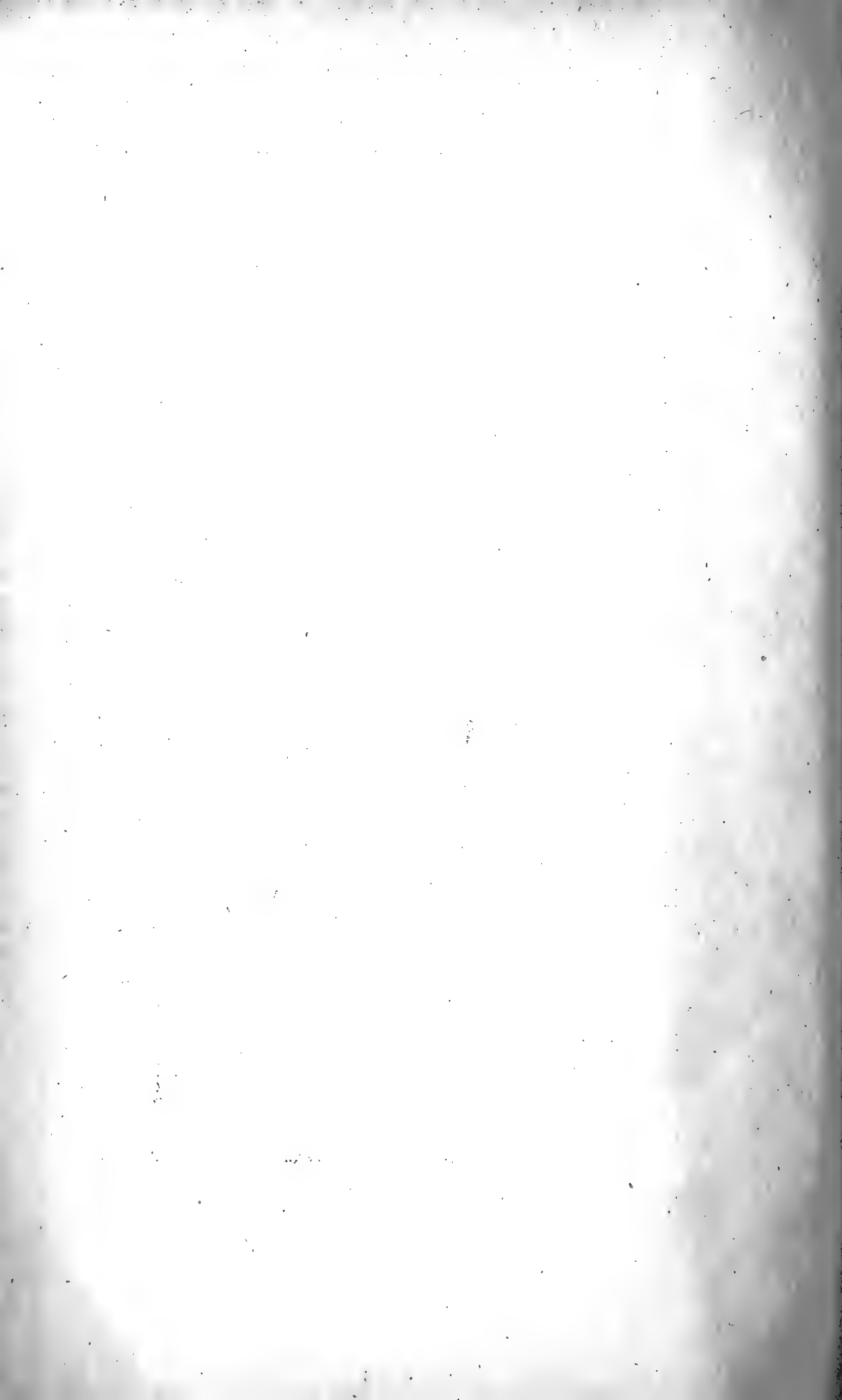
In the second objection, Professor Bragg states that Lenard's law is not rigid, and he brings forward evidence of a selective absorption of corpuscular radiation analogous to that obtained in absorption and ionization experiments. But even if selective absorption does take place and supposing that this selective absorption is of great magnitude, it is difficult to see how this affects the conclusion drawn in the paper, namely that the bombardment theory is not in harmony with experimental facts.

I may add that when the second paper was written, I was distinctly under the impression that Lenard's law was not rigorously obeyed, but its general acceptance led me to think that it was sufficiently accurate to justify an approximate calculation, and I am strengthened in this belief by the reserve with which Professor Bragg publishes his preliminary results.

Yours faithfully,

J. CROSBY CHAPMAN.





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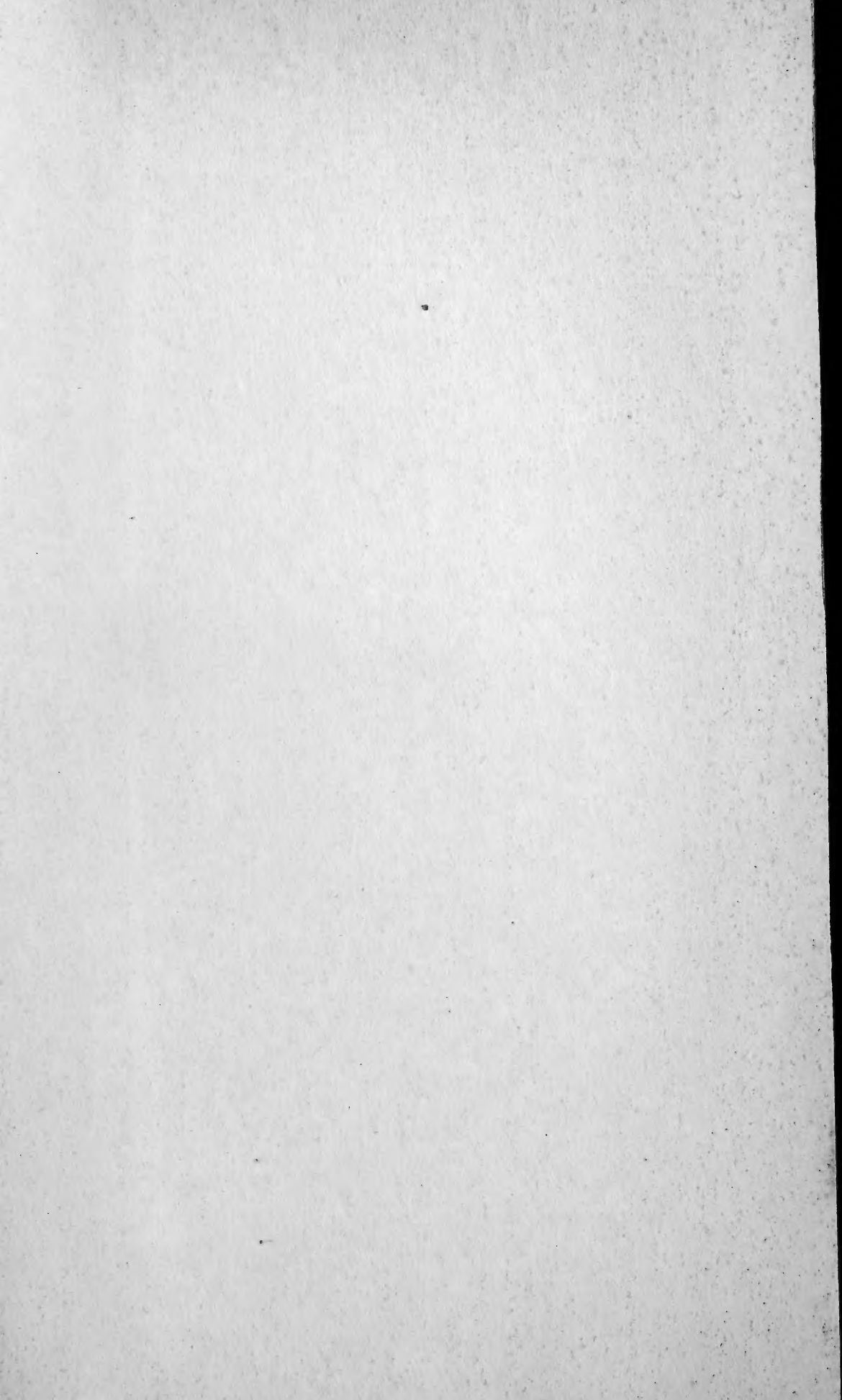
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