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AND
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"Nec aranearum 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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"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 condat,
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.

ALERE FLAMMAM

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ERRATA.

Page 519, line 20, *for* few cubic centimetres *read* few cubic millimetres.
Page 520, line 4 from bottom, *for* glass *read* gas.

PLATES.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JULY 1908.

I. *The Problem of a Spherical Gaseous Nebula.*

By the late Lord KELVIN.

[Continued from vol. xv. p. 711.]

§ 52. WE may now apply the above equations to obtain the complete solution of our problem of § 21 :—to determine for any spherical gaseous nebula of given mass, initially in convective equilibrium, exactly what its radius was, what its central temperature and density were, and what were the temperature and density at any distance from the centre, at the time when a stated quantity of heat has been radiated into space. Looking to equation (57), we see that throughout all approximate equilibrium conditions of a constant total mass the relation

$$\sigma C^{-\frac{1}{2}(\kappa-3)} = \mathscr{M} \text{ (a constant)} \quad . \quad . \quad . \quad (62)$$

holds: and, with this condition, equation (51) shows that, during the gradual loss of heat from the nebula, the value of z for each stated mass m, concentric with the boundary, is constant. We have accordingly for the mass m

$$r = \frac{\sigma C^{-\frac{1}{2}(\kappa-1)}}{z} = \frac{\mathscr{M}}{z} \cdot \frac{1}{C} \quad . \quad . \quad . \quad . \quad . \quad (63),$$

where C varies slowly as time goes on. If we suppose C_1 to be the initial central temperature of the nebula, and C_2 its central temperature after a quantity of heat H has been lost by radiation, by applying (62) in the equations given above, we easily find (with suffixes 1 and 2 referring to the initial and final conditions respectively) the following results :—

$$\left.\begin{array}{ll} t_2=\frac{C_2}{C_1}t_1 \;; & \rho_2=\left(\frac{C_2}{C_1}\right)^3\rho_1 \\ r_2=\frac{C_1}{C_2}r_1 \;; & R_2=\frac{C_1}{C_2}R_1 \\ I_2=\frac{C_2}{C_1}I_1 \;; & W_2=\frac{C_2}{C_1}W_1 \end{array}\right\} \quad . \; . \; . \; . \quad (64);$$

in which $t_2, t_1, \rho_2, \rho_1, r_2, r_1$, all refer to points on the spherical surface enclosing a stated mass m. The total heat lost by radiation may now be written—

$$H=(W_2-W_1)-(I_2-I_1)=\frac{C_2-C_1}{C_1}(W_1-I_1) \quad . \quad (65);$$

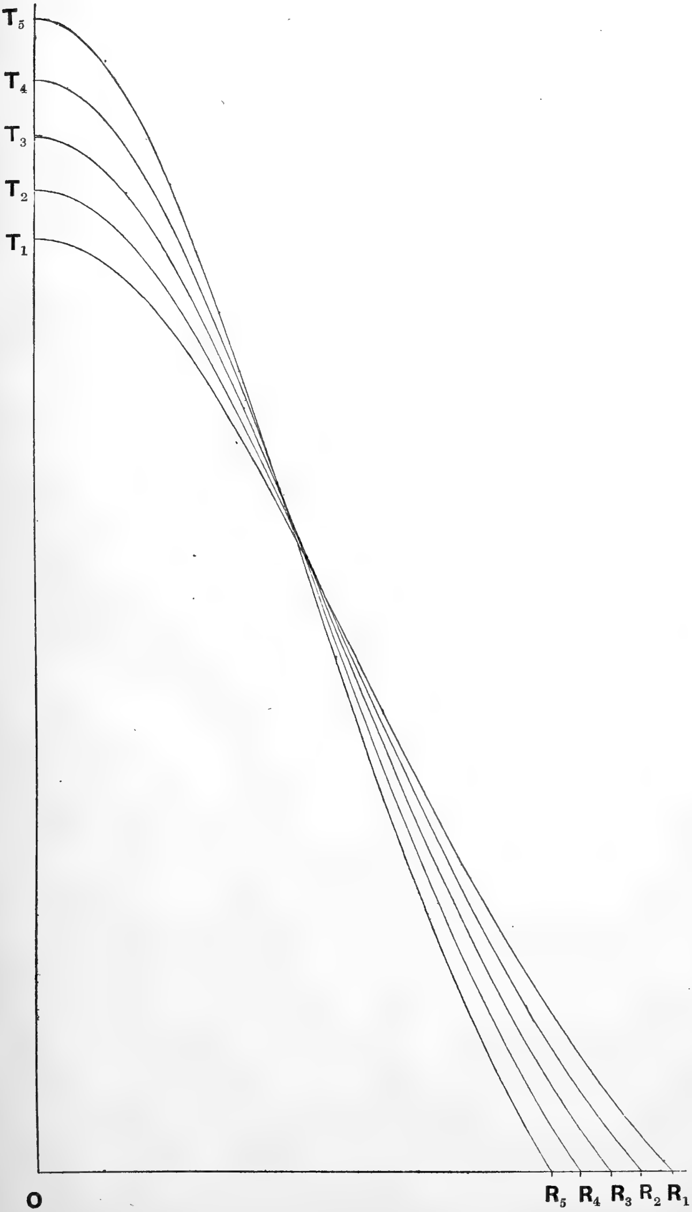
and for an infinitesimal change in the condition of the whole mass at any time this becomes

$$\delta H=\frac{\delta C}{C}(W-I) \quad . \; . \; . \; . \; . \quad (66).$$

§ 53. These are interesting results. Remembering that $I_1=\kappa/3.W_1$, we see by (65) and (66) that the central temperature of a globe of gas P in equilibrium increases, through gradual loss of heat by radiation into space. We then see also by (64) that the internal energy of a globe of gas **P**, continuing in a condition of approximate equilibrium while heat is being radiated away across its boundary, would go on increasing, and the work done by the mutual gravitation of its parts would go on increasing, till the gas in the central regions became too dense to obey Boyle's Law. At the same time the radius of the globe would diminish. In other words, the repulsive power which the globe of gas P possesses by virtue of its internal energy, while in approximate equilibrium, is, owing to gradual loss of energy by radiation, at each instant just insufficient to exactly balance the attractive force due to the mutual gravitation of its parts. The globe is therefore compelled to contract: and, as the heat due to the contraction is not radiated away so quickly as it is produced, the shrinkage of the globe is accompanied by augmentation of its internal energy.

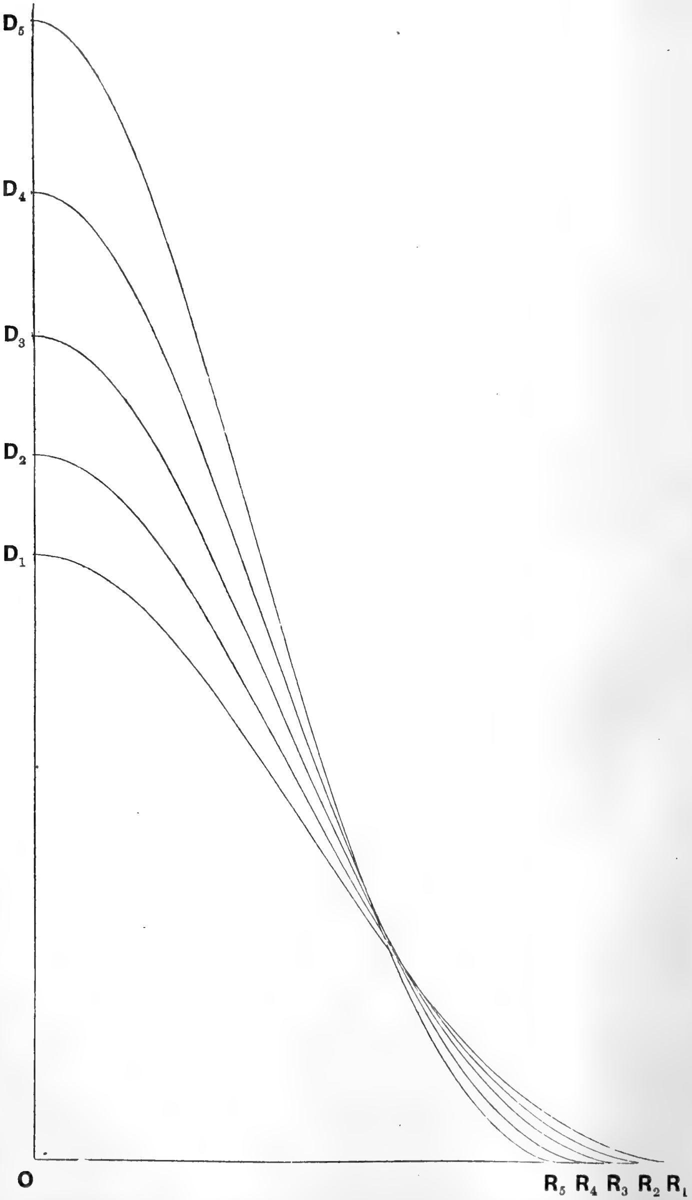
In figures 1 and 2 curves are shown illustrating five successive stages, numbered 1, 2, 3, 4, 5 respectively, in the history of a constant mass of any monatomic gas ($\kappa=1{\cdot}5$; $k=1\frac{2}{3}$) in approximate convective equilibrium while heat is

Fig. 1.



$T_1 R_1$, $T_2 R_2$, $T_3 R_3$, $T_4 R_4$, $T_5 R_5$, are temperature curves for a constant mass of monatomic gas in equilibrium, at five stages of its history, numbered 1, 2, 3, 4, 5, in order of time, while it is losing heat by radiation into space.

Fig. 2.



$D_1 R_1$, $D_2 R_2$, $D_3 R_3$, $D_4 R_4$, $D_5 R_5$, are density curves, corresponding respectively to the temperature curves $T_1 R_1$, $T_2 R_2$, $T_3 R_3$, $T_4 R_4$, $T_5 R_5$, of figure 1.

being radiated from it into space. The abscissas represent distance from the centre. The ordinates in figure 1 represent temperature reckoned from absolute zero; $OT_1 \ldots OT_5$, being proportional to 1, 1·052, 1·108, 1·169, 1·235: figure 2 gives the corresponding density curves.

§ 54. The remarkable result we have arrived at for P gases (for which alone, as we have seen, convective equilibrium can be realised), that the internal energy of a given mass in approximate convective equilibrium increases through gradual loss of heat by radiation into space, was first suggested as a possibility by Homer Lane; the suggestion being given in his paper referred to in § 2. To understand it more fully, go back to equation (62), and observe that in the case of P gases σ is continually diminishing, while the globe is shrinking through loss of heat. The adiabatic constant A, which determines the relation between temperature and density throughout the fluid at any instant, must therefore also continually diminish as time goes on [see (22) above]. Thus, we find from equation (19) that, although the density and temperature of the gas near the centre of the sphere are increasing, as we see from figures 1 and 2, and the total energy is increasing, in reality the temperatures at places of the same density are continually diminishing. And this diminution of temperature at places of the same density causes a diminution of the elastic resistance of the gas to compression which allows the gravitational forces to effect a contraction of the gaseous mass.

§ 55. It seems certain that, as the condensation illustrated in figures 1 and 2 continues with increasing total energy, a time must come when the resistance to compression of the matter in the central regions must become much more than in accordance with the laws of perfect gases; and after that occurs, the cooling at the surface, with continual mixing of cooled fluid throughout the interior mass, must ultimately check the process of becoming hotter in the central regions, and bring about a gradual cooling of the whole mass.

§ 56. The application of the above theory of approximate convective equilibrium to the sun, regarded as a mass of matter in the monatomic state, requires that the law of increase of density from the surface inwards should be such that the density at the centre is about six times the mean density (see Appendix, § 16). The mean density of the sun is about 1·4, the density of water being taken as unity. From this fact itself it seems certain that the sun is not gaseous as a whole. Disregarding, therefore, the high velocities which we know to exist in portions of the sun's atmosphere, and which are, according to the definition given in § 3, inconsistent with a condition of convective equilibrium, we are still forced to conclude that Homer Lane's exquisite mathematical theory gives no approximation to the present condition of the sun, because of his great average density. "This was emphasised by Professor Perry in the seventh paragraph, headed 'Gaseous Stars,' of his letter to Sir Norman Lockyer on 'The Life of a Star' (Nature, July 13, 1899), which contains the following sentence :—

'It seems to me that speculation on this basis of perfectly gaseous stuff ought to cease when the density of the gas at the centre of the star approaches 0·1, or one-tenth of the density of ordinary water in the laboratory' "*.

§ 57. According to a promise in the 1887 paper to the Philosophical Magazine "On the equilibrium of a gas under its own gravitation only," I now give examples of the application of this theory of convective equilibrium to spherical masses of argon and of nitrogen; choosing, for illustration, amounts of matter equal to the masses of the sun, earth, and moon, with density at the centre 0·1 in each case.

Assuming

$$t = \mathrm{C}\Theta\left[x\mathrm{C}^{-\frac{1}{2}(\kappa-1)}\right] \quad . \quad . \quad . \quad . \quad (67)$$

as the solution of (24), which gives central density 0·1, we find from equation (19)

$$0{\cdot}1 = \left(\frac{\mathrm{SC}}{\mathrm{A}}\right)^{\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68);$$

and, as in this case we suppose the total mass M of the nebula to be known, we can determine C by applying equation (25) above. Thus

$$\frac{\mathrm{M}}{\mathrm{E}} = \frac{(\kappa+1)\mathrm{S}\sigma\mathrm{C}^{-\frac{1}{2}(\kappa-3)}}{e^2}\Theta'_{\kappa}(q) \quad . \quad . \quad . \quad (69),$$

where q denotes the value of x for which $\Theta_{\kappa}(x)=0$. Eliminating A and σ by means of equations (22) and (68), we obtain

$$\mathrm{C} = \left(\frac{e}{\mathrm{S}}\right) \cdot 3770 . \left[\Theta'_{\kappa}(q)\right]^{-\frac{2}{3}} \frac{1}{\kappa+1}\left(\frac{\mathrm{M}}{\mathrm{E}}\right)^{\frac{2}{3}} \quad . \quad . \quad (70).$$

---

* Quoted from "On Homer Lane's Problem of a Spherical Gaseous Nebula," 'Nature,' Feb. 14, 1907.

From equations (68) and (22) we can determine the following expressions for A and σ :—

$$\frac{\mathrm{A}}{e} = \cdot 8122\left[\Theta'_\kappa(q)\right]^{-\frac{2}{3}} \frac{\cdot 1^{\frac{\kappa-3}{3\kappa}}}{\kappa+1}\left(\frac{\mathrm{M}}{\mathrm{E}}\right)^{\frac{2}{3}} \quad . \quad . \quad (71)$$

$$\frac{\sigma}{\sqrt{(e\mathrm{S})}} = \left(\frac{e}{\mathrm{S}}\right)^{\frac{\kappa}{2}} \cdot 1366\left[\cdot 1366 . \Theta'_\kappa(q)\right]^{-\frac{\kappa}{3}} \frac{\cdot 1^{\frac{\kappa-3}{6}}}{(\kappa+1)^{\frac{1}{2}(\kappa-1)}}\left(\frac{\mathrm{M}}{\mathrm{E}}\right)^{\frac{\kappa}{3}} \quad (72).$$

The radius of the outer boundary of the nebula is given by

$$\mathrm{R} = \frac{\sigma}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (73),$$

where

$$x\mathrm{C}^{-\frac{1}{2}(\kappa-1)} = q \quad . \quad . \quad . \quad . \quad . \quad . \quad (74).$$

We have therefore $\mathrm{R} = \sigma q^{-1}\mathrm{C}^{-\frac{1}{2}(\kappa-1)}$, which, by means of equations (53) and (55), may be written in the form

$$\frac{\mathrm{R}}{e} = 2\cdot 6527\left[\Theta'_\kappa(q)\right]^{-\frac{1}{3}} q^{-1}\left(\frac{\mathrm{M}}{\mathrm{E}}\right)^{\frac{1}{3}} \quad . \quad . \quad . \quad (75).$$

For argon we have $k = 1\frac{2}{3}$, or $\kappa = 1\cdot 5$; and $\mathrm{S} = 5\cdot 767$ kilometres ; and for nitrogen we have $k = 1\cdot 4$, or $\kappa = 2\cdot 5$; and $\mathrm{S} = 8\cdot 256$ kilometres. With these values of S and κ, inserted in the above formulas, we obtain the results shown in the following table :—

Matter in nebula.	Total mass, that of	Central density.	Central temperature in Centigrade degrees above absolute zero.	Central pressure in metric tons per sq. kilometre.	Radius of boundary in kilometres.	Adiabatic Constant in kilometres.
Argon.	Sun.	·1	$1\cdot 105 \times 10^8$	$2\cdot 33 \times 10^{14}$	$3\cdot 04 \times 10^6$	$1\cdot 08 \times 10^7$
,,	Earth.	·1	$2\cdot 342 \times 10^4$	$4\cdot 95 \times 10^{10}$	$4\cdot 42 \times 10^4$	$2\cdot 30 \times 10^4$
,,	Moon.	·1	$1\cdot 243 \times 10^3$	$2\cdot 63 \times 10^9$	$1\cdot 02 \times 10^4$	$1\cdot 22 \times 10^2$
Nitrogen.	Sun.	·1	$6\cdot 383 \times 10^7$	$1\cdot 92 \times 10^{14}$	$4\cdot 79 \times 10^6$	$4\cdot 82 \times 10^5$
,,	Earth.	·1	$1\cdot 353 \times 10^4$	$4\cdot 07 \times 10^{10}$	$6\cdot 97 \times 10^4$	$1\cdot 02 \times 10^3$
,,	Moon.	·1	$7\cdot 185 \times 10^2$	$2\cdot 16 \times 10^9$	$1\cdot 61 \times 10^4$	54·3

§ 58. The curves of figures 3 and 4 represent temperature and density at different distances from the centres of nebulas for which κ has the values 1·5, 2·5, 3, and 4. The temperature curves are drawn from the numbers given in the third columns of Tables I. . . . IV. of the Appendix : the density curves, from the numbers given in the fourth columns.

Fig. 3.

T $R_{1\cdot5}$ is the curve of temperature, and $D_{1\cdot5}$ $R_{1\cdot5}$ is the curve of density, for a monatomic gas ($k=1\frac{2}{3}$). T $R_{2\cdot5}$, and $D_{2\cdot5}$ $R_{2\cdot5}$ are corresponding curves for a diatomic gas ($k=1\cdot4$).

Fig. 4.

T R_3 is the curve of temperature, and D_3 R_3 is the curve of density, for a gas for which $k=1\frac{1}{3}$. T R_4 and D_4 R_4 are corresponding curves for a gas for which $k=1\frac{1}{4}$.

With properly chosen scales of ordinates and abscissas, the curves shown may represent the condition of any gaseous mass, corresponding to any of the solutions (26) above. Thus, with scales so chosen that $OR_\kappa = R = \sigma q^{-1} C^{-\frac{1}{2}(\kappa-1)}$, and $OT = C$, each curve, TR_κ, represents the temperature reckoned from absolute zero; and with $OD_\kappa = (SC/A)^\kappa$, each curve, $D_\kappa R_\kappa$, represents the density, in a nebula composed of gas for which κ has one of the values given above, when the central temperature is C.

Each curve shown meets the axis of R at a finite angle; this angle being so small for the density curves that they appear to meet OR tangentially.

APPENDIX.

By George Green.

§ 1. In order to determine the conditions of temperature, pressure, and density, at any distance from the centre of a spherical mass of gas in convective equilibrium, held together by the mutual gravitation of its parts, it is necessary to find a solution of the equation,

$$\frac{d^2t}{dx^2} = -\frac{t^\kappa}{x^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

In this equation,

x is inversely proportional to r, the distance of any point from the centre of the sphere:

$$\left[r = \frac{\sigma}{x}\right]$$

t is the temperature of the gas at any point of a spherical surface, of radius r:

t^κ is proportional to the density where t is the temperature:

$$\left[\rho = \left(\frac{St}{A}\right)^\kappa\right]$$

$\frac{dt}{dx}$ is proportional to the mass of gas within the surface of radius r:

$$\left[\frac{dt}{dx} = \frac{e^2}{(\kappa+1)S\sigma}\frac{m}{E}\right]$$

and κ is equal to $1/(k-1)$, where k is the ratio of specific heats of the gas considered (see §§ 22 . . . 24 of the above paper).

§ 2. Solutions of this equation can be found which correspond to a mass of gas around a solid or liquid nucleus. These may become of interest later. Solutions can also be found which correspond to an infinite sphere of gas, with an infinite density at the centre. But the solutions which it is now desirable to obtain are those which can be applied to the case of a spherical mass of gas which has a finite density at at the centre. This is expressed mathematically by saying that at $x=\infty$, we have $t=\mathrm{C}$, $\dfrac{dt}{dx}=0$.

Lord Kelvin has shown, in his paper "On the equilibrium of a gas under its own gravitation only," Phil. Mag., March 1887, and in § 25 of the preceding paper, that, when any complete solution $\mathfrak{F}(x)$ has been found, it is possible to derive from it a general solution with one disposable constant C, $\mathrm{C}\mathfrak{F}\left[x\mathrm{C}^{-\frac{1}{2}(\kappa-1)}\right]$. Accordingly, it is convenient to deal only with the particular solution for which $t=1$; $\dfrac{dt}{dx}=0$; at $x=\infty$, denoted by $\Theta_{\kappa}(x)$, and called the Homer Lane Function.

§ 3. Homer Lane, in his paper "On the theoretical temperature of the sun," gives analytical solutions of equation (1) for the cases $k=1\frac{2}{3}$ and $k=1{\cdot}4$, which correspond to a monotomic and to a diatomic gas respectively. His method of obtaining these solutions is equivalent to the following. Assume

$$t=\Theta_{\kappa}^{*}(x)=1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\frac{\alpha_3}{x^6}+\ldots\text{ etc.} \quad . \quad . \quad (2)$$

to be the required solution of (1), where α_1, α_2, α_3, etc. are to be determined. Then

$$\frac{d^2\Theta_{\kappa}}{dx^2}=\frac{2.3.\alpha_1}{x^4}+\frac{4.5.\alpha_2}{x^6}+\frac{6.7.\alpha_3}{x^8}+\text{etc.} \quad . \quad . \quad (3).$$

And the coefficients α_1, α_2, α_3, etc. can be determined from the equation—

$$\left(\frac{2.3.\alpha_1}{x^4}+\frac{4.5.\alpha_2}{x^6}+\frac{6.7.\alpha_3}{x^8}+\text{etc.}\right)=-\frac{\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\frac{\alpha_3}{x^6}+\text{etc.}\right)^{\kappa}}{x^4} \quad . \quad (4).$$

The solutions given by Homer Lane are, in the present notation,

$$\Theta_{1\cdot5}(x)=1-\frac{1}{6x^2}+\frac{1}{80x^4}-\frac{1}{1440x^6}+\frac{1}{31104x^8}-\ldots\text{ etc.} \quad (5);$$

$$\Theta_{2\cdot5}(x)=1-\frac{1}{6x^2}+\frac{1}{48x^4}-\frac{5}{2016x^6}+\frac{125}{435456x^8}-\ldots\text{ etc.} \quad (6).$$

These terms are sufficient to give a satisfactory determination of t for all values of x equal to or greater than unity; that is, at all points in the gas within distance σ from the centre of the sphere, where the radius of the boundary is σ/q, and q is the value of x for which $\Theta_\kappa(x)=0$.

The labour of calculating additional terms of these series being very great, and no great precision being necessary, Homer Lane merely employed a step-by-step process, involving the use of numerical differences, to obtain approximately the value of t at points whose distance from the centre of the sphere was greater than that corresponding to x unity in equations (5) and (6). When a fairly small value of t had been reached by this method, he was able to complete the calculation as far as $t=0$ $(x=q)$ by means of approximate formulas which can be derived in a manner similar to that described above.

§ 4. With a view to obtaining greater accuracy in the results for monatomic gases, Mr. T. J. J. See has extended Homer Lane's series (5) as far as the term containing x^{20}; and with the aid of additional terms, obtained by means of logarithmic differences of preceding terms, he has calculated the values of t, ρ, m, etc., at a place very close to the boundary of the gas. From this he has been able to find with great accuracy the radius of the spherical boundary, and the total mass of gas, corresponding to the Homer Lane Function $\Theta_{1\cdot 5}(x)$ (see § 17). These results are published in a paper entitled "Researches on the physical constitution of the heavenly bodies" (*Astr. Nachr.* No. 4053, Bd. 169, Nov. 1905). They were found after Table I., on page 20 of the present paper, had been completed by the entirely different method given below, and they are a confirmation of its usefulness.

§ 5. Eight years after the publication of Homer Lane's famous paper, the problem of the convective equilibrium of a spherical mass of gas under its own gravitation only was dealt with very fully by A. Ritter, in a series of papers entitled "Untersuchungen über die höhe der Atmosphäre und die Constitution gasförmiger Weltkörper," published in *Wiedemann's Annalen*, 1878–1882. Numerical solutions of equation (1) are given for the following values of κ, 1·5, 2, 2·44, 3, 4, 5; these solutions being obtained wholly by a graphical process, similar to the process described in § 7 below.

§ 6. Professor Schuster, in a short paper to the British Association at Southport in 1883, pointed out that it was possible to obtain solutions of equation (1) in finite terms in the two cases $\kappa=1$, and $\kappa=5$ ($k=2$ and $k=1{\cdot}2$). For $\kappa=1$, the solution, in the present notation, is—

$$\Theta_1(x)=x\sin\frac{1}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7);$$

a result which was first given by Ritter. For $\kappa=5$, the solution is

$$\Theta_5(x)=\frac{x\sqrt{3}}{\sqrt{(3x^2+1)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

§ 7. The method of obtaining numerical solutions of equation (1) which has been adopted throughout the present paper, is derived from that indicated by Lord Kelvin on page 291 of his paper to the Philosophical Magazine, March 1887, referred to in § 2 above. An arbitrary trial curve, t_0, fulfilling the initial conditions $t=\mathrm{A}$; $\frac{dt}{dx}=\mathrm{A}'$; at $x=a$; is taken for t. From this curve, t_0, a curve representing $-\frac{t^\kappa}{x^4}$, or $\frac{d^2t_1}{dx^2}$, is obtained by direct calculation. One integration performed on this calculated curve gives the means of drawing $\frac{dt_1}{dx}$; and the curve representing t_1, which is obtained by integrating $\frac{dt_1}{dx}$, is then found to be a closer approximation to the true curve for t than the curve t_0 chosen arbitrarily. This process may be repeated to obtain t_2, using the curve t_1 as a new trial curve for t: and so on. When t_i differs very little from t_{i-1}, t_i may be regarded as a very close approximation to the true curve for t.

§ 8. It was found that the best way to carry out this plan of obtaining a numerical solution by means of two successive integrations was to choose the interval of integration, from any point at which t and $\frac{dt}{dx}$ were known, sufficiently small that the trial value chosen for t, for the point at the end of the interval, could be determined with any degree of accuracy required, by means of numerical differences of the values of t already determined for the end points of preceding intervals. The arbitrary trial curve is in this case a curve which coincides with the true curve in each interval preceding the one considered, and in this interval it closely approximates to the true curve. It has been found that one application of the process of double integration to this trial curve gives t and

$\frac{dt}{dx}$ at the end of the interval with any accuracy desired; the accuracy depending on the smallness of the interval chosen. By taking the curves for $-\frac{t^\kappa}{x^4}$ and $\frac{dt}{dx}$ as straight lines within each successive interval treated, and by making a roughly estimated allowance at each step for the error thus introduced, the process can be carried out very quickly and quite satisfactorily, as a process of step-by-step calculation, without the assistance of carefully drawn curves.

§ 9. The accuracy of the above process can easily be proved analytically for the case of any very short interval; but when such a process is applied to a succession of intervals, there is certain to be a cumulative error, which may, or may not, increase without limit as the work proceeds. So far as it is possible to judge, however, the process of § 8 seems to be practically applicable to obtain numerical solutions of differential equations of the form

$$\frac{d^2t}{dx^2}=f(x, t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9),$$

provided f has the opposite sign from t. It has been applied with very satisfactory results to the two equations—

$$\frac{d^2t}{dx^2}=-t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10),$$

and

$$\frac{d^2t}{dx^2}=-\frac{t^5}{x^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11),$$

for each of which the direct verification of the solutions obtained is possible; the solution of the latter equation obtained was $\Theta_5(x)$, which is given in § 6 above.

In these cases, and in the case of any Homer Lane Function, if t, throughout a number of intervals, becomes greater than its true value, the absolute value of $\frac{d^2t}{dx^2}$ also becomes greater than its true value, and $\frac{dt}{dx}$ is therefore tending to become less than it would otherwise be. Hence the successive additions to t in each interval in which it is greater than its true value are, or tend to become, less than they would be with a correct t. Thus, when t has become too great in any interval, throughout the succeeding intervals it tends to return to its true value rather than to go without limit away from it. From similar considerations it may be judged that when t has become less than its true value, in the succeeding intervals it tends to return towards its true value.

§ 10. The numerical values of the Homer Lane Function $\Theta(x)$ with its differential coefficient $\Theta'(x)$, in the interval from $x=\infty$ to $x=q$, given in Tables I. . . . IV., and the values of the Boylean Function $\Psi(x)$, and the function $\Psi'(x)/\Psi(x)$, in the interval from $x=\cdot25$, to $x=\cdot1$, given in Table V., have all been obtained by the method of § 8. In each of the Homer Lane Functions, a beginning of the calculation was made from the following approximate equation :—

$$\Theta_\kappa(x) \doteqdot 1-\frac{1}{6x^2}+\frac{\kappa}{120x^4}- \quad . \quad . \quad . \quad (12),$$

easily derived from equations (2) and (4) above. From $x=\infty$ to $x=\cdot25$, the Boylean Function was calculated by a method described below.

After Tables I. . . . IV. had been completed, as it was still desirable to be able to verify the results obtained by the step-by-step process at some point close to the final point, q, and as the labour of calculating successive terms of the series (2) soon becomes very great, while the number of the terms required to give a sufficiently good result also becomes greater and greater as x diminishes, the form of expansion given in § 11 below was tried, and found to be useful.

§ 11. Assume as a solution of equation (1),

$$\Theta_\kappa(x)=\frac{1}{\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\frac{\alpha_3}{x^6}+\text{etc.}\right)^n} \quad . \quad . \quad (13).$$

We can write $\Theta''_\kappa(x)$ in either of the following forms :—

$$\frac{-n\left(\frac{2.3.\alpha_1}{x^4}+\frac{4.5.\alpha_2}{x^6}+\frac{6.7.\alpha_3}{x^8}+\text{etc.}\right)\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\text{etc.}\right)+n(n+1)\left(\frac{2\alpha_1}{x^3}+\frac{4\alpha_2}{x^5}+\frac{6\alpha_3}{x^7}+\text{etc.}\right)^2}{\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\frac{\alpha_3}{x^6}+\text{etc.}\right)^{n+2}};$$

$$\frac{-\frac{2.3.\alpha_1 n}{x^4}}{\left.1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\text{etc.}\right)^{n+1}}-\frac{n\left(\frac{4.5.\alpha_2}{x^6}+\frac{6.7.\alpha_3}{x^8}+\text{etc.}\right)\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\text{etc.}\right)-n(n+1)\left(\frac{2x_1}{x^3}+\frac{4\alpha_2}{x^5}+\text{etc.}\right)^2}{\left(1+\frac{\alpha_1}{x^2}+\frac{\alpha_2}{x^4}+\frac{\alpha_3}{x^6}+\text{etc.}\right)^{n+2}}.$$

If we now choose n in the first form, so that $(n+2)=\kappa n$, and equate the numerator to $-\frac{1}{x^4}$, we obtain

$$\Theta''_\kappa(x)=-[\Theta_\kappa(x)]^\kappa/x^4.$$

And the coefficients α_1, α_2, α_3, etc. can be determined from the following equations :—

$$\left.\begin{aligned}
&2.3.a_1 = \frac{1}{n};\ 4.5.a_2 = (\beta.1^2 - 2.3)a_1^{\ 2};\ 6.7.a_3 = (2\beta.1.2. - 2.3. - 4.5)a_1 a_2;\\
&2i(2i+1)a_i = \mathop{\mathrm{S}}_{r=1}^{r=\frac{i-2}{2}} \{2\beta.r(i-r) - 2r(2r+1) - (2i-2r)(2i-2r+1)\}a_r a_{i-r}\\
&\qquad\qquad + \left\{\beta\left(\frac{i}{2}\right)^2 - i(i+1)\right\} a^{\ 2}_{\frac{i}{2}}\ (i\ \text{even});\\
&2i(2i+1)a_i = \mathop{\mathrm{S}}_{r=i}^{r=\frac{i-1}{2}} \{2\beta.r(i-r) - 2r(2r+1) - (2i-2r)(2i-2r+1)\}a_r a_{i-r} (i\ \text{odd});\\
&\text{where}\qquad \beta = 4(n+1) = \frac{4(\kappa+1)}{(\kappa-1)}.
\end{aligned}\right\}(14$$

Similarly, if we choose n so that $(n+1) = \kappa n$, and then choose α_1 so that $2.3.\alpha_1.n = 1$, the first term of the second form of $\Theta''_\kappa(x)$ becomes $-[\Theta_\kappa(x)]^\kappa/x^4$; and the second term, equated to zero, gives us the following equations to determine α_2, α_3, ... , etc. :—

$$\left.\begin{aligned}
&4.5.a_2 = \beta a_1^{\ 2};\ 6.7.a_3 = (2\beta.1.2 - 4.5)a_1 a_2;\ 8.9.a_4 = (2\beta.1.3. - 6.7)a_1 a_3 + (\beta.2^2 - 4.5)a_2^{\ 2};\\
&2i(2i+1)a_i = \{2\beta.1.(i-1) - (2i-2)(2i-1)\}a_1 a_{i-1} + \mathop{\mathrm{S}}_{r=2}^{r=\frac{i-2}{2}} \{2\beta.r(i-r) - 2r(2r+1)\\
&\qquad - (2i-2r)(2i-2r+1)\}a_r a_{i-r} + \left\{\beta\left(\frac{i}{2}\right)^2 - i(i+1)\right\} a^{\ 2}_{\frac{i}{2}}\ (i\ \text{even});\\
&2i(2i+1)a_i = \{2\beta.1.(i-1) - (2i-2)(2i-1)\}a_1 a_{i-1} + \mathop{\mathrm{S}}_{r=2}^{r=\frac{i-1}{2}} \{2\beta.r(i-r) - 2r(2r+1)\\
&\qquad - (2i-2r)(2i-2r+1)\}a_r a_{i-r} (i\ \text{odd});\ \text{where}\ \beta = 4(n+1) = \frac{4\kappa}{(\kappa-1)}.
\end{aligned}\right\}($$

§ 12. In the particular case of equation (1) for which $\kappa = \infty$ $(k=1)$, and which corresponds to an ideal gas which obeys Boyle's Law for all pressures, the differential equation becomes

$$\frac{d^2 \log \rho}{dx^2} = -\frac{\rho}{x^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

Assume as the solution of this equation which gives $\rho = 1$, when $x = \infty$,

$$\rho = \Psi(x) = \frac{1}{\left(1 + \frac{\alpha_1}{x^2} + \frac{\alpha_2}{x^4} + \frac{x_3}{x^6} + \text{etc.}\right)^n} \quad . \quad (17).$$

We may, in this case also, write $\frac{d^2 \log \Psi(x)}{dx^2}$ in the two forms:—

$$\frac{-n\left(\frac{2.3.a_1}{x^4}+\frac{4.5.a_2}{x^6}+\text{etc.}\right)\left(1+\frac{a_1}{x^2}+\frac{a_2}{x^4}+\text{etc.}\right)+n\left(\frac{2a_1}{x^3}+\frac{4a_2}{x^5}+\text{etc.}\right)^2}{\left(1+\frac{a_1}{x^2}+\frac{a_2}{x^4}+\frac{a_3}{x^6}+\text{etc.}\right)^2};$$

$$\frac{-\frac{2.3.a_1 n}{x^4}}{\left(1+\frac{a_1}{x^2}+\frac{a_2}{x}+\frac{a_3}{x^6}+\text{etc.}\right)}-\frac{n\left(\frac{4.5.a_2}{x^6}+\frac{6.7.a_3}{x^8}+\text{etc.}\right)\left(1+\frac{a_1}{x^2}+\frac{a_2}{x^4}+\text{etc.}\right)-n\left(\frac{2a_1}{x^3}+\frac{4a_2}{x^5}+\text{etc.}\right)^2}{\left(1+\frac{a_1}{x^2}+\frac{a_2}{x^4}+\frac{a_3}{x^6}+\text{etc.}\right)^2}.$$

By taking $n=2$ in the first of these forms, and $n=1$ in the second, and proceeding exactly as in § 11, we obtain two expressions for $\Psi(x)$ in the form (17), the coefficients α_1, α_2, α_3, etc. being again determined from the series of equations (14), when $n=2$, and from equations (15), when $n=1$.

§ 13. At present only the numerical values given by the above solutions are of importance; and for this purpose, the expression (13) with $n=\frac{2}{\kappa-1}$ has been used to calculate the Homer Lane Functions, and the expression (17) with $n=2$ to calculate the Boylean Function. The following table gives the logarithms of several of the coefficients α_1, α_2, etc. for the functions given in Tables I. . . . V.; the letter n indicating that the term is negative:—

κ	1·5	2·5	3	4	∞
log a_1	$\overline{2}{\cdot}61979$	$\overline{1}{\cdot}09691$	$\overline{1}{\cdot}22185$	$\overline{1}{\cdot}39794$	$\overline{2}{\cdot}92082$
log a_2	$\overline{3}{\cdot}08468$	$\overline{3}{\cdot}41567$	$\overline{3}{\cdot}44370$	$\overline{3}{\cdot}31876$	$\overline{4}{\cdot}84164$ n
log a_3	$\overline{5}{\cdot}81361$	$\overline{5}{\cdot}94369$	$\overline{5}{\cdot}82045$	$\overline{6}{\cdot}91736$	$\overline{5}{\cdot}13921$
log a_4	$\overline{6}{\cdot}59587$	$\overline{6}{\cdot}45524$	$\overline{6}{\cdot}10924$	$\overline{7}{\cdot}23612$	$\overline{7}{\cdot}61229$ n
log a_5	$\overline{7}{\cdot}39883$	$\overline{8}{\cdot}96928$	$\overline{8}{\cdot}46991$	$\overline{9}{\cdot}5540$ n	$\overline{8}{\cdot}19003$
log a_6	$\overline{8}{\cdot}21416$	$\overline{9}{\cdot}49350$	$\overline{10}{\cdot}72486$	$\overline{11}{\cdot}8517$	$\overline{10}{\cdot}83708$ n
log a_7	$\overline{9}{\cdot}03834$	$\overline{10}{\cdot}01706$	$\overline{11}{\cdot}19035$	n	$\overline{11}{\cdot}5332$
log a_8	$\overline{11}{\cdot}86917$	$\overline{12}{\cdot}54628$	$\overline{14}{\cdot}84984$		n
log a_9	$\overline{12}{\cdot}70515$	$\overline{13}{\cdot}07368$	$\overline{14}{\cdot}26996$		
log a_{10}	$\overline{13}{\cdot}54520$	$\overline{15}{\cdot}60715$	$\overline{16}{\cdot}9440$ n		
log a_{11}	$\overline{14}{\cdot}38854$	$\overline{16}{\cdot}13498$	$\overline{17}{\cdot}9204$		
log a_{12}	$\overline{15}{\cdot}23460$	$\overline{18}{\cdot}67438$	n		
log a_{13}		$\overline{19}{\cdot}1967$			
log a_{14}		$\overline{21}{\cdot}7511$			
log a_{15}		$\overline{22}{\cdot}2475$			
log a_{16}		$\overline{24}{\cdot}8548$			
log a_{17}		$\overline{25}{\cdot}4061$			
log a_{18}		$\overline{27}{\cdot}6267$			

§ 14. In each of the functions (13) and (17) the coefficients become positive and negative alternately; and for small values of x, close enough to q, the series ultimately diverge. If x is not too small, several terms at the beginning of the series converge fairly rapidly, and give a close approximation to the result. The following values of the Homer Lane Function calculated by means of the numbers given above are correct to the last figure shown :—

$$\Theta_{1\cdot5}(\cdot4) = \cdot3159\ ;\ \Theta'_{1\cdot5}(\cdot4) = 2\cdot133\ ;\ \Theta_{1\cdot5}(\cdot35) = \cdot2007\ ;\ \Theta'_{1\cdot5}(\cdot35) = 2\cdot464\ ;$$
$$\Theta_{2\cdot5}(\cdot3) = \cdot24186\ ;\ \Theta'_{2\cdot5}(\cdot3) = 2\cdot0078\ ;\ \Theta_{2\cdot5}(\cdot25) = \cdot13768\ ;\ \Theta'_{2\cdot5}(\cdot25) = 2\cdot1448\ ;$$
$$\Theta_{3}\ (\cdot25) = \cdot2093\ ;\ \Theta'_{3}\ (\cdot25) = 1\cdot922\ ;\ \Theta_{3}\ (\cdot2) = \cdot111\ ;\ \Theta'_{3}\ (\cdot2) = 2\cdot00\ ;$$
$$\Theta_{4}\ (\cdot25) = \cdot3180\ ;\ \Theta'_{4}\ (\cdot25) = 1\cdot582\ ;\ \Theta_{4}\ (\cdot2) = \cdot2359\ ;\ \Theta'_{4}\ (\cdot2) = 1\cdot695.$$

By comparing these results with the corresponding values of the Homer Lane Function given in Tables I. . . . IV., we see that the numbers obtained by the step-by-step process of § 8 are sufficiently accurate for our purpose. It is possible to calculate q and $\Theta'_{\kappa}(q)$ from the values of $\Theta_{\kappa}(x)$ and $\Theta'_{\kappa}(x)$ at a point at which they are given with sufficient accuracy by (13) above, by means of the approximate formulas used by Homer Lane and referred to in § 3 above. It will be seen later, however, that Homer Lane's calculated results agree with those given in the tables.

§ 15. We can now estimate from the numbers given in § 14 the degree of probable error in the values of q and $\Theta'(q)$ found by the step-by-step process. Similar reasoning to that of § 9, by which we show that errors arising in the working out of this process do not tend to increase as the work proceeds, leads to the following results :—

The value of q (·2737) in Table I. is correct to the nearest figure, while $\Theta'_{1\cdot5}(q)$ (2·707) is less than it ought to be by about 1 in 600; the value of q (·18676) in Table II. is too high, the error being less than 1 in 3000, while $\Theta'_{2\cdot5}(q)$ (2·188) is probably too high, the true value lying close to 2·188. In Tables III. and IV. q and $\Theta'(q)$ may be taken as correct to about 1 in 200. In Table V., the final values of the Boylean Function are believed to be correct to one per cent.

Greater accuracy has been aimed at in the case $\kappa = 2\cdot5$ than in any of the other cases, owing to its theoretical importance, being applicable to stars composed of gases such as our terrestrial atmosphere. This was the case dealt with by Lord Kelvin in his 1887 paper, referred to in § 2 above. The numerical results given in that paper were obtained by an approximate process using radii of curvature calculated for successive small arcs of the curve ; and they are in satisfactory agreement with the results given in Table II.

§ 16. One important numerical result which can be derived from the values of q_κ and $\Theta'_\kappa(q)$ is the value of the ratio $\frac{\text{central density}}{\text{mean density}}$ in a nebula composed of any gas for which κ is 1·5, 2·5, 3, or 4. This ratio is given by the expression

$$\varrho = \frac{\text{central density}}{\text{mean density}} = \frac{1}{3.\Theta'_\kappa(q).q^3_\kappa}.$$

For $\kappa = 1{\cdot}5$ (monatomic gases)

$$\varrho = \frac{1}{3 \times 2{\cdot}707 \times 0{\cdot}2737^3} = 6{\cdot}006.$$

For $\kappa = 2{\cdot}5$ (diatomic gases)

$$\varrho = \frac{1}{3 \times 2{\cdot}188 \times 0{\cdot}18676^3} = 23{\cdot}39,$$

or, accurate to nearest figure,

$$\varrho = \frac{1}{3 \times 2{\cdot}188 \times 0{\cdot}18673^3} = 23{\cdot}40.$$

(For $\kappa = 2{\cdot}44$ or $k = 1{\cdot}41$, Ritter gives the value of ϱ as 23.)

For $\kappa = 3$, and $\kappa = 4$, the values of the ratio are 54·2 and 625 respectively.

For $\kappa = 5$, the ratio is infinite.

§ 17. The following table of results is given for comparison :—

	$q_{1\cdot5}$	$\Theta'_{1\cdot5}(q)$	ϱ	$q_{2\cdot5}$	$\Theta'_{2\cdot5}(q)$	ϱ
Homer Lane	·2735	2·741	5·943	·18674	2·188	23·40
See	·27368	2·7097	6·0014			
Ritter	·274	2·70	6			

§ 18. In each of Tables I. . . . V. below, the second column gives the value $1/x$, which is also the value of r when σ is unity in equations (23) and (32) of Lord Kelvin's paper. In Tables I. . . . IV., column 3 enables us to find the curve of temperature, and column 4 the curve of density, for any spherical nebula for which κ has the value, 1·5, 2·5, 3, or 4 (see equations (26) and (19) of the paper): column 5 gives the mass of gas within each sphere of radius r [see equation (51)]. In Table V., column 3 enables us to determine the density at any point in a spherical mass of ideal Boylean gas, and column 4 the mass of gas within radius r (see equations (40) and (41) of § 36).

TABLE I.

x	r	$\Theta_{1\cdot5}$	$\Theta_{1\cdot5}^{1\cdot5}$	$\Theta'_{2\cdot5}$
∞	0	1·0000	1·0000	0
40	·0250	·9999	·9998	$5{\cdot}20\times10^{-6}$
20	·0500	·9996	·9994	$4{\cdot}16\times10^{-5}$
10	·0100	·9983	·9975	$3{\cdot}33\times10^{-4}$
8	·1250	·9974	·9961	$6{\cdot}50\times10^{-4}$
6	·1667	·9954	·9931	·00154
5	·2000	·9934	·9901	·00265
4	·2500	·9896	·9844	·00511
3	·3333	·9816	·9725	·01235
2	·5000	·9590	·9391	·0402
1	1·0000	·8447	·7764	·2884
·95	1·0526	·8292	·7551	·3309
.90	1·1111	·8114	·7309	·3817
·85	1·1765	·7909	·7034	·4430
·80	1·2500	·7669	·6716	·5174
·75	1·3333	·7388	·6350	·6083
·70	1·4286	·7057	·5928	·7198
·65	1·5385	·6664	·5440	·8573
·60	1·6667	·6194	·4875	1·027
·55	1·8182	·5640	·4236	1·236
·50	2·0000	·4949	·3482	1·491
·49	2·0408	·4797	·3322	1·547
·48	2·0833	·4640	·3161	1·606
·47	2·1277	·4477	·2996	1·666
·46	2·1739	·4307	·2827	1·728
·45	2·2222	·4130	·2654	1·792
·44	2·2727	·3948	·2481	1·858
·43	2·3256	·3759	·2305	1·925
·42	2·3810	·3563	·2127	1·993
·41	2·4390	·3360	·1948	2·061
·40	2·5000	·3151	·1769	2·130
·39	2·5641	·2934	·1589	2·199
·38	2·6316	·2711	·1412	2·267
·37	2·7027	·2481	·1236	2·334
·36	2·7778	·2244	·1063	2·399
·35	2·8571	·2002	·0896	2·460
·34	2·9412	·1753	·0734	2·517
·33	3·0303	·1499	·0580	2·569
·32	3·1250	·1239	·0436	2·614
·31	3·2258	·0976	·0305	2·652
·30	3·3333	·0709	·0189	2·680
·29	3·4483	·0441	·00926	2·698
·28	3·5714	·0171	·00223	2·706
$q=$·2737	3·6536	·0000	·00000	2·707

TABLE II.

x	r	$\Theta_{2·5}$	$\Theta_{2·5}^{2·5}$	$\Theta'_{2·5}$
∞	0	1·00000	1·00000	0
100	·0160	·99998	·99994	$3·33 \times 10^{-7}$
50	·0200	·99993	·99983	$2·67 \times 10^{-6}$
25	·0400	·99973	·99933	$2·13 \times 10^{-4}$
10	·1000	·99834	·99584	·000332
8	·1250	·99740	·99351	·000659
6	·1667	·99539	·98851	·00153
5	·2000	·99337	·98350	·00264
4	·2500	·98966	·97436	·00513
3	·3333	·98174	·95496	·01201
2	·5000	·95960	·90203	·03917
1	1·0000	·85194	·66992	·26287
·98	1·0204	·84655	·65937	·27671
·96	1·0417	·84087	·64837	·29148
·94	1·0638	·83488	·63689	·30726
·92	1·0870	·82857	·62493	·32414
·90	1·1111	·82192	·61245	·34218
·88	1·1364	·81488	·59943	·36150
·86	1·1628	·80745	·58585	·38219
·84	1·1905	·79959	·57184	·40437
·82	1·2195	·79127	·55695	·42816
·80	1·2346	·78246	·54157	·45368
·78	1·2821	·77312	·52555	·48109
·76	1·3158	·76321	·50887	·51052
·74	1·3514	·75269	·49153	·54214
·72	1·3889	·74152	·47348	·57613
·70	1·4286	·72963	·45474	·61266
·68	1·4706	·71700	·43531	·65193
·66	1·5152	·70355	·41518	·69415
·64	1·5625	·68922	·39436	·73951
·62	1·6129	·67395	·37289	·78822
·60	1·6667	·65767	·35077	·84050
·58	1·7241	·64032	·32808	·89654
·56	1·7857	·62179	·30487	·95652
·54	1·8519	·60203	·28122	1·02058
·52	1·9231	·58094	·25724	1·08883
·50	2·0000	·55845	·23306	1·16130
·48	2·0833	·53447	·20883	1·23805
·46	2·1739	·50890	·18475	1·31868
·44	2·2727	·48170	·16104	1·4029
·42	2·3810	·45277	·13794	1·4903
·40	2·5000	·42206	·11573	1·5801
·38	2·6316	·38956	·09472	1·6709
·36	2·7778	·35524	·07521	1·7613
·34	2·9412	·31912	·05753	1·8493
·32	3·1250	·28129	·04197	1·9326
·30	3·3333	·24187	·02877	2·0084
·29	3·4483	·22161	·02312	2·0425
·28	3·5714	·20103	·01812	2·0736
·27	3·7037	·18015	·01377	2·1013
·26	3·8462	·15901	·01008	2·1254
·25	4·0000	·13766	·007031	2·1454
·24	4·1667	·11612	·004595	2·1613
·23	4·3478	·09444	·002741	2·1731
·22	4·5455	·07267	·001424	2·1813
·21	4·7619	·05083	·000583	2·1858
·20	5·0000	·02896	·000143	2·1876
·19	5·2632	·00708	·0000042	2·1879
$q = ·18676$	5·3545	·00000	·00000000	2·1880

TABLE III.

x	r	Θ_3	Θ_3^3	Θ'_3.
∞	0	1·0000	1·0000	0
100	·010	1·0000	1·0000	3·33 × 10^{-7}
50	·020	·9999	·9998	2·66 × 10^{-6}
25	·040	·9997	·9992	2·13 × 10^{-5}
10	·100	·9983	·9949	3·32 × 10^{-4}
5	·200	·9934	·9803	2·63 × 10^{-3}
4	·250	·9897	·9694	5·11 × 10^{-3}
3	·333	·9818	·9464	·0129
2	·500	·9598	·8842	·0386
1	1·000	·855	·625	·252
·875	1·143	·818	·547	·348
·750	1·333	·766	·450	·493
·625	1·600	·692	·331	·714
·500	2·000	·583	·198	1·046
·375	2·667	·425	·0768	1·497
·250	4·000	·209	·00913	1·922
·240	4·167	·190	·00685	1·944
·230	4·348	·170	·00495	1·963
·220	4·546	·151	·00342	1·979
·210	4·762	·131	·00224	1·993
·200	5·000	·111	·00136	2·002
·190	5·263	·0908	·000748	2·010
·180	5·556	·0707	·000353	2·014
·170	5·882	·0505	·000129	2·016
·160	6·250	·0303	·0000279	2·017
·150	6·667	·0102	·00000166	2·0175
$q=$·145	6·897	·0000	·00000000	2·0175

TABLE IV.

x	r	Θ_4	Θ_4^4	Θ'_4
∞	0	1·0000	1·0000	0
100	·010	1·0000	1·0000	3·33 × 10^{-7}
50	·020	·9999	·9997	2·66 × 10^{-6}
25	·040	·9997	·9989	2·13 × 10^{-5}
10	·100	·9983	·9934	3·32 × 10^{-4}
5	·200	·9934	·9737	2·625 × 10^{-3}
4	·250	·9897	·9595	5·070 × 10^{-3}
3	·333	·9819	·9295	1·180 × 10^{-2}
2	·500	·9603	·8505	3·780 × 10^{-2}
1	1·000	·8604	·548	·2327
·875	1·143	·8265	·467	·3157
·750	1·333	·780	·370	·437
·625	1·600	·715	·261	·615
·500	2·000	·623	·151	·872
·375	2·667	·493	·0591	1·214
·250	4·000	·318	·0102	1·582
·200	5·000	·236	·00310	1·697
·190	5·263	·219	·00230	1·715
·180	5·556	·202	·00165	1·731
·170	5·882	·184	·00115	1·746
·160	6·250	·167	·000773	1·759
·150	6·667	·149	·000494	1·770
·140	7·143	·131	·000298	1·778
·130	7·692	·114	·000166	1·785
·120	8·333	·0957	·0000837	1·790
·110	9·09	·0777	·0000358	1·793
·100	10·00	·0598	·0000128	1·795
·090	11·11	·0418	·00000306	1·796
·080	12·50	·0239	·000000325	1·797
·070	14·29	·0069	·000000002	1·797
$q=$·0667	14·99	·0000	·000000000	1·797

TABLE V.

x	r	$\Psi(x)$	$\Psi'(x)/\Psi(x)$
∞	0	1·0000	0
100	·010	·99998	$3{\cdot}33\times10^{-7}$
50	·020	·99993	$2{\cdot}67\times10^{-6}$
25	·040	·9997	$2{\cdot}13\times10^{-5}$
10	·100	·9984	·000333
5	·200	·9934	·002656
2	·500	·9597	·04065
1	1·000	·8531	·3029
·8	1·250	·7851	·5625
·6	1·667	·6649	1·204
·5	2·000	·5713	1·895
·4	2·500	·4462	3·27
·3	3·333	·2907	5·71
·25	4·000	·2076	7·91
·245	4·082	·1994	8·18
·240	4·167	·1913	8·46
·235	4·255	·1833	8·75
·230	4·348	·1753	9·06
·225	4·444	·1673	9·38
·220	4·545	·1595	9·71
·215	4·651	·1518	10·06
·210	4·762	·1443	10·42
·205	4·878	·1368	10·80
·200	5.000	·1295	11·20
·195	5·128	·1223	11·61
·190	5·263	·1153	12·04
·185	5·405	·1085	12·50
·180	5·556	·1017	12·97
·175	5·714	·0952	13·47
·170	5·882	·0889	13·99
·165	6·061	·0828	14·53
·160	6·250	·0769	15·10
·155	6·452	·0712	15·71
·150	6·667	·0657	16·34
·145	6·897	·0605	17·01
·140	7·143	·0554	17·71
·135	7·407	·0506	18·45
·130	7·692	·0461	19·23
·125	8·000	·0418	20·06
·120	8·333	·0377	20·95
·115	8·696	·0339	21·89
·110	9·091	·0303	22·88
·105	9·524	·0269	23·95
·100	10·000	·0238	25·10

II. *On the Changes of Pressure which accompany Point Discharge through Hydrogen, containing Oxygen and Nitrogen.* *By* A. P. Chattock, *Professor of Physics, and* A. M. Tyndall, *B.Sc., Lecturer in Physics, University College, Bristol* *.

THE need for the experiments described in this paper arose in connexion with an attempt upon which we have been intermittently engaged for some years, to measure the molecular complexity of the ions in point discharge through gases at normal temperature and pressure.

Our original plan was to discharge through pure hydrogen from a point against a platinum or palladium plate, in the hope that these substances might absorb the ions and hold them long enough for a measurement of the resulting pressure change to be made.

If the volume and pressure of the hydrogen are V and P, and a decrease of pressure of p is observed after discharging c coulombs, the corresponding change of volume, for P constant, is $\mathrm{V}p/\mathrm{P}=v$.

Now the volume of hydrogen given off by one coulomb in a water voltameter is 0·116 c.c. at 0° C. and 760 mm. Hence the number of complete molecules which must have been removed from the gas, or at least have ceased to exist as separate pressure-producing bodies when the charge on one monovalent ion is passed through it is

$$\frac{v}{2\times 0{\cdot}116\times c}=\mathrm{N},$$

where v is the change of volume at 0° C. and 760 mm. (The 2 comes in because a molecule of hydrogen contains two monovalent ions.)

In what follows the expression "per ion" always means "per hydrogen atom set free in a water voltameter placed in series with the discharge vessel."

Suppose now that the ions carrying the point discharge are in some way removed from the gas when they reach the electrodes. If each ion consists of a single atom of hydrogen, N will be 0·5; but if it carries with it a cluster of hydrogen atoms, N will be half the number of atoms in the cluster.

We found, as was to be expected, that the purity of the hydrogen exercised an enormous influence on the contractions observed, and therefore on the calculated values of N; quite

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* Communicated by the Authors.

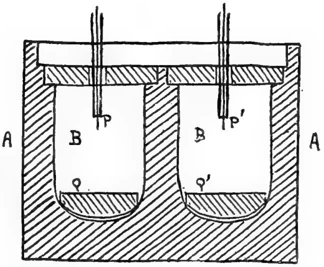
minute traces of oxygen or air sending N up to over 100 for negative discharge. But there seemed to be a lower limit to the contraction in the purest hydrogen which roughly corresponded to N=1. This was for a copper plate *.

As will be shown further on, there are reasons for thinking that this limiting value may really be due to the effect we were looking for. To be sure of this it was necessary first to make certain that impurity was not its cause; and we therefore studied in some detail the effects on p of small quantities of oxygen and nitrogen in the hydrogen. The following is a preliminary account of this work.

Method of the Experiments.

In fig. 1 is shown a section of the discharge vessel. PP′ are discharge points of the finest procurable platinum wire, sheathed in glass tubes to within a few millimetres of their extremities; QQ′ brass blocks to the flat upper surfaces of which plates of various metals could be soldered. P and P′ were not of course used at the same time.

Fig. 1.



To reduce the warming effects of the current as much as possible, the discharge vessel was formed of a block of copper AA, 10×12·5×15 cub. cms., in which were two platinum-lined cavities BB, 7·2 cm. deep and 5·0 cm. in diameter, connected respectively to opposite ends of a sensitive tilting pressure-gauge capable of indicating changes of pressure down to about 10^{-8} atmosphere †.

Heat produced in one of the cavities was thus after a short

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* With platinum and palladium plates the case is apparently complicated by the evolution of gas which, under suitable circumstances, may turn the contraction into an expansion.

† An account of this gauge is to be published shortly in connexion with a discussion of the design of instruments of this type.

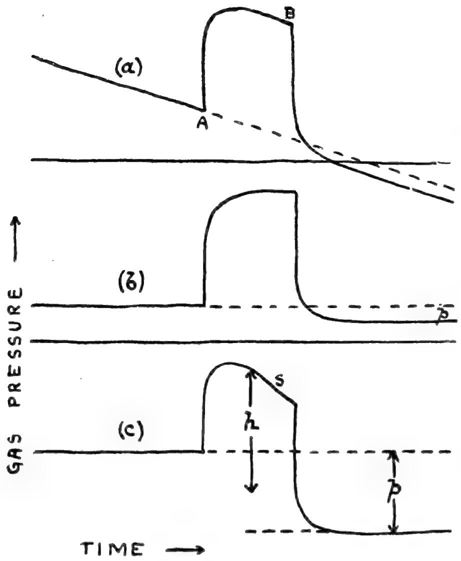
time brought to affect both ends of the gauge, and so became inoperative on the latter long before the rise of temperature it produced had vanished.

It was found that with the currents used (up to about 2·2 micro-amps.) the heating effects as indicated by the gauge were practically over in 3 or 4 minutes after stopping the discharge, for distances of about 2 cm. between point and plate. For shorter distances the time was also shorter of course. The currents were obtained from a Wimshurst, and were measured by a galvanometer between A and the earthed terminal of the machine.

Gauge and discharge vessels were shielded from external heat effects by two cardboard cases, one outside the other, double-walled, and filled with sawdust and wool—their joint thickness being about 9 inches.

The gauge contained water. To prevent water-vapour from reaching the discharge vessels each limb of the gauge was trapped with mercury. It was found, however, that water slowly worked its way past this mercury—probably by creeping between it and the glass—and small tubes of phosphorus pentoxide were therefore introduced between the gauge and the discharge vessels. These tubes were also

Curves I.



useful in absorbing the water-vapour formed during discharge; the gas having to pass through them in entering and leaving B.

The usual method of experimenting was to observe the gauge every two minutes for 8 minutes before and for about a quarter of an hour after the discharge. In Curve I *a* is given the record of a complete experiment of this kind for the purest hydrogen we were able to obtain. A is the beginning and B the end of the discharge. The greater part of the rise of pressure between A and B is seen to be temporary, and is no doubt mainly due to heat. There is also a noticeable drift of the gauge zero, which owing to the extreme sensitiveness of the gauge we were unable to avoid, and which altered in a more or less regular manner with the temperature of the room. We found that within the limits of about twenty minutes to half an hour we could depend on the change in this drift being small and uniform, but not for much longer intervals. Curve 1 *b* represents Curve 1 *a* with the drift eliminated. It shows that the discharge has brought about a small permanent lowering of the gas pressure by the amount p. Curve 1 *c* represents a similar set of readings for hydrogen containing a trace of oxygen, the drift having been again eliminated.

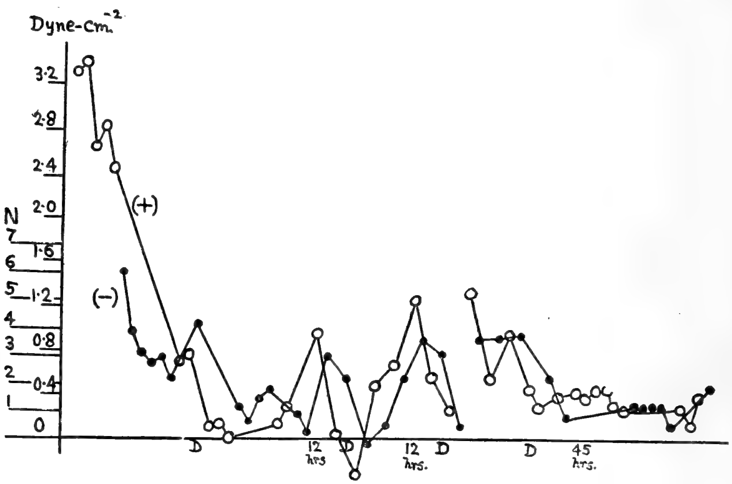
Discharge in Pure Hydrogen.

When the amount of oxygen present is above about one part by volume in a million of hydrogen, negative discharge gives higher values of p than positive. But as the hydrogen is purified below this point by continued discharge and absorption of the water-vapour formed, the values of p for positive and negative discharge, in addition to becoming very small, seem to approach equality, in the case of discharge against a copper plate.

To illustrate this we have plotted as ordinates in Curves II. the values of p for a series of two-minute discharges of 2·16 microamperes against the copper plate used in most of our work.

The exact initial amount of oxygen present in this particular case was unknown, but in the light of what follows we may put it at about 0·001 per cent. The observations are arranged horizontally in the order in which they were made. For convenience of identification the points for positive discharge (circles) and for negative (dots) are connected, each set by a separate line; but it will be understood that they were obtained, positive and negative, as they occur along the horizontal axis—not all the positives first and then all the negatives.

Curves II.



As a rule the time between each observation and the next was about a quarter of an hour, but at special points, as when a night intervened, the longer interval is given in hours by the number below. At the points marked by D a discharge of negative electricity (2 microamperes) was kept up for about half-an-hour, the corresponding values of p being unobtainable on account of the drift. The break in the curves indicates a fresh filling of the apparatus with "pure" hydrogen after pumping out sufficiently to reduce the original impurity about 80 times.

It will be seen that with the first filling a wait of some hours is always accompanied by a rise in the values of p. This is due to the diffusion into the discharge vessel of unpurified hydrogen from the space above the mercury of the pressure-gauge, connecting tubes, &c. Discharge, on the other hand, brings the values down as it should.

With the second filling the gas was so much purer to start with that these effects are almost absent.

In neither case would it be easy to say which sign of discharge gives the higher value of p, and by the end of the second curves the two signs are obviously about equally effective. The common value of p is then roughly 0·3 dyne per sq. cm., which corresponds with N = 1·1.

This residual contraction of 0·3 is a rough average of what appears to be a limit—a rather variable limit it is true—below which repeated discharges will not permanently take us. Now in all cases where contraction has been known to be due to combination of oxygen with the hydrogen, it has been recognizable by two marked characteristics. Negative electricity has produced a larger effect than positive (for small amounts of oxygen many times larger); and if the discharges have been repeated often enough the effect has ceased, presumably because the oxygen has come to an end *. Neither of these statements is true of the residual contraction, and it therefore seems unlikely that this can be due to a trace of impurity.

On the other hand, its amount is roughly proportional to the quantity of electricity passed from the point; that is to the number of ions.

For these and other reasons we are at present inclined to connect it with a temporary absorption of the ions themselves at the electrodes.

The limiting value of $N=1{\cdot}1$ means that about two atoms of hydrogen (if that is the only gas present) disappear per ion. This is consistent with the view that when the ions arrive at the electrodes it is only the single electrified atom, which may be thought of as holding the complex carrier together, that penetrates the electrode and gets absorbed; the unelectrified remainder being as it were brushed off at the surface of the metal and so rendered free to evaporate.

An examination of the pressure changes occurring after discharge is over does in fact suggest that these remainders do not at once evaporate on giving up the charged atoms; and we believe that with improved apparatus now in course of construction, we may be able indirectly to obtain the value of p corresponding to complete absorption of the ions, by observations on these after effects.

Be this as it may, it is only necessary here to show that hydrogen was obtained so pure that the changes of pressure produced in it were small compared with those due to the quantities of oxygen with which we experimented, and this will be found to have been the case. Repeated pumpings out and refillings brought down p to about the same average limiting values as did prolonged discharge; and as an addition of one volume of oxygen in about ten million of hydrogen would have perceptibly raised p it follows that, unless there is a lower limit to the quantity of oxygen with which hydrogen will combine under point discharge, our hydrogen must have contained less than 0·00001 per cent. of oxygen. The

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* See page 35.

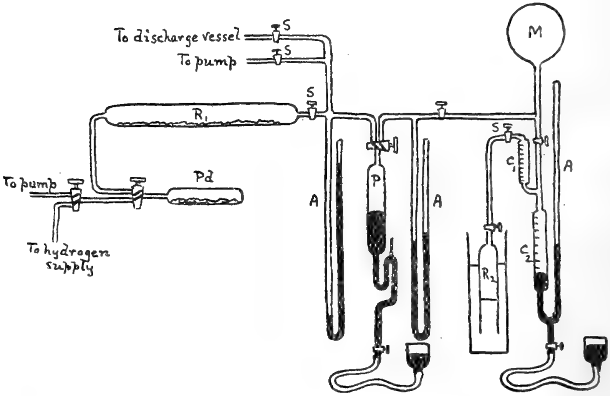
smallest percentage with which we experimented was 0·00015.

Alongside the scale of dyne-cm.$^{-2}$ in the curves is given the scale of N, calculated as already explained at the beginning of the paper. V was 233 c.c. and P was always adjusted to 75 cm. of mercury.

Method of introducing the Impurities.

Fig. 2 is a diagram of the gas apparatus. The hydrogen was obtained electrolytically from pure sulphuric acid and water; after which it was dried and absorbed by palladium black at Pd. Gas was then pumped away from the palladium until with the assistance of a little warming all impurity might be supposed to have been swept out; and the palladium vessel was connected to the receiver R_1 into which the rest of the hydrogen was passed by more vigorous heating. R_1 contained P_2O_5.

Fig. 2.



The impurity (oxygen or nitrogen) was collected in the bell-jar R_2 over sulphuric acid and introduced by way of the graduated tubes C_1C_2 into the mixing flask M (volume about 1200 c.c.).

The discharge vessels having been filled with hydrogen from R_1 to a pressure of 75 cm., this was pumped over into M by the mercury piston P. M was then warmed gently to ensure mixing and the gas pumped back again into the discharge vessels. In this way we were sure that the impurity was uniformly distributed through the hydrogen pumped over, and that calculation of the percentage present was simply a question of volumes and pressures. The pressure-gauges AAA were for measuring the latter.

Dummy experiments were of course made in which the pure hydrogen was pumped over and back before impurity was put into M; no indication that the hydrogen had been contaminated by this process could be detected when all was working properly.

The usual trouble with leaking taps was experienced. Mercury seals were used throughout to prevent air getting in, but we also used internal mercury seals in the case of the taps marked S. The plugs of these taps were hollow so that mercury could be passed into them from outside and allowed to run a short distance along the connecting tubes while the plugs were open. It was thus impossible for gas to pass the plug when closed. We also had trouble in preventing leakage between the discharge vessels and the outer air. This was finally overcome by completely immersing the copper casting in mercury.

Oxygen in Hydrogen.

The large permanent contraction that occurs when oxygen is present is roughly proportional to the current for both signs of discharge from about 2 to 9 micro-amperes. This is shown by Curves III., which were taken with hydrogen containing between 1 and 2 per cent. of oxygen.

With smaller currents negative discharge gives values of p which are too small. At 1 microampere for instance p is about 6·5 per cent. too small compared with its value for twice that current. Positive discharge does not show this discrepancy.

Similarly p is proportional, for both signs, to the duration of the current from about half a minute's interval upwards. Below this interval the time required to start the current introduces too much error for a test to be possible.

The values given in Curves III. were obtained by passing the various currents for 10 minute intervals. This happened to give time for the temperature of the gas to become steady during the last four or five minutes of the discharge; and the slope of the pressure curve in this region, when corrected for drift (S, in Curves I *c*), was therefore due to the formation of the water-vapour only.

It follows that p should be calculable from this slope (say p_1) as well as from the pressures before and after discharge (p). In Table 1 we give the ratios p/p_1 calculated from the data of Curves III.

CURVES III.

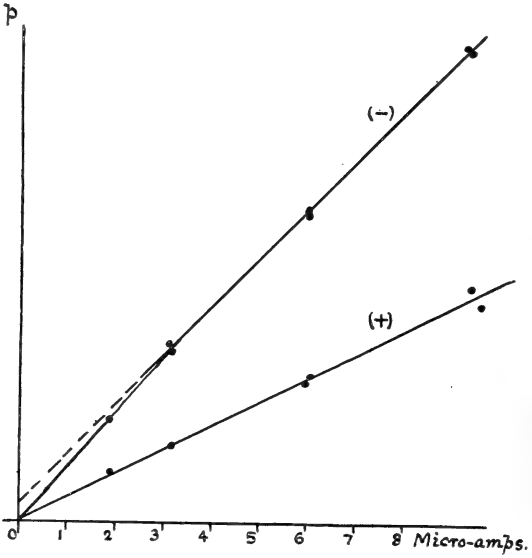


TABLE 1.

Microamperes.	p/p_1.	
	+	−
9·5	0·96	1·04
,,	1·16	1·05
6·1	1·12	1·07
,,	1·00	1·07
3·2	0·97	1·16
,,	1·09	1·03
1·9	1·34 (?)	1·11
	1·05	1·08

These ratios bring out the fact, which has since been abundantly verified, that p is greater than p_1, *i. e.* that *the contraction does not cease with the discharge*; the amount of this after effect being about 7 per cent. of the contraction during discharge, and probably the same for both signs of current.

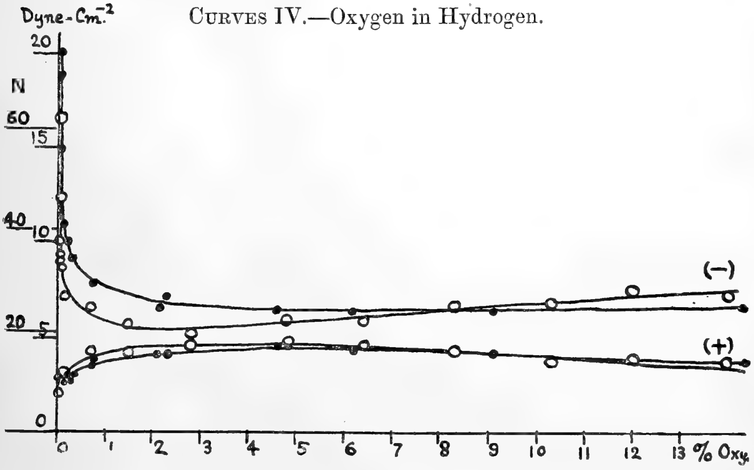
Connexion between the Percentage of Oxygen and the Contraction.

A series of various quantities of oxygen in hydrogen ranging from 0·0002 to 14 per cent. was taken and the fall of pressure, *p*, observed in each due to the passage of 2·16 micro-amperes for 2 minutes. *p* is plotted in Curves IV. with the percentage of oxygen, the points being marked by dots. The distance from point to plate was 2 cms.

It will be seen that for positive discharge through nearly pure hydrogen the gas contraction amounts to about 10 molecules per ion (N=10) and that it reaches a minimum at about 0·15 per cent. of oxygen. For negative discharge its value is about 25 molecules per ion between 14 and 2 per cent., but below this the curve rises rapidly to a high peak in the region of 0·01 per cent., corresponding to about 75 molecules per ion. (See Curves VIII. for magnified drawing of peak.) The effect of the current on the oxygen is thus far from obeying the laws of electrolysis; and this is consistent with observations of Warburg's on the effects of point discharge through oxygen and carbon dioxide.

The height of the negative peak seems to depend very much on the condition of the discharging point. After making the above observations we used the same platinum wire point for two long series in hydrogen containing nitrogen, and a third in which the nitrogen was replaced by air; and on returning to oxygen directly after these we found the height of the peak was about halved, while at the highest percentages the height of the curve had somewhat increased. With positive discharge on the other hand there was little change. This second series of oxygen observations is given in Curves IV. (circles).

Curves IV.—Oxygen in Hydrogen.



On taking out the point at the end of the above we found it coated with a light buff coloured deposit for about a millimetre up its sides, which disappeared on heating to redness.

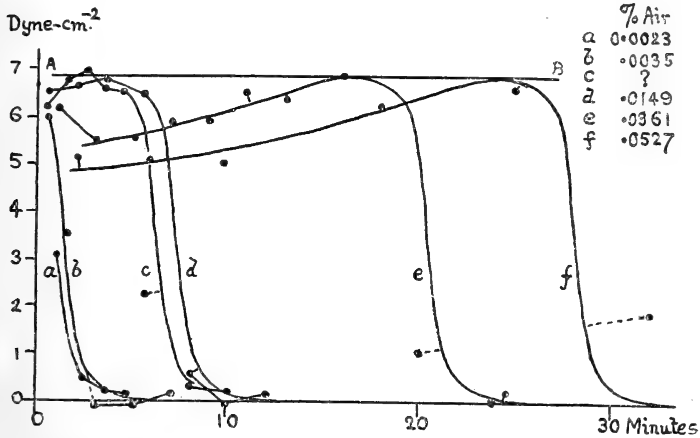
When a foreign gas like oxygen is present in any quantity in hydrogen, there is a chance of an appreciable amount of it being ionized at the discharging point along with the hydrogen itself. This may well complicate the chemical processes accompanying discharge, since not only may the hydrogen ions promote direct combination of hydrogen with oxygen, but the oxygen ions may also be responsible for a similar but independent action in a possibly different manner, to say nothing of the formation of ozone.

For this reason the most interesting, because the simplest case to consider, is that in which only a very small percentage of oxygen is present, and this is the case we have chiefly studied.

When the amount of oxygen present is small—say under 0·01 per cent.—it is possible at a single sitting by repeated discharges to reach a point where further discharges produce only the small residual contractions observed in "pure" hydrogen. This point is a very definite one. For some time before it is reached, the contraction per coulomb is nearly constant, but the drop to the smaller value occurs quite suddenly when it comes. We have determined the position of this drop for small percentages of both air and oxygen in hydrogen, with both positive and negative discharge. In all cases, the same character of curve was obtained on plotting the contraction per coulomb with the coulombs discharged. The nearly level top and the sudden drop were always marked features; the curves for air and for oxygen were practically indistinguishable, and except for the fact that negative discharge promotes combination more rapidly than positive, the same applies to the curves for the two signs of current. In illustration we give in Curves V. the results for negative discharge in air. The curves were constructed as follows—the axis of abscissæ was divided up into a series of spans representing the times in minutes the current (1·08 micro-amp.) was passed in successive discharges, and at the centre of each span was erected an ordinate giving the change of pressure produced by 1·08 micro-ampere flowing for one minute. The area of the figure thus gives the total change of pressure which occurs before the drop is reached. It will be noticed that the curves are not always the best which could be swept through the experimental points. The curves drawn were as a matter of fact obtained as explained on

p. 37, and are so nearly coincident with the points that it did not seem necessary to complicate the figure with a second set.

Curves V.—Air in Hydrogen.



The question whether this sudden drop in the contraction curve means that the whole of the oxygen has been transformed into water-vapour naturally arises here. We have not yet had the opportunity of obtaining the data necessary for a complete answer, as it involves greater modification of the apparatus than we are at present in a position to carry out, but the following arguments show that the quantity of uncombined oxygen present when the drop is reached is at most 10 per cent. of what was originally mixed with the hydrogen, and probably less.

There is nothing *à priori* impossible in the idea that practically the whole of the oxygen may enter into combination with the hydrogen, for Nernst * has shown that the equilibrium pressure of oxygen in a mixture of that gas with hydrogen and water-vapour is vanishingly small at ordinary temperatures. At the same time an agent like discharge does not necessarily result in the same equilibrium pressures as heat. Collie † has obtained measurements of true equilibrium pressures in the case of CO, O_2, and CO_2 which are quite different to the values given by Nernst for these substances. Collie worked at pressures of a few millimetres, and found that about 70 per cent. of his CO_2 had been dissociated on reaching the equilibrium point. Also Noda and Warburg ‡,

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* Nernst, *Zeit. Phys. Chem.* lvi. p. 534.

† Collie, Journ. Chem. Soc. 1901, p. 1063.

‡ Noda & Warburg, Drude's *Annalen*, xix. p. 1.

using point discharge in CO_2 at atmospheric pressure, under conditions which were therefore much more nearly comparable with ours, found that at least 3 per cent. of the CO_2 could be dissociated, and that at this point marked re-association was occurring.

In order therefore to prove that the drop in our curves corresponds with an equilibrium point for which the pressure of the oxygen is small, it is necessary to show that discharge through hydrogen containing water-vapour only does not result in much dissociation of the latter. This is the point we have not yet been able to test directly, but some light is obtainable on it by an examination of Curves V.

The water-vapour formed in the discharge vessel accumulates there, as it has to diffuse through about 18 inches of narrow quill-tubing before reaching the P_2O_5—a process which must require many hours. Hence the drop following upon the clearing out of a large percentage of oxygen occurs in the presence of more water-vapour than that following a small percentage. It will be noticed, however, that in every case where the level part of the curve is able to form, the experimental points rise to the same high value just before dropping. The horizontal line AB makes this clear *.

Now if we may take this as an indication that the same amount of oxygen is present in every case just before the drop, it will follow either that the drop is not an equilibrium point at all, or else that when it is reached the amount of oxygen has become very small; otherwise it will be impossible for the small amount of subsequent combination indicated by the later contractions to bring about equilibrium between the equal amounts of oxygen and the very unequal amounts of water-vapour in the hydrogen.

Curves V. may be regarded from a second point of view. They are so nearly level up to the drop that equal distances along the time axis mean nearly equal amounts of oxygen removed. In other words, the abscissæ up to, but not much beyond the drop, give percentages of oxygen (proportionally) to within a constant when measured from right to left. The drop curves are in fact approximately the peak plotted backwards.

In Curves VIII. (second air) is given a magnified drawing of the peak obtained for the same conditions as Curves V., except that the gas was dry and the current was larger. On the assumption that practically the whole of the oxygen is gone when the drop is reached, we have constructed a curve from

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* Curve *f*, it is true, does not rise quite so high as as the others, but this is doubtless because the discharges in this case were kept on for so many minutes that the last reading is the average of the highest with lower parts of the curve, and is therefore too low.

this peak which gives the shape Curves V. should take if the water-vapour is without effect upon them. (In constructing it account was taken of the fact that the scale of minutes is not strictly a scale of percentages, and the ordinates were reduced to correspond with a current of 1·08 microamp.)

To distinguish between the tops of *c* and *d* their points are there joined by straight lines, but everywhere else in Curves V. this constructed curve is drawn so as best to fit the points. Near the lower end of the steep part the latter are irregular as they are apt to be in that region; but the agreement is in the main good. It shows that Curves V. and VIII. are different expressions of practically the same phenomenon, though V. are for wet and VIII. for dry gas.

Now the end of the constructed curve necessarily corresponds with the absence of any added impurity, and the steep part is virtually the end. In Curves V. *c*,*d*,*e* this part is a little to the right of the lower points, suggesting that the drop has occurred before the end of the oxygen was reached; but in curve *f* it is to the left. Even if we regard the position of *f* as due to error, which there is no particular reason for doing, the other three curves indicate that not more than about 10 per cent. of the oxygen was left uncombined at the drop; and taking *f* into account makes the amount still smaller.

There is a third way in which Curves V. throw light on this matter. It is possible to obtain from them a direct comparison of the volume, v_0, of impurity originally put into the discharge vessel with the total contraction, v, measured up to the drop.

The results of this comparison for oxygen are given in Table 2. P is the percentage of oxygen (by volume)

TABLE 2.

+ Discharge.		− Discharge.	
P.	v/v_0.	P.	v/v_0.
0·00037	3·2	0·00016	2·7
·0010	2·8	·00054	3·2
·0027	2·3	·0026	2·7
·0074	2·6	·0035	3·0
		·0057	2·8
	2·7		2·9

originally in the hydrogen ; the volume of the oxygen being of course measured at the same temperature and pressure as the hydrogen with which it was afterwards mixed. The volume of the discharge vessel alone (136 c.c.) was used in calculating v_0 as the oxygen in the space above the gauge was not affected.

The mean value of v/v_0 is thus 2·8 ; and this agrees with another value, 2·7, obtained from air, on the assumption that the oxygen alone combines with the hydrogen in this case (for justification of this see below).

For both air and oxygen the ratio is a little larger for negative than for positive discharge, but the agreement between the individual values is not good enough to warrant the conclusion that this difference is real.

Now, as already explained, the water-vapour formed may be taken as having remained in the discharge vessel during the quarter of an hour of the discharge and subsequent drift readings ; and this means that if the combination occurring was that of gaseous hydrogen and oxygen the value of v/v_0 should be not greater than 1, even if the whole of the oxygen combined.

The discrepancy seems to us to be connected with the position of the combination region. On this head we hope to have more to say in a later paper, but some evidence has already been obtained which points to a gas film on the surface of the electrode as the seat of at least a large part of the chemical action. If this turns out to be correct, it may well happen that the water-vapour formed gets entangled in the film for so long that when it does evaporate the change of pressure is reckoned in with the general drift of the pressure-gauge and does not appear in p. This would of course result in the value 3 for v/v_0 if no oxygen is left uncombined at the drop. If 10 per cent. is left uncombined the ratio should be 2·7, and this is almost exactly the mean value of all the oxygen and air determinations *.

The interpretation of the ratio found is almost sure to be interesting, and light would probably be thrown on it if we could get its value for much higher percentages of oxygen ; but the labour would be too great to face with the present apparatus. To clear out 5 per cent. would take about 500 hours. With a discharge vessel one-fiftieth the present size large percentages could be used, and with these, as well as

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* Hydrogen in contact with phosphorus pentoxide contains about 0·00002 per cent. by weight of the latter (Morley, J. Am. Chem. Soc. xxvi.), but this is far too small a quantity to account for the high ratio by combining with the water-vapour formed.

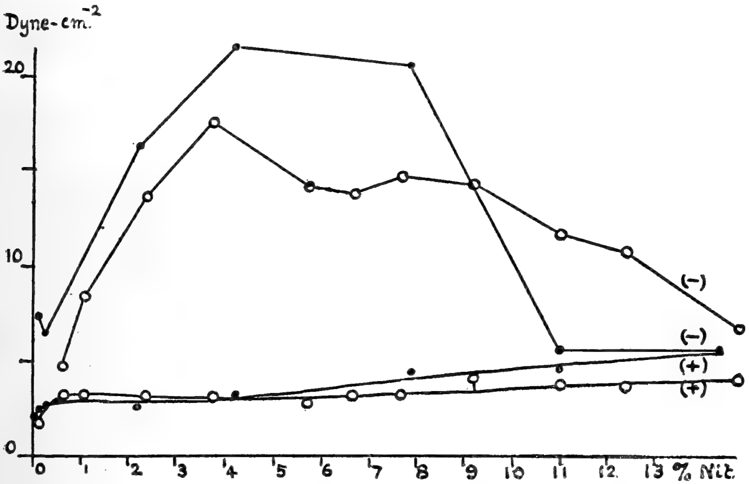
with much longer periods of discharge, the new apparatus will enable us to work.

Nitrogen in Hydrogen.

In Curves VI. (dots) are given the results of the first nitrogen series referred to above. It followed directly upon the first oxygen series, the platinum point having been left untouched in order that the geometrical conditions might be identical in the two cases.

The nitrogen was made from urea, and after bubbling through caustic potash and strong sulphuric acid was collected over the latter.

Curves VI.—Nitrogen in Hydrogen.



It has been shown by de Hemptinne * that point discharge through hydrogen and nitrogen mixed in combining proportions at a pressure of 4 cm. results in the formation of ammonia. Now ammonia formed from gaseous hydrogen and nitrogen involves a greater gas contraction per atom of hydrogen than does water-vapour from hydrogen and oxygen. For this reason, in preparing the apparatus for the first set of experiments with nitrogen, we contented ourselves with pumping out and refilling with pure hydrogen until the amount of oxygen left from the previous set was several times less than the smallest amount (0·001 per cent.) of nitrogen we intended using. It did not seem worth while

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* *Zeit. f. Phys. Chem.* xlvi. p. 13 (1903).

doing more for what were to be trial readings only, and this turns out to have been fortunate.

For examination of the nitrogen curves suggests somewhat unexpectedly that the effects observed were due not so much to the nitrogen as to the trace of oxygen still present; at any rate in the case of the lower percentages.

It will be seen that the positive curve starts at practically the same point as that for oxygen, and that the negative rises to a peak which is about as high as the oxygen peak. It is true the nitrogen peak is much more spread out along the scale of percentages, but that is of course because the *nitrogen* percentages are plotted. We have only to suppose that the nitrogen contains between 0·1 and 0·2 per cent. of oxygen to make the two peaks correspond.

Another fact which supports the oxygen theory is the ease with which we were able to clear out the active impurity. At a rate of discharge which would have required many weeks to clear out 2 per cent. of oxygen, we were able in a few hours to reduce the same percentage of nitrogen to inactivity.

On this assumption—that the contractions observed when nitrogen is the impurity are really due to traces of oxygen—we have calculated the amount of this oxygen which must have been present; expressing it as a percentage of the nitrogen, and using of course the ratio 2·8 of Table 2.

The only percentages for which the discharge happens to have been continued to the drop are the first five; and these are given in Table 3, along with the amount of oxygen calculated.

TABLE 3.

Percentage of Nitrogen.	Percentage of Oxygen in the Nitrogen.
0·0014	8·5
·010	1·1
·075	·77
·206	·40
2·22	·17

These numbers not only indicate the exhausting of a limited supply of the active agent, whatever it is, but they clearly tend towards the particular percentage (between 0·1 and 0·2) which brings the peak to the right place to correspond with the oxygen peak.

In Curves VI. (circles) are given the results of a second nitrogen series, taken directly after the first. For this the apparatus was alternately pumped out and filled with "pure" hydrogen until the nitrogen left from the first series was reduced several thousand times, and the oxygen in it probably more than a million times. The negative curve now shows signs of the fall in the height of the peak which we mentioned above, and it is impossible to say where the peak ends. We therefore cannot use the position of the peak to find the percentage of oxygen present as before. But in Table 4 is given a set of percentages worked out similarly to those in Table 3.

TABLE 4.

Percentage of Nitrogen.	Percentage of Oxygen in the Nitrogen.
0·006	?
·016	?
·065	·18
·125	·12
·62	·12
1·05	·14

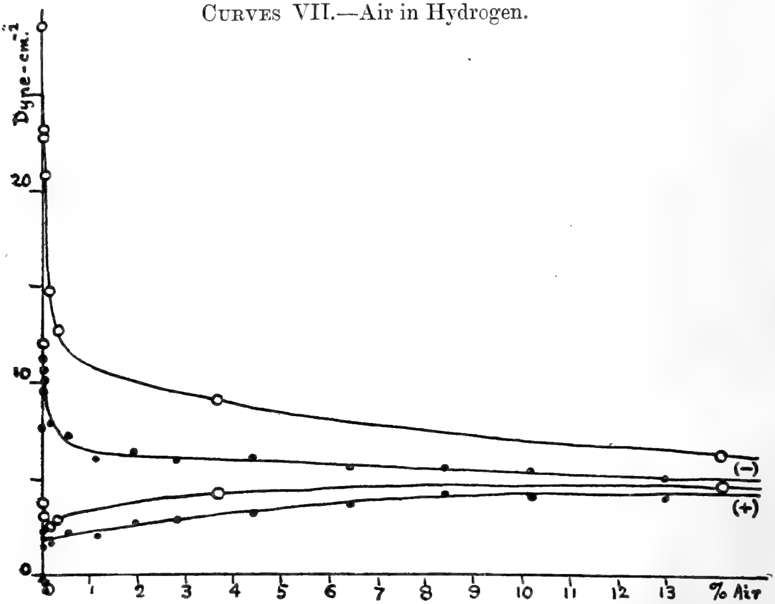
Here the first two nitrogen percentages, though larger than those in Table 3, gave values of p which were too small to rely on, and the 0·18 of the third is also rather uncertain for the same reason. There can, however, be little question that we are here dealing with quantities of impurity which bear a constant proportion to the nitrogen present with them, and which were, therefore, doubtless to be found in that nitrogen before it entered the discharge vessel.

The initial charge of oxygen, indicated by Table 3, is no longer present, but the fact that the numbers in Table 4 correspond to the limiting value of those in Table 3, and that this limiting value brings the first peak to the point which corresponds with oxygen, renders it extremely probable that in Table 4 we are also dealing with oxygen, introduced in the nitrogen.

Air in Hydrogen.

It was interesting to apply the same argument to the air series (Curves VII. dots) which was taken directly after the second nitrogen series, as the amount of oxygen present was there known.

CURVES VII.—Air in Hydrogen.



Only two percentages happen to have been taken up to the drop, and of these only the second (0·006 per cent. of air) is reliable. Calculating from this the percentage of oxygen present in the air, we obtain 17.

A second set of air discharges (Curves VII. circles) was taken after the point had been cleaned by heating to bright redness, and from this the numbers in Table 5 were calculated.

TABLE 5.

+ Discharge.		− Discharge.	
P.	P′.	P.	P′.
0·0023	20	0·0035	19
·0079	18	·0149	19
·0139	17 ?	·0361	21
		·0527	21

P is the percentage of air in the hydrogen, P′ that of oxygen in the air, calculated as in Tables 3 and 4. If we neglect the third positive determination for which the value of P is somewhat doubtful, the mean of the values of P′ comes to 20 ; this is satisfactorily close to the true value 21. Altogether it seems safe to conclude that when small quantities of oxygen and nitrogen are mixed with hydrogen at atmospheric pressure, it is the oxygen only with which the hydrogen combines.

Table 5 ends at 0·05 per cent. of air. It is, however, probable that up to 14 per cent. the oxygen alone is active ; at any rate when the nitrogen is not present in enormous excess.

In Table 6 are given the contractions observed in air at four higher percentages with the cleaned point ; and in parallel columns the contractions in oxygen at percentages one-fifth of each of these four, taken from the first set of observations on oxygen ; *i. e.* before the point became dirty.

TABLE 6.

Percentage of Air in Hydrogen.	+ Discharge.		− Discharge.		Percentage of Oxygen in Hydrogen.
	Air.	O_2.	Air.	O_2.	
0·19	0·60	0·59	3·43	3·48	0·038
0·32	0·64	0·61	2·96	3·05	0·064
3·7	0·97	0·83	2·09	1·84	0·74
14·2	1·08	0·97	1·45	1·66	2·84

The agreement is sufficiently close to render it probable that we are still dealing mainly with the oxygen in the air.

The position of the peak on the other hand is no longer a guide, as its shape has changed since heating the point. The effect on it of the condition of the point is very interesting, and we have plotted in Curves VIII. the shapes of the various peaks we have obtained, with the percentages of *oxygen* corresponding, to illustrate this.

The highest and sharpest peak is that taken in air directly after heating the point and when the latter was therefore at its cleanest ; then comes that for the first oxygen set, lower at the peak itself, but coinciding beyond about 0·01 per cent. ; and below that again the first air and the second oxygen sets taken with the point quite dirty. Each of these shows a tendency to peak formation at the lowest percentages, which vanishes further on as though it were overpowered by some opposing tendency.

We have also plotted (crosses) the curves for the two nitrogen sets, the first being dotted in for clearness. Table 3 gives for the first series the amount of oxygen present in the nitrogen up to 2·22 per cent. of the latter, and beyond that we have assumed it to bear a constant proportion to the nitrogen of 1 : 600. For the second series Table 4 shows the proportion to be constant at 1 : 770 about.

The first nitrogen curve starts with what looks like an intention of coinciding with the first oxygen curve. After two high readings, however, it falls suddenly to a low level and stays there; and it is after this fall that the peak does not again reach a high value in any subsequent curve until the heating of the point. Some permanent change in the conditions seems to have occurred—possibly connected with the large amounts of nitrogen now present (10 per cent. to 14 per cent.).

But the beginnings of the curves do not seem to have been much affected. All the five curves taken before heating the point start off along practically the same line; so that for the lowest percentages—up to about 0·003 per cent.—the condition of the point had little influence on the values of p.

The ends of the nitrogen curves are low. They are also steep, and do not seem inclined to follow the directions of the other low curves. These facts may perhaps also be attributable to the quantity of nitrogen present. It seems desirable to repeat and extend these observations with much purer nitrogen.

After the point was heated to bright redness, at which temperature it was kept for several minutes, the contractions went back to their old values for oxygen above about 0·01 per cent., but below that percentage they were completely changed.

Curves VIII. show clearly the sharpening and raising of the peak that has occurred. The curves for positive discharge too, which had so far been practically level up to percentages well above 0·06, now showed a definite tendency to form a minute peak at about 0·0005 per cent.

Heating Effect of the Discharge.

It has been shown * that when gas is blown against a plate by discharge from a point opposite, the wind produced

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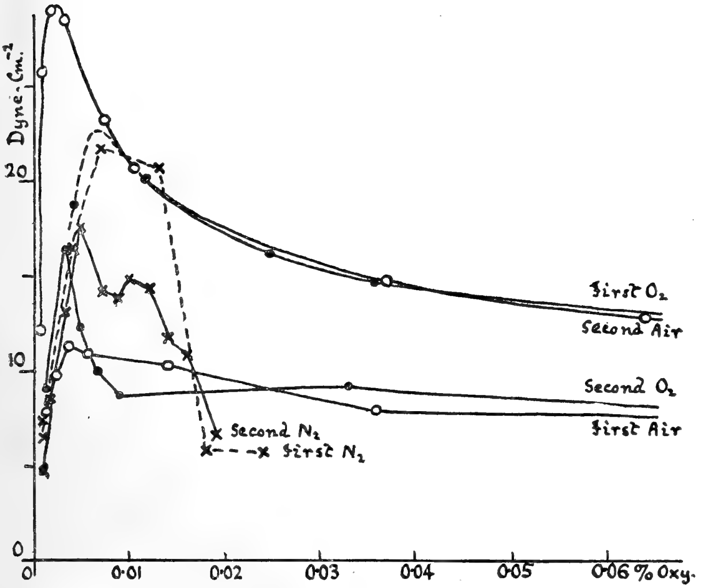
* Chattock, Phil. Mag. vol. v. p. 48 (1899); vol. vi. p. 1 (1901).

depends only on the current from the point and the specific velocities of the ions, for given geometrical conditions.



Curves VIII.—Negative Peak.

The greater the wind the more rapidly will the gas be cooled by the plate, if, as in our case, the plate is in thermal contact with a large mass of metal; and this will mean that the temporary expansion during discharge will be less, other things equal. It follows that changes in the amount of this expansion per watt will indicate changes in the specific velocities, and therefore in the sizes of the ions, if the expansion is dependent only on the temperature of the gas; large expansions implying small ions and *vice versa*.

Of course the expansion is not a certain guide to ionic dimensions as heat may not be its only cause; and the fact that in pure hydrogen with a clean point the expansion per watt is more than 100 per cent. greater for negative than for positive discharge, seems to show that the smaller size of the negative ions is not responsible for the whole of the difference between the expansions for positive and negative.

In Table 7 are given numbers which are proportional to the expansions per watt during discharge in the first set of oxygen observations; *h* being the difference between the reading of the pressure-gauge at the middle of the two minutes' discharge and the mean of the readings before and after the discharge (see Curve I. *c*).

TABLE 7.

Percentage of Oxygen in Hydrogen.	h/watts.	
	+ Discharge.	− Discharge.
0·0	5	12
·00016	6	13
·00075	6	12
·0040	6	15
·012	6	14
·025	6	9
·036	6	7
·10	5	8
·11	6	9
·15	6	8
·22	7	9
·72	6	6
2·2	7	9
2·3	6	7
4·6	6	6
6·2	7	8
9·1	7	8
14·1	7	8

It will be seen that above 0·012 per cent.—that is just where the negative peak is falling—the values for negative discharge are also falling rapidly towards a constant value. For positive discharge the values are practically constant throughout.

If we may take this as indicating that the fall of the peak is accompanied by an increase in the size of the negative ions, the conclusion receives support from an observation of Warburg's* that minute traces of oxygen added to hydrogen or nitrogen largely diminish the current from a negative point at a fixed potential, and only slightly diminish that from a positive point.

Warburg unfortunately did not work with known amounts of oxygen, so that we cannot be sure that our peak region corresponds with the region in which he observed the fall of conductivity. But the potential measurements seem to show that the two regions are the same; and if so our values of h

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* Drude's *Annalen*, ii. p. 295.

make it likely that some part of the effect of oxygen on the conductivity is due to an increase in the sizes of the ions, as Warburg himself thought possible. It will be interesting to test this by direct measurement of the ionic velocities; our new apparatus will we hope enable us to do so.

Summary of Results.

1. Oxygen present in hydrogen at atmospheric pressure and subjected to point discharge, combines with the hydrogen at the rate of about 16 molecules of oxygen per ion for positive and 25 molecules for negative between the percentages 2 and 14 by volume for the particular point used.

2. Below 2 per cent. the combination for negative rises rapidly until it may reach as many as 110 molecules per ion below 0·01 per cent.

3. Below 0·2 per cent. of oxygen the combination for positive is about constant, and roughly equal to 10 molecules per ion.

4. There is evidence that at least 90 per cent. of the oxygen can be caused to combine with the hydrogen by point discharge.

5. The presence of one part of oxygen and upwards in ten million of hydrogen can be detected and roughly measured by the methods here described.

6. The maximum contraction producible is about 2·8 times greater than the volume of the oxygen present when the water-vapour is allowed to remain in the discharge vessel.

7. When nitrogen is present with oxygen in hydrogen, even in enormous excess, the combination that occurs is mainly, and perhaps wholly, between the oxygen and the hydrogen.

8. About 7 per cent. of the contraction occurs after the discharge has ceased.

9. There is evidence which suggests that the addition of oxygen above 0·01 per cent. increases the size of the negative ions; while its effect on the positive ions is inappreciable.

10. In pure hydrogen the contraction corresponds to about 1 molecule per ion.

III. *Discharge from an Electrified Point and the Nature of the Discharge occurring through very small Distances.* *By* ROBERT F. EARHART *.

[Plate I.]

Discharge between Point and Plane.

WHEN an electrified point, such as a needle-point, is separated from a plane of opposite electrification, a discharge will occur if the potential-difference between point and plane be sufficient. In case the point is positively electrified, the potential-difference required for discharge will be greater than if the point were negatively electrified. This fact has long been known.

A series of measurements by Tamm is quoted by J. J. Thomson in 'Conduction of Electricity through Gases,' p. 499, 2nd Edition. The results there recorded for air at atmospheric pressure give a minimum potential of 2140 volts for a negative point and a value of 3760 for a positively electrified point. This potential-difference, however, is the minimum potential required to cause a perceptible leak between a point and a plane several centimetres removed: in other words, the least potential-difference required for the particular distance shown, not necessarily the least potential that will produce a discharge if the distance separating the electrodes be decreased. Recent experiments have shown that there is a minimum value for potentials required to produce an ionization of air or other gas between the electrodes, due to the field itself as the ionizing agent. This might be called the least ionizing potential. Its value for air has been determined by several observers as 350 volts.

A discharge for potential-difference less than 350 volts may be obtained if the distance between the electrodes is very minute. Such discharge at these abnormally small distances is probably not due to an ionization of gas between the electrodes, but possibly to corpuscles shot off from the electrodes. The object of this investigation is to measure the potential-difference required to cause a spark to pass between a point and plane under certain specified conditions, and to make measurements of distance to include the region where the projected corpuscles are supposed to carry the discharge; also to examine the nature of this discharge.

Measurements made by the author some years ago (Phil. Mag. [6] i. p. 147, 1901), indicate that for distances less than three wave-lengths of sodium light a discharge between a curved electrode and a plane may take place with a

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* Communicated by the Author.

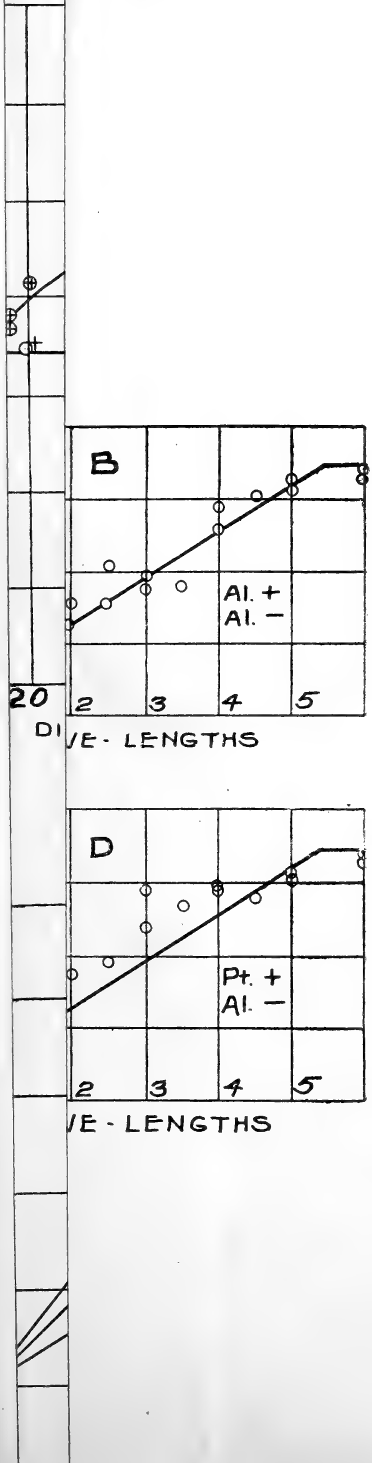

20
DI
/E - LENGTHS
B
Al. +
Al. −
2
3
4
5
/E - LENGTHS
D
Pt. +
Al. −
2
3
4
5
/E - LENGTHS

Fig. 1.

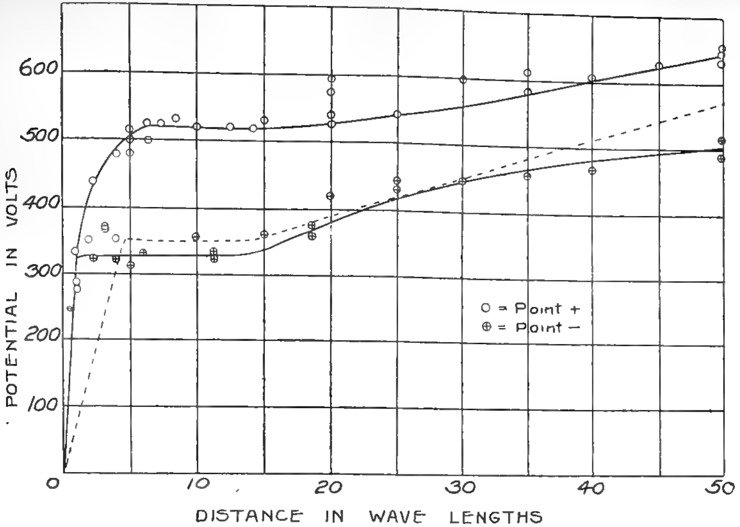


Fig. 2.

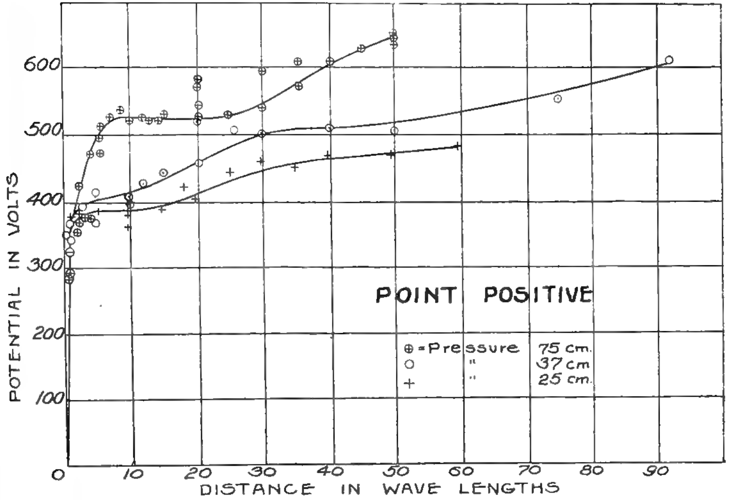


Fig. 3.

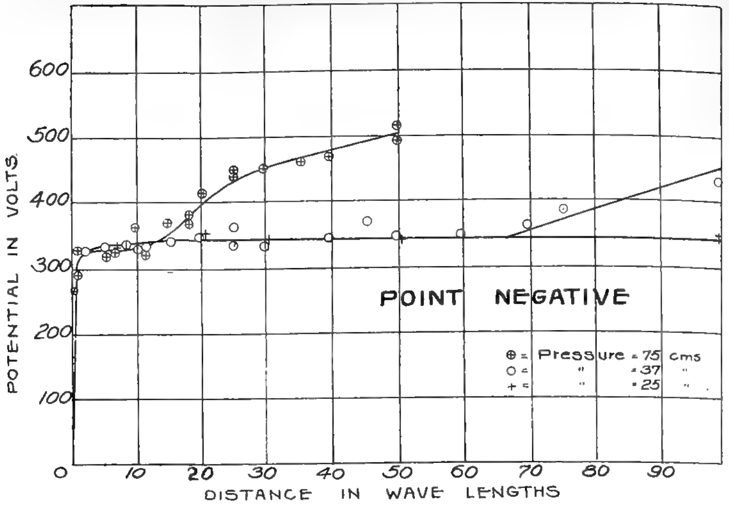
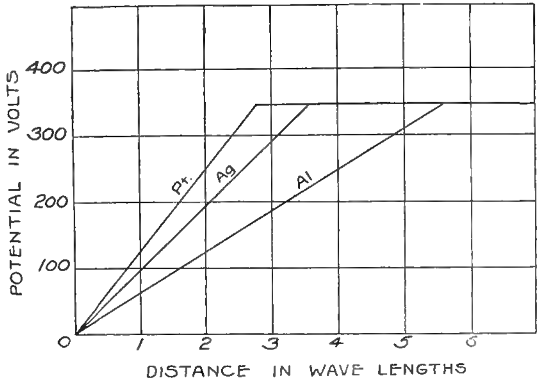
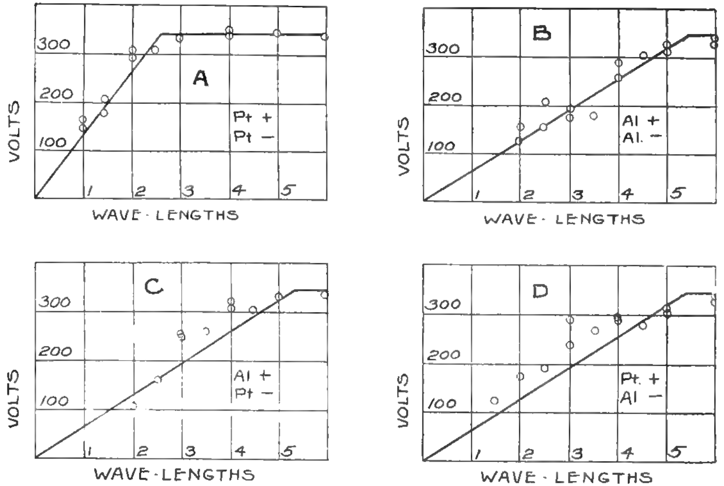


Fig. 4.



Figs. 5 A, B, C, D.



potential-difference which is not sufficient to produce an ionization of the gas. Measurements made by Kinsley (Phil. Mag. [6] ix, p. 692, 1905), Hobbs (Phil. Mag. [6] x. p. 617, 1905), and others give approximately the same result. The values obtained by Hobbs indicate that the distance through which this corpuscular discharge occurs varies with the character of the metal electrode. This will be referred to later.

The measurements made by Tamm (*Annalen der Physik*, 1901, no. 10, p. 259) were those of a potential-difference obtained by operating a static machine. This is an advantage in so far as a fine point may be used for successive discharges. Sparks of this kind do not involve much energy, and the point is but slightly modified by the passage of a single spark.

I proposed in this experiment to use a bank of storage-cells as a source of E.M.F. and to measure potential-differences by means of a Weston voltmeter placed across the spark-gap. A discharge from a needle-point under such conditions represents a much greater flow of electrical energy, and the point is damaged to such an extent as to make a new one necessary.

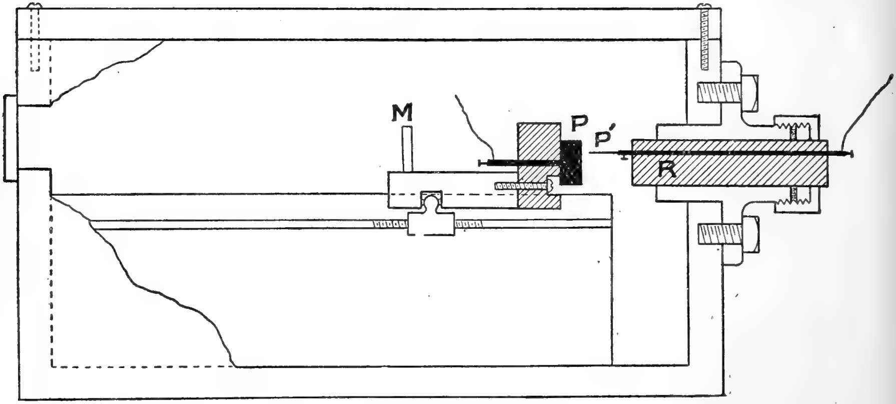
A series of preliminary measurements between point and plane were made with an alternate current source, which indicated that with a proper selection of points consistent results could be obtained. This preliminary report was made before Section B of the A. A. A. S. at the Ithaca meeting during the summer of 1906.

There are two objections to such a source of potential-difference :—(1) The polarity of the point is unknown when discharge occurs. (2) Higher harmonics may be present in the potential curve. Discharge would then occur at a potential corresponding to the peak of the curve, and the square root of mean square value, as given by the voltmeter, could not be depended upon to indicate the correct value at which discharge occurred. A suitable storage battery will at least obviate such difficulties.

The points used in this investigation consisted of No. 10 Sharp needles. A large number were examined by means of a microscope, and one which appeared as representing a fair average was selected as a master needle. Other needles were then examined by means of the microscope and were matched against the master needle.

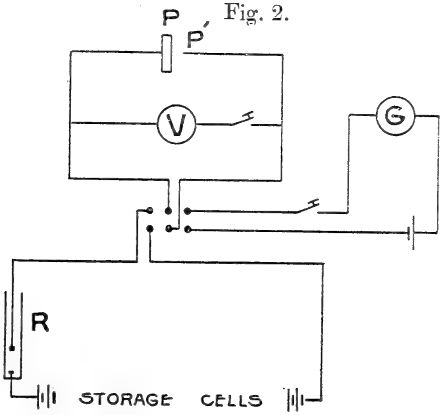
Fig. 1 indicates the manner of supporting the needle and the means used to set it against the plane. The plane consisted of a steel disk 2·54 cm. in diameter, this was ground plane but not polished. The plane P was mounted on and suitably insulated from the movable carriage of a Michelson interferometer. This carriage supports the mirror M.

Fig. 1.



The interferometer was enclosed in a heavy iron box, and was securely fastened to it so as mechanically to form part of the same. The rod in which the needle was secured by means of a set screw was $\frac{1}{16}$ of an inch in diameter. This rod passed through a cylinder of hard rubber (R). The metal rod passed through the insulating cylinder $\frac{3}{8}$ of an inch from the centre. The manner of attaching the rubber insulator and rod to the box is indicated in the figure. It was necessary to withdraw this system after a spark-discharge in order to introduce a new needle. By orienting the insulating cylinder a new needle could thus be brought to bear on a portion of the plane which had been undisturbed by the previous discharge. The motion of the interferometer carriage and plane was controlled by the usual screw motion. This was operated through a stuffing-box not shown in the figure. Suitable openings for admitting dry and dust-free air were provided. The electrical arrangement is shown in fig. 2. Here P and P′ represent the electrodes. A double-pole double-throw switch made it possible to connect these in a circuit containing a galvanometer (G) and a small e.m.f. The usual procedure was to move the plane against the point and determine the position of contact by testing with this circuit as the plane was pulled off. No difficulty was experienced in securing a definite and positive zero setting. The plane was then moved forward the desired distance, this distance being measured in terms of wave-lengths of sodium light. The double-throw switch was then thrown over, and the surfaces made part of the circuit containing the storage-cells and liquid resistance R. A Weston voltmeter, together with a suitable multiplier placed in parallel with the spark-gap, served to indicate the potential-difference of the terminals.

Fig. 2.



Dry dust-free air was the only dielectric used. Measurements were made at three pressures for point positive. Similar measurements for negative points were made at the same pressures. Very favourable temperature conditions prevailed during the entire progress of the work. The usual temperature was 21° C. No variations exceeding 1·5° above or below this temperature were noted.

Tables I. to VI. inclusive give the results obtained. These are represented graphically in Pl. I. figs. 1, 2, and 3.

Table I.—Air 75 cm. Pressure.
Point +.

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.	Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
1	282	10	517
1	292	12·5	517
1	329	14	517
2	354	15	526
2·5	432	20	545
3	361	20	587
3	366	20	598
4	354	20	526
4	488	25	531
5	517	25	532
5	499	30	599
5	470	35	583
7	499	35	610
7	526	40	604
7·5	526	45	637
8	540	50	658
10	516	50	640
10	517	50	650

Table II.—Air 37 cm. Pressure.
Point +.

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.	Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
1	347	15	446
1	376	20	526
3	395	20	456
5	364	25	517
5	426	30	503
10	409	40	508
10	395	50	503
12	428	75	564
15	446	92	611

Table III.—Air 25 cm. Pressure.
Point +.

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.	Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
1	376	20	409
2·5	385	20	423
2·5	390	25	446
5	390	30	461
10	351	35	456
10	395	40	475
10	381	45	475
15	395	50	488

Table IV.—Air 75 cm. pressure.
Point −

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.	Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
0·5	268	18	376
1	329	20	423
1	338	25	437
2·5	329	25	446
4	329	30	451
5	319	35	460
12	338	40	471
12	329	50	494
15	376	50	517
18	385		

TABLE V.—Air 37 cm. pressure.
Point −

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.	Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
1	338	30	338
3	338	35	338
5	338	40	347
10	338	45	380
10	338	50	343
15	347	60	344
20	357	70	357
25	371	75	381
25	338	100	423

TABLE VI.—Air 25 cm. pressure.
Point −

Distances in wave-lengths Na light.	Least P.D. required for discharge. Volts.
1	343
5	343
10	338
20	343
30	338
40	338
50	338
100	347
100	338

Pl. I. fig. 1 represents the results obtained with air at atmospheric pressure. Reading for a positive point is indicated by a circle and for negative by a cross within a circle ⊕. The dotted curve shows the potential-difference required for a spark to pass between a plane and a sphere, the sphere having dimensions large compared with the distances separating the surfaces. The data for this curve are taken from an article published some years ago by the author (Phil. Mag., Jan. 1901, p. 147).

Pl. I. fig. 2 represents values obtained for point positive under pressures of 75 cm., 37 cm., and 25 cm.

Pl. I. fig. 3 in a similar manner, indicates the values when the point was negative.

When discharge occurred there was evidence of a much higher temperature existing at the point when the point was negative than for point positive. For distances corresponding to the flat portion of the curve parallel to the axis of abscissæ, there was a fusion of the point provided it had been negative. A microscopic examination of a negatively discharged point showed that it had been fused down very much in the shape of a mushroom with the convex side towards the plane. Under similar conditions for a positive point, a fusing temperature had not been attained. A bluish discoloration at and near the point showed that a high temperature had been reached and the temper drawn. The flat portion of the curve parallel to the X axis shows that the discharge did not always occur from the point alone. When a potential sufficient to produce an ionization of the gas is attained, the discharge, or a portion of it at least, will occur between the parts removed a distance equal to the critical spark-length for the pressure employed. If the point lies within this distance, part of the discharge will occur from the portion of the needle lying back of the point. Hence as the needle is withdrawn no increase in the potential-difference needed for the production of a discharge will be required until the needle-point is removed to a distance exceeding the critical distance. Attention was called to this by Carr (Proc. Roy. Soc. xxi. p. 374, 1903). The results published by Hobbs in a paper previously mentioned bring out this point markedly.

The critical distance, if this is the correct interpretation, in the case of point and plane is not the same as between parallel plates, nor indeed would this be expected owing to the difference in the electric fields. My results indicate that the critical distance for a pressure of 25 cm. exceeds 100 wave-lengths of sodium light.

Paschen's law indicates that for a pressure of 25 cm. the critical distance between parallel plates would be 40 wave-lengths. This deduction is based on measurements made by Carr.

In discussing the discharge between point and plane, J. J. Thomson makes the following statement ('Conduction of Electricity through Gases,' 2nd edition, p. 511) :—"The minimum potential required for the discharge of positive electricity from a point is greater than for negative, for the minimum potential V_0 is determined by the condition that the electric field near the electrode should be strong enough to enable the positive ions to produce an adequate stream of corpuscles. Now, when the point is the cathode the positive ions have two opportunities of producing corpuscles, (1) by impact with the electrode, (2) by impact with the molecules of the gas; while when the point is the anode only the second of these is available. This would have the effect of making V_0 for the positive point greater than for the negative, and thus making the minimum potential required for point discharge greater."

The curves shown in Pl. I. figs. 2 and 3 will support, for the most part, the interpretation placed on such phenomena by Prof. Thomson. The discharge potentials given in the tables refer to dark discharge undoubtedly. Upon repeating the measurements, with the apparatus outside the box in a fairly dry atmosphere, almost identical results were obtained. In this case I was not able to perceive any luminosity at the surfaces.

The potentials at which discharge occurred could readily be determined by the behaviour of the voltmeter-needle. On decreasing the resistance in the liquid rheostat a potential would be reached when the needle came to rest, wavered and sometimes fell back; on still further decreasing the resistance slightly, the voltmeter indicated no further rise in potential. If the potential were increased sufficiently, however, a crackle could be heard and a luminous spark was obtained, the voltmeter-needle falling to zero. The potentials given in the preceding tables are those indicating the existence of the dark discharge.

For potentials less than the least ionizing potential it was extremely difficult to secure readings. The potential gradient is extremely steep, hence variations of $\frac{1}{20}$ of a wave-length would be accompanied by large changes in potential-difference readings. It is not difficult, however, to explore the region for potential-differences which ionize the gas, and by taking numerous readings for these potentials one is enable to locate quite accurately the place where the gradient changes from one of great inclination to one parallel to the axis of abscissæ.

My readings indicate that the gradient changes at a potential of 338 volts for a negatively electrified point. The distance corresponding to this potential-difference is one wave-length of Na light. It may also be remarked that for distances greater than this, the potential gradient for a positively electrified point shifts. For distances less than this, the discharge is carried by negative corpuscles or even positive ions—metal ions, perhaps, for throughout this limited region the gradient is not determined by the polarity of the point.

Character of the Discharge produced by Potentials less than those required to ionize a gas.

In order to determine whether the carriers of the discharge through these abnormally small distances are negative corpuscles or positive metal ions or both, I have made a modification of Dr. Hobbs's experiment.

It is possible for a discharge to occur between electrodes whose potential-difference is less than that required to ionize the gas. The distance through which this discharge occurs depends on the character of the electrodes.

Pl. I. fig. 4 shows the results obtained by Hobbs for electrodes of Pt, Ag, and Al. Hobbs also used Bi, Ni, Sb, Zn, and Mg. The potential gradients for these elements lie within the limits of those for Pt and Al.

In Tables VII. to XV. distances in wave-lengths are given in the first column under λ. Potential-differences in the second column are indicated by V.

TABLE VII.

Al + Al −

λ.	V.	λ.	V.
2	121	4	295
2	159	4	254
2·5	164	4·5	301
2·5	212	5	306
3	197	5	320
3	188	6	329
3·5	188	6	342

TABLE VIII.

Al + Pt −

λ.	V.	λ.	V.
2	103	4	305
2·5	169	4	301
3	258	4·5	304
3	268	5	329
3·5	277	5	329
4	305	6	338
4	320	6	338

TABLE IX.

Pt+ Al−

λ.	V.	λ.	V.
1·5	122	4	291
2	188	4	295
2·5	197	4·5	285
3	231	5	310
3	235	5	305
3	235	6	325
3	295	6	329
3·5	263		

TABLE X.

Pt+ Pt−

λ.	V.	λ.	V.
1	150	3	338
1	169	3	338
1·5	188	3	342
1·5	210	4	348
2	295	4	345
2	301	5	348
2·5	305	5	352
2·5	305	6	344

TABLE XI.

Pt+ Ag−

λ.	V.
2	225
2	235
3	320
3	306
4	348
4	343
5	352
5	352

TABLE XII.

Ag+ Pt−

λ.	V.
1·5	179
2	225
3	306
3	310
4	329
4	329
5	348
5	348
6	352
7·5	352

Table XIII.

Ag + Ag −

λ.	V.	λ.	V.
2	211	3·5	338
2·5	235	3·5	335
2·5	282	4	357
3	306	4	320
3	306	4·5	352
3	306	5	334
3·5	306	5	352

Table XIV.

Ag + Al −

λ.	V.	λ.	V.
2	110	4	305
2	197	4·5	305
2·5	132	5	320
3	225	5	320
3	291	6	325
3·5	238	6	329
4	291	6	320

Table XV.

Al + Ag −

λ.	V.	λ.	V.
2	111	4	301
2	197	4	320
2·5	137	4·5	320
3	273	5	325
3	282	6	342
3·5	291	6	338
4	305		

In all these cases Hobbs used two electrodes of the same metal. Suppose, however, that one electrode was Pt, the other made of Al. A number of possibilities are presented. 1st, If the negative corpuscle is the carrier of the discharge the gradient should be determined by the negative electrode. 2nd, If the positive metal ion is the carrier, the positive electrode should determine the gradient. 3rd, If either one could be the carrier, the potential-gradient would be determined by the electrode having the lower gradient irrespective of its polarity.

In testing this matter, apparatus similar to that employed in the point and plane experiment was used, a sphere 2·54 cm. in diameter being substituted for the point. Three metals were used in the following permutations, viz. :—

Al+, Al−	Ag+, Ag−	Pt+, Pt−
Al+, Ag−	Ag+, Al−	Pt+, Al−
Al+, Pt−	Ag+, Pt−	Pt+, Ag−

In each of these cases the discharge was determined by the metal having the lower gradient of the pair irrespective of its polarity. These results are recorded in the tables VII. to XV inclusive.

Pl. I. fig. 5 represents graphically the results for Pt and Al, *i. e.*, the extreme case. The curves for Pt+ Pt− (A) and Al+, Al− (B) are similar to those as given by Hobbs ; curves and individual readings show good agreement with his results. The curves for Pt+, Al− (C) and Al+ Pt− (D) are the same as (B), the individual readings under the stated conditions being indicated. Curves representing the same relations for the other combinations are not shown ; they indicate, however, the same behaviour, viz. :—that the metal having the lower gradient controls the discharge irrespective of its polarity.

Summary.

Within the limitations previously described the results indicate :—

1st. That the least ionizing potential for point and plane is about 338 volts in air ; a value some 12 volts less than between plane surfaces.

2nd. That the critical distance is greater for point and plane than between plane electrodes.

3rd. That the critical potential is less for a negatively electrified point than for a positive point.

4th. That the gradient for discharge occurring for potential-differences less than the least ionizing potential is steeper in the case of point and plane than for plane electrodes and is independent of the polarity of the point.

5th. That the carriers for a discharge produced by potential-differences less than the least ionizing potential are not always negative corpuscles.

Physical Laboratory,
Ohio State Univ., Columbus, Ohio,
Dec. 10th, 1907.

IV. *The Unit-Stere Theory: The Demonstration of a Natural Relation between the Volumes of the Atoms in Compounds under Corresponding Conditions and that of Combined Hydrogen.* By GERVAISE LE BAS, *B.Sc.**

PART II.

THE RELATIVE VOLUMES OF CARBON AND HYDROGEN (*a*) IN THE LIQUID OLEFINES $C_2H_{2n}|=|$ AND THE ACETYLENES $C_nH_{2n-2}|\equiv|$, (*b*) IN AROMATIC AND HYDROAROMATIC COMPOUNDS.

IN a former paper (Phil. Mag. ser. 6, vol. xiv. No. 81, pp. 324–350) the normal paraffin hydrocarbons C_nH_{2n+2} were dealt with. The apparent volume of a particular hydrocarbon under all physical conditions, from the melting to the critical point, was considered to be measured by the product of a number W, which represents the number of valencies, and a variable S, called the unit-stere, the magnitude of which depends upon the physical circumstances of the experiment. The unit-stere S is equal to the apparent volume of hydrogen in the combined state; the apparent atomic volume of carbon being equal to 4S. The relation $C=4S$ thus connects the apparent volumes of the atoms in the individual hydrocarbons under the circumstances already mentioned, and as a result the equation

$$\text{Mol. vol. of } C_nH_{2n+2}=(6n+2)S=WS$$

is always true, at least approximately.

It is obvious that no direct comparison of the apparent volumes of the atoms in each compound is possible, but the validity of the above equation can be demonstrated from a consideration of the volumes of successive members of the paraffin series under coincident conditions. The relation is however, not always quite strictly followed in such a series, and this constitutes the first limitation of the principle of strict additivity to be met with. The explanation given of this is that the relative volumes of the carbon and hydrogen atoms are very closely in the ratio of 4 : 1 in a single compound, but that the apparent volumes of like atoms may change very slightly from compound to compound under most physical conditions. Another way of stating this is that there is no one physical condition except perhaps absolute zero at which ALL the compounds of a series are really comparable. Thus the molecular volumes of a series of homologous hydrocarbons under corresponding conditions

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* Communicated by Prof. W. J. Pope, F.R.S.

are approximately in arithmetical series, sometimes exactly so. If this series divided by a second, necessarily arithmetical, that of the valency numbers, the respective ratios are constant or nearly so.

Thus,

$$\frac{V_1}{W_1} = \frac{V_2}{W_2} = \frac{V_3}{W_3} = \ldots\ldots = S,$$

a constant, which has already been referred to.

By simple arithmetical processes it is usually possible to prove that the apparent atomic volume of H is equal to the volume of the unit-stere, and the volume of carbon equal to 4S. This method is important, because it is the most direct method of proving the relation

$$C = 4H = 4\frac{V}{W}.$$

It is, however, sometimes not possible to obtain very exact values of small numbers by the method of differences, and it is also necessary to exclude other relations. The following method has been devised to supplement that given above.

Let it be supposed that the apparent volumes of a series of homologous compounds like the paraffin hydrocarbons under a number of physical conditions be obtained, then, assuming that the relation $V = WS$ is true for a single compound,

$$\begin{array}{lcl} V_1,\ V_2,\ V_3,\ \ldots\ldots & = & W_1 S,\ W_2 S,\ W_3 S, \\ V_1',\ V_2',\ V_3',\ \ldots\ldots & = & W_1 S',\ W_2 S',\ W_3 S', \\ \multicolumn{3}{c}{\ldots\ldots\ldots\ldots\ldots\ldots} \end{array}$$

If the volumes in each series be successively divided by those of the first members, then

$$\left.\begin{array}{l} \frac{V_1}{V_1},\ \frac{V_2}{V_1},\ \frac{V_3}{V_1},\ \ldots\ldots \\ \frac{V_1'}{V_1'},\ \frac{V_2'}{V_1'},\ \frac{V_3'}{V_1'},\ \ldots\ldots \\ \ldots\ldots\ldots\ldots \end{array}\right\} = 1,\ \frac{W_2}{W_1},\ \frac{W_3}{W_1},\ \ldots\ldots$$

The ratios so obtained must be additive, that is, the differences must be equal or nearly so, and also they should be reproduced by dividing the valencies of the successive compounds by the valency of the first.

Both of these conditions are fulfilled under corresponding conditions in a surprising manner, although sometimes not quite strictly.

Divide the volumes of the members of the successive series by the corresponding members of the first; then

$$\left.\begin{array}{r}V_1'/V_1,\ V_2'/V_2,\ V_3'/V_3,\ \ldots\ldots = S'/S,\\ V_1''/V_1,\ V_2''/V_2,\ V_3''/V_3,\ \ldots\ldots = S''/S,\\ \ldots\ldots\ldots\ldots\ldots\ldots = S^n/S,\end{array}\right\}\ \text{a series of constants.}$$

The reference points are generally the critical temperatures or pressures, but it has been found convenient to utilize the melting-points in the case of the more complex hydrocarbons.

It is no doubt a fact that the apparent molecular volumes under corresponding conditions are proportional to their real volumes, approximately at any rate. Let it be supposed that these are respectively equal to V_1^0, V_2^0, V_3^0, ...

Then

$$\left.\begin{array}{l}\dfrac{V_1}{V_1^0},\ \dfrac{V_2}{V_2^0},\ \dfrac{V_3}{V_3^0},\ \ldots\ldots = \dfrac{S}{S_0},\\[2ex] \dfrac{V_1'}{V_1^0},\ \dfrac{V_2'}{V_2^0},\ \dfrac{V_3'}{V_3^0},\ \ldots\ldots = \dfrac{S'}{S_0},\\[2ex] \ldots\ldots\ldots\ldots\ldots\end{array}\right\}\ \text{a series of constants of increasing magnitude.}$$

The real volumes are known to be about $\frac{1}{4}$ of the molecular critical volumes, and no doubt are equal fractions of the apparent volumes under corresponding conditions. In support of this conclusion one finds that the molecular refractions are equal fractions of the apparent volumes of the compounds under coincident conditions.

In consequence of this proportionality the molecular refractions themselves are subject to additive relations similar to those of the apparent molecular volumes of the compounds under such conditions.

UNSATURATED COMPOUNDS.

The Olefines and the Acetylenes.

In view of the very interesting relations found among the saturated paraffins under corresponding conditions, the possible extension of the theory to other series is a matter of peculiar interest. Attention will be directed in this section to unsaturated hydrocarbons, (1) the olefines $C_nH_{2n}|{=}|$ and the acetylenes $C_nH_{2n-2}|{\equiv}|$, (2) aromatic compounds.

In spite of the very great amount of experimental material very little of it is suitable for our present purpose, since most of the observations refer to some common temperature like 0° or 20°. In the case of compounds belonging to the aliphatic series, additive volume relations will be considered at the melting-point and at the boiling-point. It is natural to suppose that some constitutive effect is noticeable, as appears to be the case when other physical properties are taken into consideration. Although there is a contraction in both the olefines and the acetylenes at the melting-point, apparently due to unsaturation, none is found when the molecular volumes of the simpler homologues of the unsaturated series are considered at the boiling-point. Very much more experimental work will have to be done before it is possible to draw any very general conclusions, and under as great a variety of physical conditions as possible. Only the barest outlines of the theory can be presented under the circumstances, and it is possible that it will have to be modified in certain of its details in the light of fuller knowledge, and with much more extended experimental material than is available at present.

(a) *The Olefines*, $C_nH_{2n}|{=}|$. (Krafft, *Ber.* 1886, xvi. p. 3018.)

TABLE I.

Table of Volumes of the Olefines at the M.P.

No.	Olefine, $C_nH_{2n}\vert{=}\vert$.	W.	V.	Δ.	$\frac{\text{M.P.}}{\text{B.P.}}$ (15 mm.)	WS −2·50.
1.	Dodecylene, $C_{12}H_{24}\vert{=}\vert$ ...	72	211·2	...	·656	211·4
2.	Tetradecylene, $C_{14}H_{28}\vert{=}\vert$ ...	84	246·9	35·7	·652	247·03
3.	Hexadecylene, $C_{16}H_{32}\vert{=}\vert$ ...	96	282·9	36·0	·647	282·7
4.	Octadecylene, $C_{18}H_{36}\vert{=}\vert$ ...	108	318·6	35·7	·644	318·3
	Mean value			35·8		
				12×2·98		

The value of S used in the calculation of the molecular volume is 2·970—a number which is justified by the very close approximation of the calculated to the observed values.

The contraction for unsaturation is 2·50 at the melting-point in the above cases.

In order to obtain a more extended view, it is, however, necessary to study the liquid volumes of the olefines above the melting-point. For this reason, calculations similar to those followed for the saturated paraffin series are here worked out.

TABLE II.

Table of Constants.

Olefine, $C_nH_{2n}|=|$.	W.	M.W.	M.P. (abs.).	d_{T}'.	*a*.	*β*.
Dodecylene, $C_{12}H_{24}|=|$ ...	72	168	242°	·7954	−·0008997	−·00000022
Tetradecylene, $C_{14}H_{28}|=|$ ...	84	196	261°	·7936	−·0008869	−·00000017
Hexadecylene, $C_{16}H_{32}|=|$ ...	96	224	277°	·7917	−·0008556	−·00000040
Octadecylene, $C_{18}H_{36}|=|$ ...	108	252	291°	·7910	−·000872	...

The method which is adopted for calculating the amount of the contraction is expressed by the following formula :—

$$\text{M.V. of } C_nH_{2n+2} - \text{M.V. of } C_nH_{2n}|=| = \Delta \text{ for } H_2 + |=|,$$

$$|=| = -\Delta + \text{Vol. of } H_2.$$

The apparent volume of H at corresponding temperatures, that is, those which are equidistant from the respective melting-points, are given in the tables of results for the normal paraffins. Column 4 gives V the molecular volumes of the olefines at the different temperatures, and column 5 the volumes V′ for the corresponding normal paraffins.

TABLE III.

Dodecylene, $C_{12}H_{24}|=|$. M.W. 168. W. 72. M.P. −31°.

$$d_{T} = \cdot 7954\{1 - \cdot 0008997\,t - 00000022\,t^2\}.$$

t.	Calc. sp. gr.	Observed sp. gr.
−31°	......	·7954
± 0	·7731	·7729 ·7732
+15	·7621	·7620
+30	·7511	·7511

T.	*d*.	$\frac{d_T}{d_{T'}}$.	V.	V′.	Δ.	H_2.	$|=|$.
242	·7954	1·0000	211·21	219·93	−8·72	5·94	−2·78
252	·7882	0·9910	213·14	221·84	−8·70	6·00	−2·70
262	·7810	0·9819	215·11	223·86	−8·75	6·05	−2·70
272	·7739	0·9730	217·08	225·91	−8·83	6·10	−2·73
282	·7664	0·9636	219·21	228·06	−8·85	6·15	−2·70
292	·7592	0·9544	221·29	230·23	−8·94	6·22	−2·72
302	·7518	0·9452	223·45	232·49	−9·04	6·28	−2·76
312	·7445	0·9360	225·67	234·77	−9·10	6·34	−2·73
					Mean contraction	=	−2·73

Values of V/W in $C_{12}H_{24}$ |=|. W. 72.

T.	V.	V+|=|.	V/W.	Vol. of $C_{12}H_{26}$.	V/W.
M.P.	211·21	213·94	2·971	219·93	2·970
„ +10°	213·14	215·87	2·998	221·84	2·997
„ +20°	215·11	217·84	3·025	223·86	3·025
„ +30°	217·08	219·81	3·053	225·91	3·053
„ +40°	219·21	221·94	3·082	228·04	3·081
„ +50°	221·29	224·02	3·111	230·23	3·111
„ +60°	223·45	226·18	3·141	232·49	3·142
„ +70°	225·67	228·40	3·171	234·77	3·173

Tetradecylene, $C_{14}H_{28}$ |=|. M.W. 196. W. 84. M.P. −12°.

$$d_T = \cdot 7936\{1 - \cdot 0008869\,t - \cdot 00000017\,t^2\}$$

t.	Calc. sp. gr.	Observed sp. gr.
−12°............	......	·7936
0	·7851	·7852
15	·7745	·7745
30	·7637	·7638

T.	$d_{T'}$.	$\frac{d_T}{d_{T'}}$.	V.	V′.	Δ.	H_2.	|=|.
261	·7936	1·0000	246·90	255·40	−8·50	5·94	−2·56
271	·7865	0·9911	249·20	257·68	−8·48	6·00	−2·48
281	·7795	0·9822	251·43	260·03	−8·60	6·05	−2·55
291	·7723	0·9732	253·78	262·45	−8·67	6·10	−2·57
301	·7652	0·9642	256·14	264·88	−8·74	6·16	−2·58
311	·7580	0·9552	258·57	267·34	−8·77	6·22	−2·55
				Mean contraction |=|			−2·55

Values of V/W for $C_{14}H_{28}$ |=|.

T.	V.	V+|=|.	V/W.	Vol. of $C_{14}H_{30}$.	V/W.
M.P.	246·90	249·45	2·970	255·4	2·970
„ +10°	249·20	251·75	2·997	257·68	2·996
„ +20°	251·43	253·98	3·023	260·03	3·023
„ +30°	253·78	256·33	3·051	262·45	3·051
„ +40°	256·14	258·69	3·080	264·9	3·080
„ +50°	258·57	261·12	3·109	269·97	3·108

Hexadecylene, $C_{16}H_{32}$. M.W. 224. W. 96. M.P. 4°.

$$d_T = \cdot 7917\{1 - \cdot 0008556\, t - \cdot 000000\, t^2\}.$$

t.	Calc. sp. gr.	Observed sp. gr.
+4°	......	·7917
15	·7842	·7842
37·1	·7689	·7689

T.	$d_{T'}$.	$\frac{d_T}{d_{T'}}$.	V.	V'.	Δ.	H_2.	$\vert=\vert$.
277	·7917	1·0000	282·94	291·47	−8·53	5·94	−2·59
287	·7849	0·9914	285·37	294·05	−8·68	6·00	−2·68
297	·7780	0·9827	287·92	296·66	−8·74	6·05	−2·69
307	·7710	0·9739	290·53	299·34	−8·80	6·10	−2·71
					Mean contraction $\vert=\vert$		−2·66

Values of V/W for $C_{16}H_{32}$ $|=|$.

T.	V.	V+$\vert=\vert$.	V/W.	Vol. of $C_{14}H_{30}$.	V/W.
M.P.	282·94	285·60	2·975	291·47	2·974
,, +10°	285·37	288·03	3·000	294·05	3·000
,, +20°	287·92	290·58	3·027	296·66	3·027
,, +30°	290·53	293·19	3·054	299·34	3·054

Octadecylene, $C_{18}H_{36}$ $|=|$. M.W. 252. W. 108. M.P. 18°.

$$d_T = \cdot 7910\{1 - \cdot 000872\, t\}.$$

t.	Calc. sp. gr.	Observed sp. gr.
+18°	......	·7910
22·1	·7881	·7880
35·6	·7788	·7790

T.	$d_{T'}$.	$\frac{d_T}{d_{T'}}$.	V.	V'.	Δ.	H_2.	$\vert=\vert$.
291°	·7910	1·0000	318·58	327·11	−8·53	5·94	−2·59
301°	·7841	0·9913	321·39	329·95	−8·56	6·00	−2·56
311°	·7771	0·9825	324·28	332·89	−8·61	6·05	−2·56
321°	·7702	0·9738	327·17	335·89	−8·72	6·10	−2·62
					Mean contraction $\vert=\vert$		−2·55
					Mean of four		−2·62

Values of V/W for $C_{18}H_{36}$ |=|.

T.	V.	V+|=|.	V/W.	Vol. of $C_{18}H_{38}$.	V/W.
M.P.	218·58	321·13	2·973	327·11	2·973
,, +10°	321·39	323·94	2·999	329·95	2·999
,, +20°	324·28	326·83	3·026	332·89	3·026
,, +30°	327·17	329·72	3·053	335·89	3·053

So far as can be seen, the contractions for unsaturation are independent both of the temperature and of the complexity of the above olefines—or at least there is no clear difference between the numbers. The contractions for unsaturation depend only upon the olefine bonds, for the apparent volumes of the atoms in the saturated portions of the molecules possess similar volumes under particular conditions to those of the normal paraffins. The mean value of |=| is 2·62.

By the simple process of adding the mean value of the contraction for each olefine to the apparent volume under each of the conditions, and then dividing by the valency number W, the validity of the valency rule is shown, which rule of course depends upon the fact that C=4H in each case. The apparent molecular volumes of the compounds are thus expressed as the sum of two terms one of which is proportional to the valency numbers W, and the other is constant.

M.V. of C_nH_{2n} |=| $=6n\text{S}-2{\cdot}62=\text{WS}-$|=| $\text{S}=2{\cdot}970$ at the melting-point.

TABLE IV.

Table showing the Values of V/W for the Olefines at equal intervals of Temperature from the Melting-points.

T.	$C_{12}H_{26}$.	$C_{12}H_{24}$ |=|.	$C_{14}H_{28}$ |=|.	$C_{16}H_{32}$ |=|.	$C_{18}H_{36}$ |=|.
M.P.	2·970	2·971	2·970	2·975	2·973
,, +10°......	2·997	2·998	2·997	3·000	2·999
,, +20°......	3·025	3·025	3·023	3·027	3·026
,, +30°......	3·053	3·053	3·051	3·054	3·053
,, +40°	3·081	3·082	3·080		
,, +50°......	3·111	3·111	3·109		
,, +60°......	3·142	3·141			
,, +70°......	3·173	3·171			

The above table shows in a remarkable way that the apparent volumes of the compounds above the melting-point become comparable at equal intervals of temperature therefrom, exactly as was found to be the case with the normal paraffins. It is thus concluded:—*that the relation* M.V. *of* $C_nH_{2n}\vert=\vert = 6n\text{S} - 2{\cdot}62 = \text{WS} - \vert=\vert$ *found to be true for the olefines at the melting-point is also true for temperatures which are at equal intervals therefrom.*

It is possible to show by a method adopted for the saturated normal paraffins that under the conditions just stated additive relations hold, and also that the valency rule is alone capable of explaining the facts. In this instance dodecane $C_{12}H_{26}$ is taken as the standard substance, and use is made of the apparent volumes under the different circumstances, plus the contractions $\vert=\vert$.

Table V.

Table showing the validity of the Valency Rule for the Olefines.

T.	$C_{12}H_{26}$.	$C_{12}H_{24}+\vert=\vert$.	$C_{14}H_{28}+\vert=\vert$.	$C_{16}H_{32}+\vert=\vert$.	$C_{18}H_{36}+\vert=\vert$.
M.P.	1·0000	0·9728	1·1342	1·2986	1·4601
,, +10°......	,,	0·9731	1·1349	1·2983	1·4602
,, +20°......	,,	0·9731	1·1350	1·2980	1·4599
,, +30°......	,,	0·9730	1·1346	1·2978	1·4595
,, +40°......	,,	0·9732	1·1344		
,, +50°......	,,	0·9730	1·1342		
,, +60°......	,,	0·9728			
,, +70°......	,,	0·9729			
Mean values ...	1·0000	0·9730	1·1345	1·2981	1·4599
Theoretical (4:1 rule)...	$\frac{74}{74}$	$\frac{72}{74}$	$\frac{84}{74}$	$\frac{96}{74}$	$\frac{108}{74}$
	1·0000	0·9730	1·1351	1·2973	1·4595
Errors	......	±0	+0·0006	−0·0008	−0·0004

The above table shows in a striking way that the relations attaching to the apparent molecular volumes of the olefines under the above circumstances are additive, for the differences between the mean values of the ratios are nearly equal to ·1620.

Also, the validity of the valency rule, under the different conditions, is evident from the fact, that the mean values of the ratios follow very closely those obtained by dividing the valency numbers of the various olefines by the valency number of dodecane $C_{12}H_{26}$.

The remarkable consistency of the numbers representing the ratios suggests the possibility of obtaining approximate values of V/W; and thus of the apparent volumes of hydrogen, without taking the contractions into consideration. This is done by finding by difference the apparent volumes of the homologous increment CH_2 and then dividing by 6. The following table shows the closeness of the correspondence between the values of V/W obtained in this way and those derived by taking the contractions into account.

Table VI.

Volumes of V/W for the Olefines by differences.

T.	Vol. of $C_{14}H_{28}$ |=|.	Vol. of $C_{12}H_{24}$ |=|.	Δ for $2CH_2$.	$\frac{\Delta}{12}$.	V/W from $C_{12}H_{26}$.	Diff.
M.P.	246·90	211·21	35·69	2·975	2·970	+0·005
„ +10°...	249·20	213·14	36·06	3·005	2·997	+0·008
„ +20°...	251·43	215·11	36·32	3·027	3·025	+0·002
„ +30°...	253·78	217·08	36·70	3·058	3·053	+0·005
„ +40°...	256·14	219·21	36·93	3·078	3·080	−0·002
„ +50°...	258·57	221·29	37·28	3·106	3·109	−0·003
					Mean difference ...	+0·002

The differences only affect the third decimal place and the mean error is quite small, and this in spite of the unavoidable discrepancies introduced by this method of calculation. The apparent volumes of carbon and hydrogen are thus similar in the paraffin and the olefin series at the melting-point and at equal intervals of temperature therefrom.

It has been shown that the specific gravities of the normal paraffins at equal intervals of temperature from the respective melting-points are equal to fractions of their specific gravities at those points. It is remarkable that similar relations are true for the olefins, and since these substances are not believed to be associated, the probability that the 4 : 1 rule is a natural relation is greatly increased.

The results that have been obtained by a study of the saturated normal paraffins and of the olefins are placed side by side in the following table (p. 70) for purposes of comparison.

TABLE VII.

Comparison between the Values of $\frac{d_T}{d_{T'}}$ for the Paraffins and the Olefines under similar circumstances.

T.	$C_{12}H_{26}$	$C_{12}H_{24}$ |=|	$C_{14}H_{30}$	$C_{14}H_{28}$ |=|	$C_{16}H_{34}$	$C_{16}H_{32}$ |=|	$C_{18}H_{38}$	$C_{18}H_{36}$ |=|
M.P.	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
„ +10°	0·9913	0·9910	0·9911	0·9911	0·9913	0·9914	0·9913	0·9913
„ +20°	0·9824	0·9819	0·9822	0·9822	0·9826	0·9827	0·9826	0·9826
„ +30°	0·9735	0·9730	0·9732	0·9732	0·9738	0·9739	0·9738	0·9738
„ +40°	0·9644	0·9636	0·9642	0·9642				
„ +50°	0·9552	0·9544	0·9556	0·9556				
„ +60°	0·9459	0·9452						
„ +70°	0·9368	0·9360						

The conclusion is that:

the specific gravities of the olefines C_nH_{2n} |=| *at equal intervals of temperature from the melting-points are equal fractions of their specific gravities at those points.*

(b) *The Acetylene Hydrocarbons*, C_nH_{2n-2} |≡|.

The data for the acetylenes are those of Krafft (*Ber.* 1887, xvii. p. 1371), and are for the liquid state at the melting-point.

TABLE VIII.

The Volume relations of the Acetylenes at the M.P.

No.	Acetylene, C_nH_{2n-2} |≡| .	W.	V (obs.).	Δ.	WS.	WS−3.	$\frac{W-1}{V}$.
1.	Dodecylidene, $C_{12}H_{22}$ |≡| ...	70	205·0		207·9	204·9	2·971
				35·5			
2.	Tetradecylidene, $C_{14}H_{26}$ |≡| ...	82	240·5		243·54	240·54	2·970
				35·6			
3.	Hexadecylidene, $C_{16}H_{32}$ |≡| ...	94	276·1		279·18	276·18	2·970
				35·6			
4.	Octadecylidene, $C_{18}H_{36}$ |≡| ...	106	314·82		314·82	311·82	2·970
	Mean values...	...	....	35·6			

The calculated molecular volumes are seen to be in excellent agreement with the observed values, and the ratio

$\frac{V}{W-1}$ is equal to the mean value of the unit-stere, viz. 2·970. The difference for C_2H_4 is 35·6, which equals $12 \times 2{\cdot}967$. It follows that the volumes for hydrogen and carbon are the same in the acetylenes at the melting-point as in the normal saturated paraffins under similar circumstances.

The contraction for unsaturation is evidently not far from 3 units per gramme molecule—a number which happens to be about equal to the apparent volume of hydrogen at the melting-point. The significance of the ratio $\frac{V}{W-1}$ is thus obvious. The contraction for the acetylenes also appears to be a little larger than that for the olefines.

Owing to the fact that data exist for the formulation of interpolation equations similar to those which have been used in the discussion of the members of the two former series, it is possible to examine the volumes of the acetylenes above the melting-point in a similar way.

The ranges of temperature over which Krafft's determinations extend are sufficiently restricted to justify the use of linear formulæ, as a comparison between the observed and the calculated specific gravities show. Interpolation formulæ have been worked out for the three acetylenes dodecylidene $C_{12}H_{22}$ $|\equiv|$. tetradecylidene $C_{14}H_{26}$ $|\equiv|$, and hexadecylidene $C_{16}H_{30}$ $|\equiv|$, the constants for which appear in the appended table.

Table IX.

Table of Constants.

No.	Acetylene, C_nH_{2n-2} $\lvert\equiv\rvert$.	W.	M.W.	M.V.	d_T'.	α.
1.	Dodecylidene, $C_{12}H_{22}$ $\lvert\equiv\rvert$ ...	70	166	264	·8097	−·00092
2.	Tetradecylidene, $C_{14}H_{26}$ $\lvert\equiv\rvert$ ...	82	194	279·5	·8064	−·00090
3.	Hexadecylidene, $C_{16}H_{32}$ $\lvert\equiv\rvert$ ...	94	222	293	·8039	−·00087

As before, V represents the molecular volume of the acetylene, and V′ that of the corresponding saturated normal paraffin under similar circumstances.

TABLE X.

Dodecylidene, $C_{12}H_{22}\,\vert\equiv\vert$. M.W. 166. M.P. 264°.

$$d_\mathrm{T} = \cdot 8097\{1 - \cdot 00092\,t\}.$$

t.	Calc. sp. gr.	Observed sp. gr.
−9°	......	·8097
±0	·8029	·8030
+15°	·7918	·7917
+32·5........	·7788	·7788

T.	d_T'.	$\dfrac{d_\mathrm{T}}{d_\mathrm{T}'}$.	V.	V′.	Δ.	H_4.	$\vert\equiv\vert$
264°............	·8097	1·0000	205·0	219·93	−14·93	11·88	−3·05
274	·8022	0·9908	206·92	221·84	−14·92	11·99	−2·93
284	·7948	0·9816	208·86	223·86	−15·00	12·10	−2·90
294	·7873	0·9724	210·85	225·91	−15·06	12·21	−2·85
304	·7799	0·9632	212·85	228·04	−15·19	12·33	−2·86
314	·7724	0·9540	214·91	230·23	−15·32	12·44	−2·88
					Mean contraction $\vert\equiv\vert$		−2·91

Values of V/W for Dodecylidene $C_{12}H_{22}\,\vert=\vert$.

T.	V.	V+ $\vert\equiv\vert$.	V/W.	V. of $C_{12}H_{26}$.	V/W.
M.P.	205·0	207·91	2·970	219·93	2·972
,, +10°	206·92	209·83	2·996	221·84	2·998
,, 20	208·86	211·77	3·025	223·86	3·325
,, 30	210·85	213·76	3·054	225·91	3·053
,, 40	212·85	215·76	3·082	228·04	3·082
,, 50	214·91	217·82	3·112	230·23	3·111

Tetradecylidene, $C_{14}H_{26}\,\vert\equiv\vert$.

$$d_\mathrm{T} = \cdot 8064\{1 - \cdot 00090\,t\}.$$

t.	Calculated sp. gr.	Observed sp. gr.
6·5°	......	·8064
15·2	·8001	·8000
30	·7092	·7093

T.	d_T.	$\dfrac{d_\mathrm{T}}{d_\mathrm{T}'}$.	V.	V′.	Δ.	4H.	$\vert\equiv\vert$
6·5°	·8064	1·0000	240·57	255·4	−14·83	11·88	−2·95
16·5	·7991	0·9910	242·78	257·71	−14·93	11·99	−2·94
26·5	·7918	0·9820	244·98	260·03	−15·05	12·10	−2·95
36·5	·7864	0·9730	247·26	262·49	−15·23	12·22	−3·02
					Mean contraction		−2·97

Values of V/W for Tetradecylidene $C_{14}H_{26}|\equiv|$.

T.	V.	V+ $\vert\equiv\vert$.	V/W.	V. of $C_{14}H_{30}$.	V/W.
M.P.	240·57	243·54	2·970	255·4	2·970
,, +10°	242·78	245·75	2·997	257·71	2·996
,, +20	244·98	247·95	3·024	260·03	3·023
,, +30	247·26	250·23	3·052	262·49	3·052

Hexadecylidene, $C_{16}H_{30}|\equiv|$.

$$d_T = \cdot 8039\{1 - \cdot 00087\, t\}.$$

t.	Calc. sp. gr.	Observed sp. gr.
20°	......	·8039
30°	·7969	·7969

T.	d_T'.	$\frac{d_T}{d_T'}$.	V.	V+ $\vert\equiv\vert$.	V/W.	V. of $C_{16}H_{34}$.	V/W.
293°..	·8039	1·0000	276·15	279·15	2·972	291·47	2·974
303	·7969	0·9913	278·59	281·59	2·996	294·05	3·000
313	·7899	0·9826	281·05		3·022	296·66	3·027
323	·7829	0·9739	283·54		3·048	299·34	3·054

The contraction due to unsaturation is about 3 units per gramme molecule in these acetylenes, although the apparent volumes of carbon and hydrogen atoms are the same as for the normal saturated paraffins.

The general formula for the acetylenes is thus:—

$$\text{M.V. of } C_nH_{2n-2}|\equiv| = 6n\text{S} - 2\text{S} - 3 = \text{WS} - |\equiv|.$$

It will now be convenient to compare the value of S for the different acetylenes, plus the amounts of the contraction, that is to say, the volumes of H in these compounds, with the values found for the paraffins under similar circumstances.

TABLE XI.

Table showing the validity of the Valency Rule for the Acetylenes.

T.	$C_{12}H_{26}$.	$C_{12}H_{22}$ $\vert\equiv\vert$.	$C_{14}H_{26}$ $\vert\equiv\vert$.	$C_{16}H_{30}$ $\vert\equiv\vert$.	$C_{18}H_{34}$ $\equiv$
M.P.	2·970	2·970	2·970	2·972	2·970
,, +10° ...	2·997	2·997	2·997	2·996	
,, +20	3·025	3·025	3·024	3·022	
,, +30	3·053	3·054	3·052	3·048	
,, +40	3·081	3·082			
,, +50	3·111	3·112			

The above values are significant because they represent the volumes of H in the acetylenes under the different circumstances.

The following alternative method, which has already been utilized, is valuable for the purpose of demonstrating the validity of the valency rule in a different way. Use is made of the observed volumes of the acetylenes at the different temperatures, plus the contractions as in the former table.

TABLE XII.

Table showing the validity of the Valency Rule for the Acetylenes.

T.	$C_{12}H_{26}$.	$C_{12}H_{22}\,|\equiv|$.	$C_{14}H_{26}\,|\equiv|$.	$C_{16}H_{30}\,|\equiv|$.	$C_{18}H_{34}\,|\equiv|$.
M.P.	1·0000	0·9453	1·1073	1·2692	1·4315
,, +10° ...	,,	0·9459	1·1078	1·2693	
,, +20......	,,	0·9473	1·1076	1·2688	
,, +30......	,,	0·9453	1·1077	1·2684	
,, +40......	,,	0 9461			
,, +50......	,,	0·9461			
Mean values ...	1·0000	0·9460	1·1081	1·2689	1·4315
W/W′	$\frac{74}{74}$	$\frac{70}{74}$	$\frac{82}{74}$	$\frac{94}{74}$	$\frac{106}{74}$
	1·0000	0·9459	1·1081	1·2702	1·4324
Errors	......	−0·0001	+0·0005	+0·0013	+0·0009

The above table shows unmistakably that the volume relations of the acetylenes under the conditions are essentially additive, and further that the valency rule with the requisite modification for unsaturation, is alone capable of adequately expressing the results.

It is thus concluded that the general formula M.V. *of* $C_nH_{2n-2}\,|\equiv| = 6nS - 2S - |\equiv|$ *holds good not only at the melting-point but also at equal intervals of temperature therefrom.*

The average contraction for unsaturation is evidently not far from 3 units for these acetylenes, and it is apparently constant, both as regards complexity and temperature, at least in the cases that have been considered.

It now remains to tabulate the results that have been obtained with reference to the values of $\frac{d_T}{d_T'}$.

TABLE XIII.

The validity of the Law of Coincident States.

T.	$C_{12}H_{26}$	$C_{12}H_{24}$ =	$C_{12}H_{22}$ ≡	$C_{14}H_{30}$	$C_{14}H_{28}$ =	$C_{14}H_{26}$ ≡	$C_{16}H_{34}$	$C_{15}H_{32}$ =	$C_{15}H_{30}$ =
M.P. ...	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
„ +10°	0·9913	0·9910	0·9908	0·9910	0·9910	0·9910	0·9913	0·9913	0·9913
„ +20	0·9824	0·9819	0·9816	0·9820	0·9821	0 9820	0·9826	0·9826	0·9826
„ +30	0·9735	0·9730	0·9724	0·9730	0·9731	0·9730	0·9738	0·9738	0·9738
„ +40	0·9644	0·9636	0·9632						
„ +50	0·9552	0·9544	0·9540						

It is concluded that the following rule holds for the acetylenes as it does for the paraffins and the olefines.

The specific gravities of the acetylenes at equal intervals of temperature from the melting-points are equal fractions of their specific gravities at those points.

The law of additivity and the law of coincident states are thus considered to be true under similar circumstances for the members of the three series which have been studied, namely: the normal saturated paraffins, the olefines, and the acetylenes, and they are mutually dependent.

The Simpler Olefines and other Unsaturated Compounds at the Boiling-Point.

A study of the complex saturated paraffins in the neighbourhood of the melting-point, has led to the conclusion that there is an *extra* contraction when two or four hydrogen atoms have been eliminated. It will be interesting to find out if this is true when the volumes of the compounds are examined at the boiling-point.

An extended study of the data at this point shows that there is no extra contraction to be considered, that is to say, the olefines and the acetylenes differ in volume from the saturated paraffins by an amount equal to the volumes of the hydrogen atoms by which they differ in composition. Horstmann has made a very thorough study of the differences to be observed between the volumes of saturated and olefinoid compounds at the boiling-point, and has found that the elimination of two hydrogen atoms is responsible for a contraction of about 7·4 c.c. per gramme molecule. This number has already been shown to represent the volume of H_2 under the circumstances. The evidence in favour of the relation C=4H is thus reasonably certain as it has been obtained under a great variety of circumstances. It is also worthy of note that the above-mentioned constant differences observed by Horstmann, which have long been known, now find their place in a scheme of molecular volumes.

The data referring to unsaturated compounds are far too incomplete both as regards the number and variety of substances observed and as regards the ranges of temperatures to attempt to account for the different results respecting the effect of unsaturation on molecular volumes which have been obtained at the melting- and boiling-points respectively.

The following table shows that at the boiling-point the normal paraffins and the unsaturated series of hydrocarbons fall into one scheme owing to the fact that carbon and hydrogen respectively possess approximately the same volumes in each. This is also true of hydrocarbon residues saturated and unsaturated.

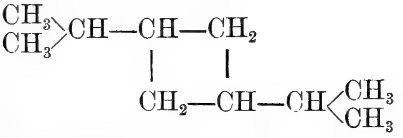
TABLE XIV.

The Volume Relations of the Atoms in Unsaturated Compounds at the Boiling-Point.

Compounds.	W.	V.	Δ.	V/W.	Author.
Pentane, C_5H_{12}	32	117·8	2×3·85	3·68	Young.
Amylene, C_5H_{10}	30	110·1	4×3·32	3·67	Schiff.
Valerylene, C_5H_8	28	104·5		3·73	Buff.
Hexane, C_6H_{14}	36	139·8	2×3·70	3·68	Young.
Hexylene, C_6H_{12}	34	132·4	4×3·42	3·68	Schiff.
Diallyl, C_6H_{10}	32	126·1		3·71	,,
Heptane C_7H_{16}	44	162·56	2×3·88	3·69	Young.
Heptylene C_7H_{14}	42	154·8		3·68	Schiff.
Octylene, C_8H_{16}	48	177·6		3·70	,,
Propyl alcohol, C_3H_8O	22	81·5	2×3·65	3·70	Zander.
Allyl alcohol, C_3H_6O	20	74·2		3·71	,,
Propyl amine, C_3H_9N	24	85·7	2×3·60	3·57	Schiff.
Allyl amine, C_3H_7N	22	78·5		3·57	,,
Tripropylamine $N(C_3H_7)_3$	60	222·4	6×3·62	3·70	Zander.
Triallylamine $N(C_3H_5)_3$	54	200·7		3·71	,,
Propyl acetate, $C_5H_{10}O_2$	...	128·8	2×3·60	...	Schiff.
Allyl acetate, $C_5H_8O_2$	...	121·6		...	,,
Propyl chloride C_3H_7Cl	...	91·7	2×3·65	...	,,
Allyl chloride. C_3H_5Cl	...	84·4		...	,,

It will be observed that the oxygen in the alcohols and the nitrogen in the amines possess volumes respectively equal to 2 S and 3 S, thus following the law of valency. It is also seen that the differences for H_2 in the acetates and chlorides are about the same as in the other compounds. Their volume relations are thus clearly additive. The fact that such small differences as those of H_2 are fairly concordant, and that the volume of H is found by this means to be equal to S, and consequently to H in the paraffin hydrocarbons at the boiling-point, is sufficiently remarkable. The numbers 3·7 and 14·8 for hydrogen and carbon respectively thus replace the numbers 5·5 and 11 in Kopp's scheme.

Diamylene $C_{10}H_{20}$ is a derivative of the olefine series and is formed by the polymerization of two molecules of amylene. It is not, however, supposed to belong to the olefine series, but to possess the formula



$$\begin{array}{l} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\text{—}CH\text{—}CH_2 \\ \qquad\qquad\ \ | \qquad\ \ | \\ \qquad\qquad CH_2\text{—}CH\text{—}CH\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix} \end{array}$$

(*Ber.* 1890, xxix. p. 1550).

Diamylene is thus a ring compound, which fact may be expected to be indicated by its molecular volume.

M.V. of $C_{10}H_{20}$ at B.P.	211·7
2 vols. of amylene C_5H_{10}	220·3
Contraction	8·6

This contraction is far too considerable to be ascribed to unsaturation, and must be attributed to the profound change in its chemical constitution indicated by its ring structure. The real contraction is, however, greater than that shown above, for the value of S in a compound of the complexity $C_{10}H_{20}$ is 3·71 (*cp.* Octane C_8H_{10} W 50 $S=3·72$, tripropylamine $N(C_3H_7)_3$ W 60 $S=3·71$). The normal volume of $C_{10}H_{20}$ is thus $3·71 \times 60 = 222·6$. Contraction 10·9. Contractions such as the above are a second departure from the principle of additivity, and are due to the effect of ring structure on molecular volumes, a matter which will be discussed more fully when aromatic and hydroaromatic compounds are considered.

The Aromatic Hydrocarbons and other Cyclic Compounds at the Boiling-Point.

(i.) A consideration of the apparent Atomic Volumes of Carbon and Hydrogen in the Side Chains at the Boiling-Point.

The compounds that are commonly called aromatic and hydroaromatic belong to a totally different class to those which have been discussed in previous papers. Whereas the latter are usually considered to consist of straight chains, the former are distinguished by more or less complex nuclei, the constituent atoms of which are supposed to possess a cyclic arrangement.

Before an attempt is made to work out the volume relations of the atoms in the nucleus, it will be necessary to consider the side chains, particularly those consisting of aliphatic hydrocarbon residues. It might be anticipated from their character that they should possess volumes comparable with those of equivalent residues in the hydrocarbons. This is indeed shown to be the case from the fact that the addition of the homologous increment CH_2 causes an increase of 22 units at the boiling-point—a number similar to that which has been found from an examination of the molecular volumes of the paraffin hydrocarbons under similar circumstances.

The fact that the nucleus and the side chains have little reciprocal influence other than that which might be attributed to the two parts of an aliphatic hydrocarbon on each other, is strikingly shown by subtracting the volumes of the complexes $n\mathrm{CH}_2$ from the volumes of each benzene, and so obtaining the volume of the nucleus. In all cases the volume of the free nucleus, as found by experiment, is reproduced by making the subtraction already referred to.

The experimental study of the benzene derivatives is largely due to Schiff and also to Lossen and Zander.

TABLE XV.

The Volumes of the Nucleus and the Side Chains in Monocylic Compounds.

Hydrocarbon.		V.	Δ.	Calculated Volume of the Nucleus.
Benzene,	C_6H_6	96		[96]
Toluene,	C_7H_8	118·3	22·3	96·1
Xylene,	C_8H_{10}	140·3	22	95·9
Mesitylene,	C_9H_{12}	162·8	22·5	96·2
Cymene,	$C_{10}H_{14}$	184·9	22·1	96·1
Mean		...	22·2	96·07
Pyridine,	C_5H_5N ...	89·3		[89·3]
β Picoline,	C_6H_7N ...	111·5	22·2	89·3
Hexahydroxylene,	C_7H_{14} ...	141·8		[141·8]
Hexahydroxylene,	C_8H_{16} ...	164·3	22·5	142·1

The conclusion to be drawn from the above figures is that the side chains occupy similar volumes to those of equivalent paraffin hydrocarbon residues, and that the volume of the nucleus in derivatives of this kind remains the same as that of the free nucleus. It follows that the volume of combined hydrogen is $\frac{22{\cdot}2}{6} = 3{\cdot}7$ and of combined carbon 14·8 as before.

(ii.) The volumes of the six extra Hydrogen atoms in Hydroaromatic Compounds.

The six extra hydrogen atoms in hydroaromatic compounds may be viewed in the light of side chains, in which case they might be supposed to possess volumes similar to those of hydrogen atoms in the paraffin hydrocarbons under similar circumstances. It will be found that they usually do. Exceptions are found in the cases of hexamethylene and hexahydropyridine or piperidine. The extra hydrogens in these compounds appear to be more closely associated with the nucleus than is the case with hydrocarbon side chains.

Table XVI.

Table showing the Volume of H_6 in Hydroaromatic Compounds. I.

Compound.	V.	6 H.	H.
Benzene, C_6H_6	96	20·3	3·38
Hexamethylene, C_6H_{12}	116·3		
Pyridine, C_5H_5N	89·3	19·5	3·25
Piperidine $C_5H_{11}N$	108·8		

The smaller value of H found by difference indicates that the six extra hydrogens are closely associated with the nucleus. A more extended study of benzene and hexamethylene under corresponding conditions shows that this conclusion is correct.

This, however, ceases to hold when one or more side chains are added to the nuclei, as the following table will show.

Table XVII.

Table showing the Volume of H_6 in Substituted Aromatic Compounds. II.

Compound.	V.	6H	H.
Toluene, C_7H_8	118·3	23·8	3·97
Hydrotoluene, C_7H_{14}	142·1		
Xylene, C_8H_{10}	140·3	24·0	4·00
Hexahydroxylene, C_8H_{16}	164·3		
Naphthalene, $C_{10}H_8$	147·2	24·0	4·00
Naphthyl hydride, $C_{10}H_{14}$	171·2		

The volume of a single hydrogen in these compounds is about 4, that is, a little higher than its volume in the paraffins. The number is, however, much higher than that found in the unsubstituted hydroaromatic compounds, and this may be attributed to the effect of the side chains or to spatial considerations. Curiously enough, the unsaturated part of the naphthalene has precisely the same effect as that of an aliphatic side chain.

It is thus concluded—

(*a*) That the volume of CH_2 is 22·2 on the average in the homologues of benzene.

(*b*) The volume of the *extra* hydrogens in the hydroaromatic hydrocarbons varies from 3·25 to 4 at the boiling-point.

(iii.) The apparent Atomic Volumes in the Nucleus at the Boiling and the Critical Points.

Having studied the volumes of carbon and hydrogen in the side chains, it is now necessary to examine the nuclei more particularly. It is natural to suppose that the apparent volumes of carbon and hydrogen still stand in the relation of 4 to 1 in the nucleus, although their absolute values might differ from those in the paraffins under similar circumstances. The following table gives the value of V/W for a number of single ring compounds, none of the hydrogens being displaced by substituents. Thus the relation C = 4 H is assumed. Nitrogen in pyridine and piperidine is considered to possess the volume 3 S in accordance with its fundamental valency number, that is to say, it is equal to 3 H.

TABLE XVIII.

Table showing the values of V/W for a number of simple cyclic arrangements.

Compound.		$V_{B.P.}$	W.	V/W.	V_K.	W.	V/W.
Benzene,	C_6H_6	96	30	3·20	256·3	30	8·54
Hexahydrobenzene,	C_6H_{12}......	116·3	36	3·23	306·7	36	8·52
Pyridine,	C_5H_5N ...	89·3	28	3·19	$\Delta = 49·6$	for	H_6.
Piperidine,	$C_5H_{11}N$ ...	108·8	34	3·20	H	=	8·3.
Paraffins		...	...	3·70	...	...	9·66

The above table shows very clearly that the relation between the volumes of carbon and hydrogen is the same in the nucleus as in the side chains, and as in the paraffins.

Incidentally, nitrogen is shown to possess the volume 3 S, so that H : C : N = 1 : 4 : 3.

A remarkable result of the above calculations is that no allowance for the so-called double bonds is to be made in benzene and its homologues. This is especially noticed in an extended study of benzene and hexamethylene to be made later (see Table XXII.).

The absolute apparent volumes of carbon and hydrogen in the compounds included in the table are considerably smaller than those found in aliphatic hydrocarbon chains under similar circumstances. It is clearly inadmissible to compare their volumes, and to work out volume relations, without first taking into account their different constitutions : this may be done by allowing a definite contraction for ring-structure.

Conclusion.—The relative volumes of C and H are still as 4 : 1 in the nuclei, but their absolute values differ from those in the side chains or in the paraffin hydrocarbons.

(iv.) The Amount of the Contraction in Aromatic Compounds for Ring-structure at the Boiling-Point.

Because benzene and its derivatives have almost the same volumes as those of certain homologous paraffin hydrocarbons, Kopp supposed that the apparent atomic volumes of C and H at the boiling-point are 11 and 5·5 respectively. This conclusion no doubt was arrived at because of a similarity in the volumes of certain paraffin hydrocarbons and a series of homologous benzene derivatives. The above compounds are shown in the following table.

Table XIX.

Table of comparison of the Volumes of Aromatic and Paraffin Hydrocarbons at the B.P.

Aromatic Compounds.	V.	Paraffins.	V.
Benzene, C_6H_6	96	Butane, C_4H_{10}	95·9
Toluene, C_7H_8	118·3	Pentane, C_5H_{12}	117·8
m-Xylene, C_8H_{10}	140·0	Hexane, C_6H_{14}	139·93
Mesitylene, C_9H_{12}	162·8	Heptane, C_7H_{16}	162·66
Cymene, $C_{10}H_{14}$	184·5	Octane, C_8H_{16}	186·26
		sec. Octane, C_8H_{16}	184

Kopp's reasoning was somewhat as follows :—

M.V. of Benzene, C_6H_6 96
M.V. of Butane, C_4H_{10}.................. 96

Thus 2 vols. of C = 4 vols. of H, and C = 2 H.
But 1 vol. of $CH_2 = 22$.
Therefore

$$1 \text{ vol. of C} = \frac{22}{2} = 11, \text{ and } 1 \text{ vol. of H} = \frac{11}{2} = 5{\cdot}5.$$

The similarities found in the above table, however, are illusive, for the two series are not comparable ; that is to say, the apparent volumes of the atoms in the nucleus of aromatic compounds are not the same in size as those in the paraffin hydrocarbons. The well-known difference in their constitutions is marked by a very important difference in their volumes, a constitutive effect which is of the nature of a contraction.

The complex C_6H_6 in the paraffin hydrocarbon series possesses a volume of $30 \times 3{\cdot}7 = 111$ at the boiling-point, so that on passing from the aliphatic to the aromatic series a contraction of $111 - 96 = 15$ occurs. This is characteristic of all compounds possessing the hexacyclic ring.

Vol. of complex, C_6H_6 .... $96 + 15 = 111$.
Vol. of butane, C_4H_{10} .... 96.

Therefore 2 vols. of C = 4 vols. of H + 15 = 8 vols. of H, and 1 vol. of C = 4 vols. of H = 4 S.

$$\text{But } 1 \text{ vol. of H} = \frac{22}{6} = 3{\cdot}66;\ 1 \text{ vol. of C} = 22 - 7{\cdot}3 = 14{\cdot}7$$
$$= 4 \times 3{\cdot}67.$$

It must be remarked that the similarity between the amount of the contraction and an integral number of unit-steres of hydrogen volumes is quite a coincidence and does not hold under other conditions.

Direct evidence for the above contraction is found in the following :—

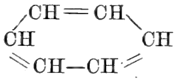
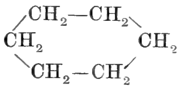
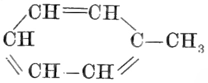
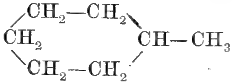
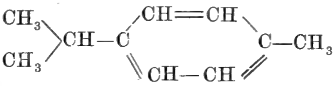
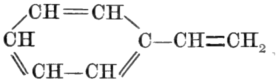
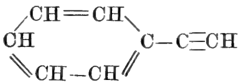
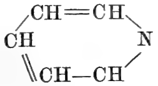
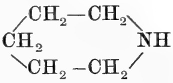
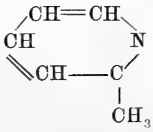
M.V. of Heptylene,	C_7H_{14}	154·8	12·5
M.V. of 6 Hydrotoluene,	C_7H_{14}	142·3	
M.V. of Octylene,	C_8H_{16}	177·6	13·3
M.V. of 6 Hydroxylene,	C_8H_{16}	164·3	

The above comparisons have already been made by Horstmann (*Ber.* 1890, xx. p. 766). The following further evidence may be adduced :—

M.V. of Benzene,	$C_6H_6 + 6\,H = (C_6H_{12}) =$	$96 + 22{\cdot}2 = 118{\cdot}2$	14·2
M.V. of Hexylene,	C_6H_{12}	132·4	
M.V. of *p* Xylene,	$C_8H_{10} + 6\,H = (C_7H_{14}) =$	$140{\cdot}5 + 22{\cdot}2 = 162{\cdot}7$	14·9
M.V. of Octylene,	C_7H_{14}	177·6	

TABLE XX.

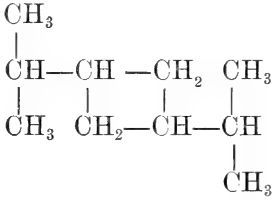
The following gives the values of the Contractions for a number of Hexacyclic Compounds.

Compound.	Formula.	V.	W.	$n \times 3{\cdot}7$.	Δ.
Benzene, C_6H_6 ...		96	30	111·0	−15
Hexamethylene, C_6H_{12}		116·3	36	133·2	−16·9
Toluene, C_7H_8 ...		118·3	36	133·2	−14·9
Hexahydrotoluene C_7H_{14}		141·8	42	155·2	−13·4
Cymene, $C_{10}H_{14}$. .		184·4	54	200	−15·6
Styrolene, C_8H_8...		131·2	40	148	−16·8
Phenlyacetylene, C_8H_6		126·2	38	140·6	−14·4
Pyridine, C_5H_5N. N=35...........		89·3	28	103·6	−14·3
Piperidine, $C_5H_{11}N$		108·8	34	125·8	−17·0
α Picoline, C_6H_7N		111·7	34	125·8	−14·1
Mean	....	...	...	...	−15·2

It is seen from the above table that a contraction of about 15 is observable in compounds possessing a hexacyclic ring. Paraldehyde $C_6H_{12}O_3$, which is a fatty derivative, with a cyclic structure, also manifests a similar contraction (15·8). Certain other compounds, such as thiophene, pyrrol, furfurla, also possess a very marked contraction, that is one of about 11 units. This smaller value is due to the fact that the complexity of these rings is less than those given in the above table. A consideration of the above compounds is reserved for the present.

Diamylene $C_{10}H_{20}$ may, however, be mentioned here.

Formula :



V. 211·3, W. 60, $n \times 3·7$ 222·0, contraction — 10·7.

This case of diamylene, as well as that of paraldehyde, is a striking verification of the idea that there is always a contraction when a compound possesses cyclic structure.

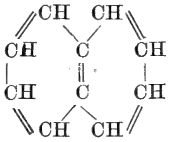
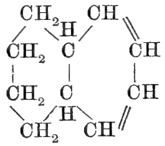
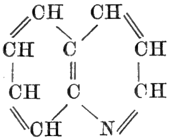
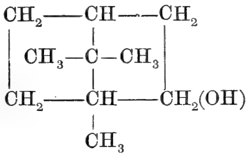
It is now necessary to consider rings of higher complexity than that of benzene for instance (Table XXI. p. 85).

The last compound is referred to in Trans. Chemical Society, 1906, cxi. p. 312. Camphor, which is also considered, may be shown to be subject to a contraction of 30·9 ; but since it is only intended to deal in this paper with those compounds which follow the law of valency, as it is generally understood, a number of ring compounds for which data referred to the boiling-point exist cannot be now considered.

The results brought out by Table XXI. show unmistakably that not only is there a special contraction when a compound possesses ring-structure, but that also the amount of the contraction is a function of the complexity of the ring. The above compounds which are distinguished by similar ring structure are the subjects of similar contractions. The average value of the contraction is shown to be −30·6. It is remarkable that borneol, and of course camphor, substances which have only recently been shown to possess bridged rings, should manifest contractions similar to those of naphthalene or quinolene, which are bicyclic. Camphene would no doubt manifest a similar contraction.

TABLE XXI.

Table showing the Contraction for Double Rings.

Compound.	Formula.	V.	W.	$n \times 3{\cdot}7$.	Δ.
Naphthalene, $C_{10}H_8$.		147·2	48	177·6	−30·4
Naphthyl hydride, $C_{10}H_{14}$		171·2	54	200	−28·8
Quinoline, $C_{10}H_7N$. N=3 S.		187·4	59	218·3	−30·4
Borneol, $C_{10}H_{18}O$. -O- = 2 S.		190·5	60	222	−31·5
Mean contraction ...	....	...	...	...	−30·6

A determination of the molecular volume of a compound at the boiling-point enables us not only to show that it is cyclic, but also, to some extent, the nature of the ring independently of whether it is aliphatic or aromatic.

If the case of carvene $C_{10}H_{16}$ be considered, it will be found to be subject to a contraction similar to that characteristic of benzene compounds, and thus the ring is shown not double.

M.V. of carvene $C_{10}H_{16}$ at the B.P. is 190·3 ; W=56.
Volume of the complex $C_{10}H_{16}$ in the fatty series is

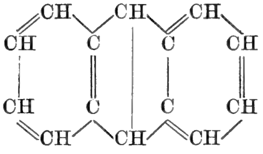
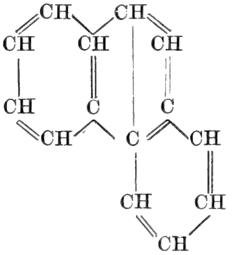
$$=58\times 3{\cdot}7=207{\cdot}2\ ;\ \text{contraction}\ -16{\cdot}9.$$

The following table includes two isomeric ring-compounds of high complexity, namely anthracene and phenanthrene.

They will be shown to manifest still greater contractions than those which have been associated with the cyclic compounds previously considered. This the following table shows.

Table XXII.

Table giving the Contractions associated with Anthracene and Phenanthrene.

Compound.	Formula.	V.	W.	$n \times 3·7$	Δ.
Anthracene, $C_{14}H_{10}$		195·5	66	244·2	48·7
Phenanthrene, $C_{14}H_{10}$		196·2	66	244·2	48

The contractions brought out by the above calculations are quite considerable. No doubt chrysene $C_{18}H_{12}$ would manifest a still higher contraction.

The above investigations show that when compounds possess what is usually considered to be cyclic structure a notable contraction occurs. The contractions have magnitudes which are probably dependent on the number of atoms in the nuclei, and on the kind of nucleus. It is scarcely to be doubted that significant additive relations are also to be noticed under all corresponding conditions. Only the barest outline of the theory can here be given, but it is hoped to amplify it as other compounds come up for consideration. A point of practical utility is likely to be found in the possibility of identifying cyclic or nuclear structure in aliphatic compounds, a matter for which there is very little physical evidence at present at command. A paper on this subject is in preparation.

The Volume Relations of Benzene and Hexamethylene under corresponding conditions.

It will be found that a similar thorough treatment is possible for benzene and hexamethylene as was the case with the paraffin hydrocarbons. The references are Young, Trans. Chem. Soc. 1889.

(a) *At identically reduced Pressures.*

TABLE XXIII.

Relation between the Values of V/W and also of V/V_K for C_6H_6 and C_6H_{12} under corresponding conditions.

C_6H_{12}, W=36.					C_6H_6, W=30.			
P/P_K.	T/T_K.	V.	V/W.	V/V_K.	T/T_K.	V.	V/W.	V/V_K.
·001474	·5096	106·3	2·95	·3466	·5098	87·86	2·93	·3424
·002949	·5354	108·14	3·00	·3526	·5359	89·45	2·98	·3489
·005898	·5646	110·32	3·06	·3597	·5648	91·24	3·04	·3560
·011797	·5985	112·97	3·14	·3684	·5989	93·50	3·12	·3648
·022411	·6330	115·85	3·20	·3777	·6334	95·91	3·22	·3742
·044232	·6759	119·82	3·33	·3907	·6765	99·19	3·30	·3870
·088465	·7277	125·37	3·48	·4088	·7282	103·60	3·45	·4053
·14744	·7714	130·89	3·64	·4263	·7725	108·49	3·61	·4233
·20642	·8041	135·68	3·77	·4424	·8052	112·49	3·75	·4389
·29488	·8428	142·54	3·96	·4648	·8429	117·95	3·93	·4602
·44232	·8901	153·27	4·26	·4997	·8906	127·12	4·24	·4960
·58978	·9267	165·17	4·59	·5385	·9270	137·2	4·57	·5353
·73721	·9566	180·13	5·00	·5873	·9566	149·8	4·98	·5845
·82568	·9720	191·74	5·32	·6252	·9725	160·19	5·34	·6250
·94363	·9914	220·87	6·13	·7201	·9915	182·3	6·07	·7113
·97313	·9960	235·96	6·55	·7693	...	...	...	...
1·00000	1·0000	306·7	8·52	1·0000	1·0000	256·3	8·54	1·0000

The above table is very instructive. It shows in the first place that the volumes of benzene and hexamethylene are very nearly in the ratio 30 : 36 under conditions of corresponding pressure. This ratio is similar to that between the valency numbers. It is thus seen that the ratio of the volumes of carbon and hydrogen is still as 4 : 1, although the series is quite different to that of the paraffin hydrocarbons. Such a regularity is most remarkable, and the probability is very great that the additive relations found to exist under corresponding conditions will ultimately be found to be connected with a kind of liquid structure which has been little suspected.

The volume relations of the atoms in benzene and hexamethylene at the critical point may also be investigated in a direct way.

M.V. of C_6H_{12}	306·7
M.V. of C_6H_6	256·3
Volume of 6H	50·4

Therefore H has a volume of 8·4.

The volume of

$$6C = \text{vol. of } C_6H_6 - \text{vol. of } H_6 = 256{\cdot}3 - 50{\cdot}4$$
$$= 205{\cdot}9$$

The volume of

$$6C = \text{vol. of } C_6H_{12} - \text{vol. of } H_{12} = 306{\cdot}7 - 100{\cdot}8$$
$$= 205{\cdot}9$$

The volume of C is thus $= \frac{205{\cdot}9}{6} = 34{\cdot}3 = 4 \times 8{\cdot}57$.

It is thus conclusively shown that the volumes of benzene and hexamethylene are proportional to their valency numbers at the critical point, and that the volumes of carbon and hydrogen are respectively as 4 to 1, which is the same as the relation existing between their valency numbers. This has been shown to be approximately true at all corresponding pressures.

One other point connected with the above table deserves attention. It has been shown that the homologues of benzene as well as benzene itself possess volumes at the boiling-point which are the same, or nearly the same, as those of certain hydrocarbons of the paraffin series. Thus benzene C_6H_6 has a volume at the boiling point, which is the same as that of butane C_4H_{10} (96), and this is also approximately true at the critical point. V_K for benzene 256·3 ; V_K for butane 251 approx. The volume of toluene C_7H_8 at the boiling-point is also similar to that of pentane C_5H_{12}. Hexamethylene C_6H_6 has a volume (116·3) not very different from that of pentane 117·8. It is found that if the volumes of pentane and hexamethylene be compared under conditions of corresponding pressures from the critical vapour-pressure downwards, the parallelism between the two series of molecular volumes is maintained. No doubt the molecular volumes of butane and benzene under similar conditions are the same or nearly so. These results are of course due to the validity of the law of corresponding states.

It may not be without interest to show in one table that the law of corresponding states and the law of additivity are approximately true for C_6H_6 and C_6H_{12}.

TABLE XXIV.

Table showing the validity of the Law of Corresponding States and of Additivity for C_6H_6 and C_6H_{12}.

C_6H_6.			C_6H_{12}.		
P/P_K.	V.	V/V_K.	V′.	V'/V'_K.	V'/V.
·001474	87·86	·3432	106·3	·3466	1·209
·005898	91·24	·3560	110·32	·3597	1·208
·022411	95·91	·3742	115·85	·3777	1·208
·088465	103·60	·4042	125·37	·4084	1·210
·20642	112·49	·4385	135·68	·4423	1·206
·44232	127·12	·4960	153·27	·4997	1·206
·73721	149·8	·5845	180·13	·5873	1·202
·94363	182·3	·7112	220·87	·7202	1·211
1·00000	256·3	1·0000	306·7	1·0000	1·197

Mean .... 1·206
Theoretical (4 : 1 rule) .... 1·200

The above results show in the first place that the ratio V/V_K for C_6H_{12} is somewhat larger than that for C_6H_6. This is also true of the ratios V/W.

Secondly, the ratio V'/V, which gives the volume of hexamethylene relative to benzene, is very nearly equal to the quotient of their respective valency numbers.

Table XXV. gives the volumes of the compounds under conditions of corresponding pressure, but owing to the fact that the values T/T_K are nearly the same in the two cases, a special investigation of the volume relations of benzene and hexamethylene at corresponding temperatures is unnecessary.

TABLE XXV.

The relation of W to the Critical Coefficients of Aromatic Compounds.

Compound.	W.	P_K.	T_K.	$*\frac{T_K}{P_K}$.	$\frac{1}{W}\frac{T_K}{P_K}$.	V_K.	$\frac{P_K V_K}{T_K}$.
Pentane, C_5H_{12}	32	2510	470·2	·1873	·00585	309·2	1650
Benzene, C_6H_6	30	3639·5	561·5	·1544	·00514	256·3	1661
Hexamethylene, C_6H_{12}	36	3025·2	553·0	·1828	·00508	306·7	1677

* T_K is expressed in degrees centigrade, P_K in cms. of mercury.

While the values of $\frac{1}{W}\frac{T_K}{P_K}$ are very similar for the two compounds C_6H_6 and C_6H_{12}, they are quite different from the value attaching to C_5H_{12}. The difference amounts to about 15 per cent. of the whole. This indicates a large constitutive effect which has already been traced to ring-structure.

In order to show the great probability of similar additive relations being observable at the critical point as at the boiling point in the case of the homologues of benzene, a table is given of critical coefficients quoted by Guye (*Bull. de la Soc. Chim.* (3) xiii. p. 34). These are shown to be subject to a nearly constant diminution in $\frac{T_K}{P_K}$. The critical temperatures are absolute and the pressures are expressed in atmospheres.

Table XXVI.

Table of Critical Coefficients.

Compound.	$\frac{T_K}{P_K}$.		Plus 2·1.	W.	$\frac{1}{W}$ (crit. coeff.).
Hexane, C_6H_{12}	16·92		...	38	·445
Octane, C_8H_{18}	22·58		...	50	·451
Decane, $C_{10}H_{22}$	28·32		...	62	·459
Benzene, C_6H_6	11·25		13·35	30	·445
Toluene, C_7H_8	14·28		16·38	36	·455
o Xylene, C_8H_{10}	17·09	17·07	19·17	42	·456
m ,,	17·66				
p ,,	17·3				
Ethylbenzene	16·24				
Propylbenzene, C_9H_{12}	19·8	19·6	21·70	48	·452
Mesitylene	19·3				
Pseudocumene $C_{10}H_{14}$	19·7				
Cymene	22·8		24·90	54	·461

When the number attaching to benzene and its homologues is augmented by 2·10 and the sum divided by the valency numbers, the quotients are found to be about equal to those obtained by dividing the critical coefficients of the paraffin hydrocarbons by their respective valency numbers. It must therefore be concluded that 2·1 represents the change in $\frac{T_K}{P_K}$ which occurs on passing from the paraffins to the aromatic compounds. Since $V_K = \frac{T_K}{P_K} \times$ constant, the molecular critical volumes are proportional to the critical coefficients and are thus subject to similar additive relations. It is, however, highly probable that these would be still more clearly shown in the molecular critical volumes. The volumes of the side-chains in the benzene homologues are thus equal to corresponding paraffinoid residues, while the nucleus undergoes a contraction.

M.V. of C_6H_{12} at B.P. 116·3. M.V_K. of $C_6H_{12} = 306{\cdot}7$.
Ratio 2·64.

M.V. of C_7H_{10} (Toluene) at B.P. 118·3. Calculated M.V_K. of
$C_7H_{10} = 118{\cdot}3 \times 2{\cdot}64 = 313{\cdot}3$,

Vol. of CH_2 at the Critical Point $=$ Vol. of $C_7H_8 -$ Vol. of C_6H_6
$= 313{\cdot}3 - 256{\cdot}3 = 57$.

Vol. of H in side-chain $= \frac{57}{6} = 9{\cdot}5$,

which is about equal to that in the paraffin hydrocarbons.

SUMMARY.

It has been found that at the *melting-point* and at equal intervals of temperature therefrom the molecular volumes of the *olefines* may be expressed by the following formula:

$$\text{M. vol. } C_nH_{2n}|{=}| = 6nS - 2{\cdot}62 = WS - |{=}|$$

the *acetylenes* by the following:

$$\text{M. vol. } C_nH_{2n-2}|{\equiv}| = 6nS - 2S - 3 = WS - |{\equiv}|\,;$$

the specific gravities of the above compounds are at equal intervals of temperature from the melting-points equal fractions of the specific gravities at those points.

The molecular volume of a single *olefine* and *acetylene* is at the boiling-point expressed by the following formulæ:—

$$\text{M. vol. of } C_nH_{2n} = 6nS \text{ (Olefines).}$$

$$\text{M. vol. of } C_nH_{2n-2} = 6nS - 2S \text{ (Acetylenes).}$$

The value of S is usually about 3·7, but may vary slightly from compound to compound. In so far as 3·7 is constant the above formulæ are general for a series.

3·7 is the atomic volume of H. The atomic volume of carbon is 14·8, which numbers are also those of similar atoms in the paraffins.

Thus $C = 4S = 4\frac{V}{W}$, the symbols having the same meaning as before.

Aromatic Compounds.

It is found that the possession of ring structure on the part of a compound corresponds with an extra contraction—that is to say, the atomic volumes in ringed molecules are always less than the volumes of similar atoms in straight chain compounds, so that the total molecular volume is on the whole less than that of a similar complex in the fatty series.

The relative volumes of atoms in the nuclei are the same as those in straight chain compounds.

Thus it is found that the volumes of benzene and hexamethylene are proportional to their valency numbers from the critical point downwards, so that $C=4H$ as before.

The volumes of the atoms in aliphatic side chains are, however, the same as in the paraffins.

It has been found that the critical coefficients of benzene and its homologues manifest similar relations to those shown by the molecular volumes.

Note.—It should be mentioned that Barlow and Pope take the view that the relative volumes of the atoms in the molecular complexes, aromatic as well as aliphatic, are always maintained and that the volume of an atom in a compound is always proportional to its fundamental valency.

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V. *The Decomposition of Water Vapour by Electric Sparks.*

By ALFRED HOLT, Jun., *and* EDWIN HOPKINSON [*].

THE decomposition of a compound gas such as water-vapour, or carbon dioxide, by electric sparks, and the separation and arrangement of the resulting products about the electrodes, is of special interest since it may be expected to show how far the hypothesis of electrolysis in liquids is applicable to gases.

Almost half a century ago Perrot (*Ann. Chim. et Phys.* 1861, p. 161) showed that the decomposition of water-vapour took place along the entire path of the spark and not only in the neighbourhood of the electrodes, and that the gas collected from the anode contained an excess of oxygen, while that from the cathode contained an excess of hydrogen, their amounts being equivalent to the copper deposited in a voltameter placed in the same circuit. His experiments

[*] Communicated by the Authors.

proved, therefore, that an electric current is conducted through water-vapour in a similar manner as through liquid water.

J. J. Thomson ('Recent Researches in Electricity and Magnetism,' Appendix), in repeating the experiments of Perrot, found that the pole at which the excess of oxygen or hydrogen appeared depended on the length of the spark, for when it was extremely short and resembling an arc the hydrogen was found at the anode and the oxygen at the cathode; whereas with a long spark, the excess of hydrogen appeared at the cathode and the excess of oxygen at the anode. A critical position could be found between long and short sparks at which the excess of hydrogen was sometimes collected at the anode and sometimes at the cathode. If, under these circumstances, Leyden jars were introduced into the circuit, the hydrogen always appeared at the anode and the oxygen at the cathode, while the critical spark-length was found to be increased. This was explained by Thomson by supposing that the separation of the oxygen and hydrogen was the result of the motion of charged hydrogen towards one pole and oppositely charged oxygen towards the other, the charges on the molecules of the gases being different when the discharge resembled an arc or spark.

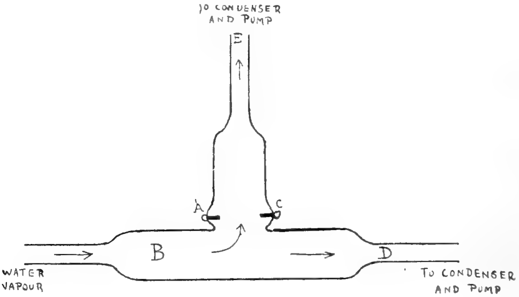
In a separate series of experiments he showed that there was an alteration in the sign of the charges on the molecules of these gases when the discharge changed from an arc to a spark, or *vice versa*.

More recently, Chapman and Lidbury (J. C. S. Trans. 1902, p. 1301) noticed that the position in which the water-vapour entered the spark had a marked effect on the separation of the products of decomposition, for the excess of oxygen always appeared at the pole situated furthest from the point at which the current of vapour entered. It followed, therefore, that a position could be found at which there was no separation, pure electrolytic gas being collected at either pole. They further observed that when the vapour entered near the anode, the amount of separation of the oxygen and hydrogen was very much less than when it entered near the cathode. Their experiments led to the conclusion that it was not possible to give a complete explanation of the phenomena by an hypothesis based solely on the theory of electrolysis in liquids.

While carrying out another investigation, one of us noticed that oxygen and hydrogen could be separated to a considerable extent by the difference between the rates at which they diffused through water-vapour at low pressure.

This separation was well shown by the following experiment:—A stream of water-vapour at about 15 mm. pressure was drawn into the tube B (fig. 1), where it divided, one half passing straight on to a condenser D and pump, while the other half passed through the spark between A and C, and on to a second condenser, E, and pump. Both condensers were kept at the same temperature, and both pumps were worked at approximately similar rates. Under these conditions it was found that the hydrogen produced by the spark diffused into the stream of vapour passing from B to D, where it appeared in excess, while a proportionate excess of oxygen was collected from E, since this gas could not readily diffuse back against the water-vapour current passing from B to E.

Fig. 1.



No. of experiment.	Vol. of excess of hydrogen collected from D.	Vol. of excess of oxygen collected from E.	Total vol. of electrolytic gas collected from D+E.
1 …………	2·14 c.c.	1·04 c.c.	11·2 c.c.
2 …………	1·94 c.c.	0·94 c.c.	10·5 c.c.
3 …………	2·20 c.c.	1·07 c.c.	10·0 c.c.

It seemed possible that the separation of the oxygen and hydrogen in the spark might really be a diffusion-phenomenon, for most of the results obtained by Perrot and by Chapman and Lidbury can be explained by this hypothesis.

When electric sparks pass through water-vapour contained in an apparatus like that used by Chapman and Lidbury, a mixture of oxygen and hydrogen is produced in the path of the spark. The hydrogen, on account of its great power of diffusion, tends to become uniformly distributed throughout the apparatus, even if a rapid current of vapour is passing through it.

The distribution of the oxygen, however, depends far more on the water-vapour current; it will be divided according to the position of the entrance-tube. When this tube is in the neighbourhood of the cathode, the greater portion of the oxygen is driven out at the anode, the result being that an excess of oxygen is found at the anode and an equivalent excess of hydrogen at the cathode.

If this entrance-tube is brought to the anode, the hydrogen, on account of its power of diffusion, again tends to become equally distributed through all parts of the apparatus. The greater portion of the oxygen, however, is now swept out at the cathode, so that it appears in excess at that pole while hydrogen is found at the anode.

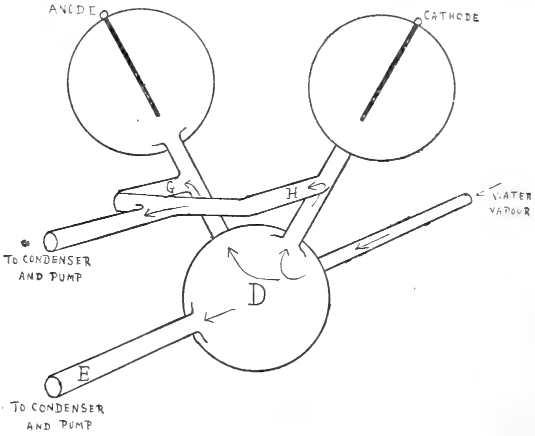
If equal quantities of oxygen are swept towards both poles, pure electrolytic gas should be collected from both anode and cathode, and Chapman and Lidbury found that this condition was reached when the entrance-tube was situated near the centre of the spark-gap.

The faster the stream of vapour passes through the apparatus the less easily does the oxygen diffuse against it, whereas the distribution of the hydrogen is almost unaffected, so the amount of separation of the decomposition products should increase as the stream of vapour becomes more and more rapid.

In order to investigate the truth of this view of the part played by diffusion, we have carried out a number of experiments with both water-vapour and carbon dioxide, for it should be impossible to obtain any separation of the oxygen and carbon monoxide produced by the passage of sparks through this latter gas, since both carbon monoxide and oxygen diffuse at almost similar rates, and would, consequently, become uniformly distributed in all parts of the apparatus.

In the first series of experiments, the discharge from an induction-coil with a large condenser was passed through a spark-tube of the shape shown in fig. 2 (p. 96). A rapid current of water-vapour entered the bulb D, which was blown in the centre of the spark-gap. The stream divided, any gas which might diffuse out of the spark was driven away through the side-tube E to a condenser which was surrounded by a freezing-mixture, while the decomposition-products remaining in the path of the spark were swept by the stream of vapour through the two side-tubes G and H, which communicated with another condenser also surrounded by a freezing-mixture.

Fig. 2.



After condensation of the vapour in the condenser, the gases, which consisted of mixtures in different proportions of oxygen and hydrogen, were removed by automatic Sprengel pumps, and were collected separately and analysed in the same manner as in the experiments of Chapman and Lidbury.

A voltameter was placed in the circuit so that comparison could be made between the amount of decomposition of the water-vapour and the quantity of electricity passing in the spark.

The rate at which the water-vapour passed through the apparatus was varied, and it was noticed that when the current of vapour was slow the separation of the oxygen and hydrogen was small, but that it increased rapidly as the stream became faster, until practically pure hydrogen was collected from the diffusion-bulb D.

If the separation of the oxygen and hydrogen is really a diffusion phenomenon, one would expect that with this apparatus the gas collected through E should contain an excess of hydrogen, while that from G and H should contain a proportionate excess of oxygen; for it is improbable that any large amount of oxygen could diffuse back into the bulb D against the rapid current of water-vapour passing from D to G and rom D to H. The faster the stream of vapour was passing, the less easily could the oxygen diffuse against it, and hence the larger the excess of hydrogen found in D.

The following results were obtained with this apparatus:—

No. of experiment.	Vol. of H liberated in voltameter.	Excess of Hydrogen from Bulb D.			Excess of Oxygen from G and H.		
		Direct estimation by volume.	Estimated by analysis.	Vol. of excess of H if 1 c.c. of H was liberated in voltameter.	Direct estimation by volume.	Estimated by analysis.	Vol. of excess of O if 1 c.c. H was liberated in voltameter.
1.	0·545 c.c.	6·06 c.c.	6·05 c.c.	11·10 c.c.	2·96 c.c.	2·89 c.c.	5·12 c.c.
2.	0·795 c.c.	8·86 c.c.	...	11·14 c.c.	4·13 c.c.	...	5·19 c.c.
3.	1·175 c.c.	7·88 c.c.	...	6·70 c.c.	3·87 c.c.	...	3·30 c.c.
4.	1·005 c.c.	6·41 c.c.	6·38 c.c.	6·35 c.c.	3·16 c.c.	3·14 c.c.	3·12 c.c.
6.	0·312 c.c.	5·11 c.c.	5·01 c.c.	16·06 c.c.	2·52 c.c.	...	8·07 c.c.

In three experiments the total gas collected from the bulb D was carefully analysed in order to see whether the percentage of oxygen contained in it diminished as the stream of vapour became more and more rapid.

In the first experiment (No. 6) the stream of vapour was comparatively slow, and the ratio $\frac{O_2}{H_2}$ was found to be

$$\frac{1·274}{7·564} = 0·169,$$

therefore the gas contained 16·9 per cent. oxygen.

In the second experiment (No. 2) the current of water-vapour was more rapid, and the ratio $\frac{O_2}{H_2}$ was

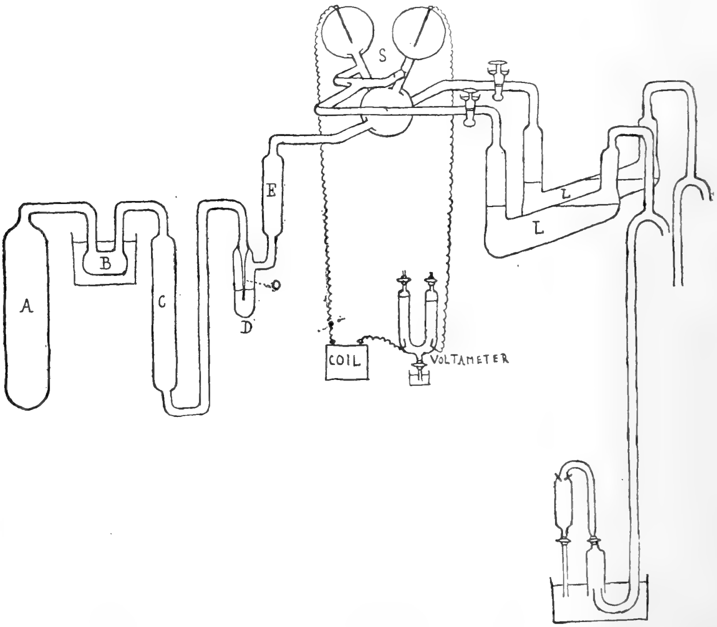
$$\frac{0·34}{9·54} = 0·035,$$

so that the gas contained only 3·5 per cent. oxygen.

In a third experiment (No. 5), in which the stream of vapour was extremely rapid, nearly pure hydrogen was obtained. These results are exactly what one would expect if the separation of the oxygen and hydrogen is a diffusion-phenomenon. A number of experiments were next performed with the same spark-tube, but a stream of carbon dioxide was substituted for the water-vapour.

The arrangement of the apparatus is shown in fig. 3.

Fig. 3.



The carbon dioxide was generated by heating in an air-bath, pure sodium bicarbonate, contained in the tube A.

The water produced by the decomposition of the bicarbonate was partly condensed in B, which was immersed in cold water, after which the gas was passed through a mixture of fused calcium chloride and anhydrous sodium carbonate contained in C so as to completely dry it. The dry gas next passed through a very fine capillary tube, O, dipping into concentrated sulphuric acid contained in the vessel D. The capillary tube was of such a bore that when there was practically a vacuum on one side of it and carbon dioxide at atmospheric pressure on the other, the gas would pass through at the rate of about five litres (at N.T.P.) per hour. This was about the mean rate of the water-vapour current in the previous experiments.

After bubbling through the concentrated sulphuric acid, any spray being removed by the glass-wool E, the gas entered the spark-tube, where, as in the water-vapour experiments, it divided into two streams. After being sparked, the gas passed through the absorber L, in which the carbon dioxide was removed by concentrated potash solution. The residual carbon monoxide and oxygen were then pumped off and analysed by explosion.

The quantity of electricity passing in the spark was again measured by a voltameter placed in the circuit.

Several experiments were carried out, but in no case could the separation of the carbon monoxide and oxygen be detected, for the gas collected from the bulb G and from H and K always contained these gases in the proportion to form carbon dioxide. The rate at which the current of carbon dioxide passed through the apparatus was varied by altering the diameter of the capillary tube O, but it was found to be entirely without effect except as regards the total amount of decomposition, which increased as the stream of gas became faster.

Since carbon monoxide and oxygen diffuse at practically the same rate, one would not expect to find any separation occurring in the spark, and the above results show that there is none.

The next series of experiments consisted of a repetition of those carried out by Chapman and Lidbury on the effect caused by the position in which the stream of gas entered the spark.

A stream of carbon dioxide was again substituted for the current of water-vapour.

The gas was allowed to enter the spark-tube at either the anode or cathode, or at any intermediate position, and the size and shape of the bulbs round the electrodes were also greatly varied, but in every experiment the products of decomposition consisted of carbon monoxide and oxygen in combining proportions.

No separation could be detected.

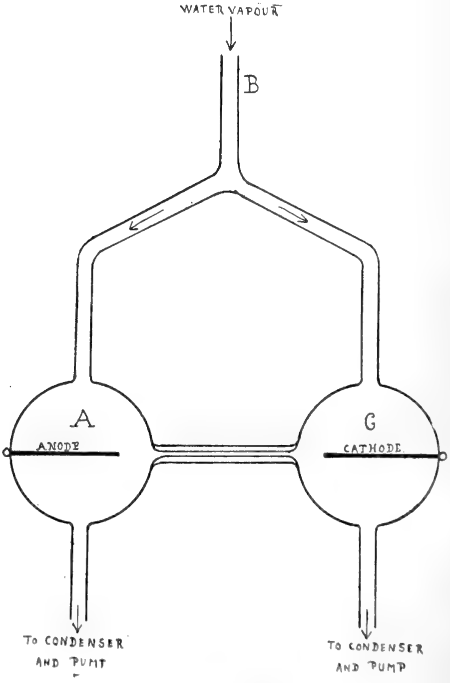
A further series of experiments were carried out in order to study the effect of passing a more rapid current of water-vapour through one end of a spark-tube than through the other. The apparatus employed is illustrated in fig. 4.

A stream of water-vapour passed along the tube B and divided, one portion passing through the bulb A to a condenser and pump, and the other passing through C to a second condenser and pump. The tube from A to C through which the spark passed had a bore of one millimetre.

By altering the temperature of one of the condensers or by changing the speed of one of the pumps, the current of water-vapour passing through A could be made either faster or slower than that passing through C.

The amount of separation of oxygen and hydrogen obtained with this apparatus was found to depend on the difference between the velocities of the two streams. When the more rapid current passed through the bulb containing the cathode, an excess of hydrogen was obtained at that pole, while oxygen appeared at the anode; but if the faster stream passed through the anode bulb, the poles at which the excesses of oxygen and hydrogen were collected were reversed.

Fig. 4.



Further, the amount of the excesses of oxygen and hydrogen was much less when the more rapid stream of vapour passed through the anode bulb.

The following details of an experiment will illustrate these observations:—

1. More rapid current through cathode bulb.

Hydrogen collected in voltameter in same circuit.	Excess of hydrogen from cathode.	Excess of hydrogen for 1 c.c. hydrogen liberated in voltameter.	Excess of oxygen from anode.	Excess of oxygen for 1 c.c. hydrogen liberated in voltameter.
3·055 c.c.	4·529 c.c.	1·482 c.c.	2·241 c.c.	0·733 c.c.

2. More rapid current through anode bulb.

Hydrogen collected in voltameter in same circuit.	Excess of hydrogen from anode.	Excess of hydrogen for 1 c.c. hydrogen liberated in voltameter.	Excess of oxygen from cathode.	Excess of oxygen for 1 c.c. hydrogen liberated in voltameter.
2·673 c.c.	0·622 c.c.	0·232 c.c.	0·173 c.c.	0·065 c.c.

These different results obtained with the same apparatus are easily explicable as a diffusion phenomenon, for when the current of water-vapour which passes down one limb is more rapid than that down the other, it is evident that there is a larger volume of gas in the quicker stream into which the hydrogen can diffuse, and since it becomes, or tends to become, equally distributed throughout the water-vapour, the greater part of it will be collected where there is the more rapid current. The oxygen can only be affected to an extent equal to one-sixteenth that of the hydrogen, so that very little more of it is found to pass into the faster than into the slower stream.

A consideration of these experiments leads to the conclusion that the products of decomposition of a compound gas are not arranged in such a manner that one constituent is liberated at the anode and the other at the cathode.

A homogeneous mixture is first formed in the path of the spark, and the separation is due to gaseous diffusion against the current of water-vapour. When both the decomposition products diffuse at nearly similar rates, there is no perceptible separation.

Though many of the phenomena attending the decomposition of a gas by electric sparks can thus be readily explained by diffusion, this explanation, in its unmodified form, is insufficient to account both for the important fact observed by Thomson that when very short sparks are used the poles at which the excesses of oxygen and hydrogen appear are reversed, and for the interesting observation made by Chapman and Lidbury, that the total amount of water-vapour decomposed and the extent of the separation of the decomposition-products is very much greater when the current of vapour enters the spark-tube in the neighbourhood of the cathode instead of near the anode.

When sparks are passed between platinum electrodes in water-vapour, some of the metal is shot or sprayed off the electrodes in the form of extremely minute particles which adhere to the surface of the glass, and gradually produce a metallic film on those portions of the spark-tube which immediately surround the anode and cathode. The amount of metal deposited from the anode is extremely small compared with that from the cathode.

The minute particles which constitute this metallic spray have in all probability a very powerful catalytic action, since they must closely resemble platinum-black, and the film which they form when deposited on the glass would also have, though in a lesser degree, the property of combining electrolytic gas.

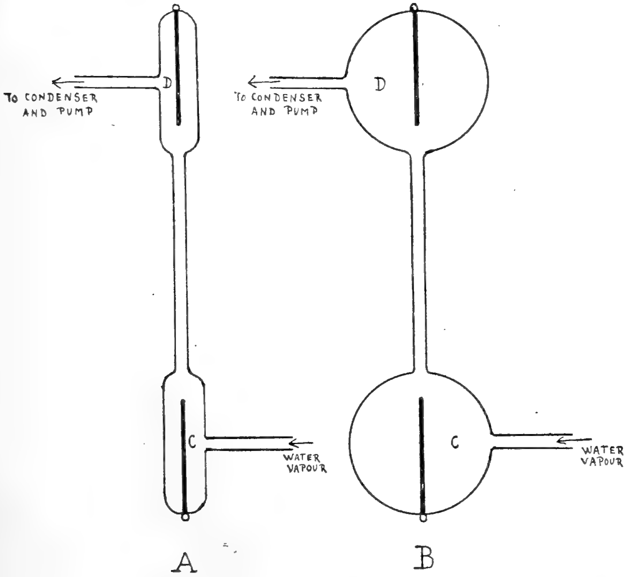
It appeared to us that this metallic spray and deposit, with its catalytic action, must influence the amount of water-vapour decomposed by the sparks, and might possibly account for the various phenomena not wholly explicable by the hypothesis of gaseous diffusion.

In order to study this catalytic action, it was necessary to carry out parallel experiments with platinum and some metal which did not give any perceptible spray under the influence of the spark, and which did not react chemically with water-vapour when heated to a moderate temperature.

Aluminium seemed very suitable for this purpose as it does not readily oxidize in water-vapour, and no metallic film can be formed from it.

A series of spark-tubes of the shape shown in fig. 5, A and B, were used, the sole difference between them being the diameter of the bulbs surrounding the electrodes, which in type A was 1 cm., and in type B 5 cms. In some tubes the electrodes were of aluminium, and in others of platinum. With this latter metal various thicknesses of electrodes were tried in order to see whether the results were affected, for the thinner the electrode the hotter would the cathode become under the influence of the spark discharge, and the amount of metal shot off increases with rise of temperature.

Fig. 5.



The stream of water-vapour at about 12 mm. pressure entered the tubes at C, and after being decomposed by the spark passed out at D to a condenser surrounded by a freezing-mixture whence the electrolytic gas was removed by a pump, and estimated by explosion. The electrode at C or D could be made anode or cathode at will by simply reversing the current.

The experiments were carried out as follows :—

The whole apparatus being completely evacuated, a current of water-vapour, the velocity of which was measured by the volume of water collected in the condenser per hour, was passed through the spark-tube, and C was made the cathode.

After ten minutes' continuous sparking the current was switched off and the electrolytic gas produced was removed by the pump and estimated. D was then made the cathode, and sparks were passed for another ten minutes, when the resulting oxygen and hydrogen were pumped off and estimated as before. The ratio of the amount of the electrolytic gas obtained when the cathode was at C to that when it was at D could then be calculated.

The two observations were made as rapidly as possible so that the rate of the stream of water-vapour might be assumed to be the same in each case. No voltameter was placed in the circuit, but care was taken that the amount of electricity passing during each ten minutes of sparking was approximately the same.

Without altering the apparatus in any way or admitting air to it, a series of pairs of experiments were made in the manner just described.

The reason for doing this, and not cleaning off the metal deposited on the glass of the spark-tube during each of these experiments, was to see to what extent the metallic film, apart from the actual spray, exercised a catalytic influence. During each ten minutes' sparking the film would become thicker and denser, while the amount of spray round the cathode would remain fairly constant, since it only depends on the spark and the consequent heating of the electrode. If, then, the ratio of the amount of electrolytic gas collected when the cathode was at C to that when it was at D was found to alter through successive pairs of experiments, it would show that the metallic film exercised a catalytic influence apart from that of the spray round the heated cathode.

The following table gives the results of some of these experiments.

No. of pairs of experiments.	Electrodes.	Diameter of bulbs round electrodes.	Vol. of electrolytic gas collected in 10 mins. when cathode was at C. A.	Vol. of electrolytic gas collected in 10 mins. when cathode was at D. B.	Ratio B/A.
1.	*Platinum* wire 0·5 mm. diameter.	1 cm.	8·58 c.c.	2·08 c.c.	0·242
2.			8·09 c.c.	1·62 c.c.	0·201
3.			8·96 c.c.	1·62 c.c.	0·181
4.	*Aluminium* wire 0·5 mm. diameter.	1 cm.	2·44 c.c.	2·49 c.c.	1·018
5.			5·96 c.c.	6·14 c.c.	1·031
6.			7·17 c.c.	7·50 c.c.	1·047
7.	*Platinum* wire 1 mm. diameter.	1 cm.	2·58 c.c.	1·78 c.c.	0·690
8.			1·99 c.c.	1·32 c.c.	0·663
9.	*Platinum* wire 0·5 mm. diameter.	5 cms.	3·18 c.c.	2·94 c.c.	0·924
10.			3·14 c.c.	2·87 c.c.	0·914

In the above table, experiments 1–3 when compared with 4–6 show the enormous effect the metal composing the electrodes exerts on the amount of electrolytic gas obtained when the stream of water-vapour enters the spark-tube at the anode and cathode respectively. Experiments 1–3 compared with 7–8 show the difference between thick and thin electrodes. In experiments 7–8, where the electrodes are thick and therefore become only slightly heated, there is a very small amount of spray, and consequently the difference in the amount of gas collected when the vapour enters at the cathode compared with that when it enters at the anode is smaller than in experiments 1–3.

Experiments 1–3 and 9–10 show the effect of large and small bulbs round the electrodes. It will be noticed that when the bulbs are large, the effect is the same as when the electrodes are very thick. This difference between the amount of gas collected when the water-vapour enters at the anode or cathode can be explained by the catalytic action of the platinum spray.

In the first experiment of any series the spark-tube is clean and C is made the cathode, as already mentioned. The vapour enters at the cathode, is partially decomposed by the spark and passes over the anode on its way out of the tube at D. The amount of spray and heating at the anode being negligible, and the surrounding glass being clean, no recombination of the electrolytic gas produced in the spark takes place.

D is next made the cathode; the electrolytic gas produced in the spark passes over its heated surface, from which particles of metal are being shot off; and some recombination of the oxygen and hydrogen occurs; consequently a smaller amount is collected than when the cathode was at C.

When the electrodes are thick the heating of the cathode is less, and a smaller amount of metal is shot off: there is therefore less recombination; and if a very thick cathode is used there may be little difference between the amounts of gas collected according as this pole is at C or D.

It will be noticed in the table that in the case of platinum each successive pair of experiments gives a lower value for the ratio B/A, that is to say the amount of recombination increases every time D is made the cathode. Since the amount of spray shot off the cathode does not vary from one experiment to the next, this increase of recombination must result from the catalytic action of the metallic film which is deposited on the walls of the tube. This film becomes denser with each experiment, and so presents a larger active surface to the electrolytic gas, as it passes over it.

When the bulbs round the electrodes are of large diameter, less oxygen and hydrogen is combined by the metallic particles, since there is a larger volume of water-vapour into which the electrolytic gas produced by the spark can diffuse, and so escape the catalytic action.

As the difference between the behaviour of aluminium and platinum when used as electrodes during the decomposition of water-vapour by electric sparks seemed of considerable interest, we were led to examine the action of other metals as well.

A number of spark-tubes of the shape shown in fig. 4 A were used, and the pairs of experiments were carried out exactly as already described. As it was not possible to obtain all the metals in wires of equal thickness, the values for the ratio B/A for one metal are not strictly comparable with those for another.

The following tables give a summary of the results obtained with different metals :—

Electrodes.	Vol. of electrolytic gas collected in 10 mins. when cathode was at C. A.	Vol. of electrolytic gas collected in 10 mins. when cathode was at D. B.	Ratio B/A.
Gold wire 0·5 mm. diameter.	6·38 c.c.	7·79 c.c.	0·929
	8·12 c.c.	7·32 c.c.	0·901
	5·66 c.c.	4·27 c.c.	0·754
Silver wire 1·0 mm. diameter.	8·41 c.c.	8·18 c.c.	0·974
	7·94 c.c.	7·71 c.c.	0·971
	7·84 c.c.	7·61 c.c.	0·970
Copper wire 1·0 mm. diameter.	7·36 c.c.	6·88 c.c.	0·936
	8·24 c.c.	7·52 c.c.	0·912
Iron wire 0·3 mm. diameter.	5·09 c.c.	5·41 c.c.	1·062
	5·22 c.c.	5·44 c.c.	1·042
Nickel wire 0·3 mm. diameter.	5·83 c.c.	5·87 c.c.	1·006
	5·75 c.c.	5·95 c.c.	1·035

Electrodes.	Vol. of electrolytic gas collected in 10 mins. when cathode was at C. A.	Vol. of electrolytic gas collected in 10 mins. when cathode was at D. B.	Ratio B/A.
Cadmium strips of foil 1·0 mm. diameter.	6·04 c.c.	6·50 c.c.	1·076
	6·41 c.c.	6·55 c.c.	1·023
Zinc strips of foil 1·5 mm. diameter.	4·65 c.c.	4·70 c.c.	1·058
	4·59 c.c.	4·95 c.c.	1·077
Tantallum filament from lamp.	4·70 c.c.	4·96 c.c.	1·056
	4·68 c.c.	4·52 c.c.	1·108
Magnesium wire 0·5 mm. diameter.	4·39 c.c.	4·75 c.c.	1·082
	4·39 c.c.	4·71 c.c.	1·074
Palladium wire about 0·4 mm. diameter.	8·54 c.c.	0·99 c.c.	0·116
	0·89 c.c.	0·31 c.c.	0·352
	0·56 c.c.	0·28 c.c.	0·510
Rhodium wire about 1·0 mm. diameter.	2·84 c.c.	1·84 c.c.	0·648
	1·70 c.c.	0·79 c.c.	0·464
	2·81 c.c.	0·95 c.c.	0·340
Ruthenium small buttons about 3 mm. diameter.	2·63 c.c.	2·23 c.c.	0·845
	2·51 c.c.	2·18 c.c.	0·803
Osmium filament from "Osmi" lamp.	7·34 c.c.	5·05 c.c.	0·685
	6·75 c.c.	3·62 c.c.	0·536
	5·36 c.c.	3·35 c.c.	0·625
Iridium wire about 1·0 mm. diameter.	6·34 c.c.	0·71 c.c.	0·112
	5·43 c.c.	0·59 c.c.	0·108
	6·38 c.c.	0·57 c.c.	0 090

It will be seen from these tables that all those metals which oxidize when heated in air behave like aluminium. They give no spray and cause no recombination of the electrolytic gas produced by the spark. They do not appear to be oxidized by the water-vapour, but possibly a very thin skin of oxide is formed which prevents any metal being shot off the cathode, for several of them have been shown by Crookes (Proc. Roy. Soc. 1891, vol. l. p. 88) to disintegrate in other gases.

Those metals which do not oxidize when heated in air to a moderate temperature, or which form a volatile oxide as in the case of osmium, behave, with the exception of silver and palladium, exactly like platinum. They disintegrate in water-vapour and bring about more or less recombination of the electrolytic gas. Silver, though spraying readily, does not appear to combine oxygen and hydrogen. Palladium behaves exceptionally, for the ratio B/A is found to steadily increase in each successive pair of experiments, instead of decreasing, as in the case of the other metals.

When this metal is in a state of very fine subdivision (palladium black), it is known to exert intense catalytic action on a mixture of oxygen and hydrogen. The metal rapidly becomes heated through the energy with which these gases are combined on its surface.

During the experiments with electrodes of this metal, it was noticed that the film deposited on the tube about D became heated when C was the cathode, a phenomenon not observed in the case of any other metal; and though the amount of gas collected when D was the cathode was found to diminish in each successive experiment, yet when C was the cathode it was found to diminish far more rapidly, especially at first, and hence caused the increase in the ratio B/A. As the film around D became heated, it was probable that the steady diminution in the amount of gas collected in each experiment when C was the cathode was the result of recombination. To see if this was the case a series of experiments was carried out in exactly the same manner and with the same spark-tube, only when C was the cathode, the metallic film round D was kept cold by water so as to prevent, as far as possible, any catalysis. The results then obtained were in exact agreement with the other platinum metals (table, p. 109).

The observations of Chapman and Lidbury that the degree of separation of the oxygen and hydrogen is less when the stream of water-vapour enters the spark near the anode than near the cathode can now receive a complete explanation.

When the vapour enters near the anode the greater part of

No. of Experiment.	Volume of electrolytic gas collected in 10 mins. when cathode was at C. A.	Volume of electrolytic gas collected in 10 mins. when cathode was at D. B.	Ratio B/A.
1.	6·739 c.c.	2·607 c.c.	0·386
2.	6·293 c.c.	0·644 c.c.	0·102
3.	6·125 c.c.	0·371 c.c.	0·060
4.	6·237 c.c.	0·317 c.c.	0·051

the oxygen is swept towards the cathode, where it appears in excess, while the hydrogen is equally distributed between the two poles. A considerable quantity of the electrolytic gas passing over the cathode is, however, recombined there, so that less oxygen is left to appear in excess at that pole, and the hydrogen collected at the anode is proportionately diminished.

If the point of entry of the stream of vapour is near the cathode, a volume of oxygen equal to that which in the former case passed over this electrode, and was partially recombined, is now driven out at the anode, but its amount is not sensibly diminished there, since hardly any recombination takes place near this latter pole.

An explanation of the results obtained by Thomson can also be given, though the conditions in his experiments and in ours were somewhat different, since his steam was at atmospheric pressure, whilst our water-vapour was at about 12 mm. pressure, and the amount of metal shot off the cathode, and hence the extent of catalysis, increases as the pressure decreases. The cathode is surrounded by particles of metal which exert a catalytic action on electrolytic gas, so that a zone of recombination is found around that pole ; and one of us has already pointed out that if a homogeneous mixture of oxygen and hydrogen (as is found in the path of the spark) is produced inside such a zone, an excess of hydrogen may be expected outside it, while the oxygen becomes concentrated within (Phil. Mag. 1907, vol. xiii. p. 630).

If the electrodes are close together, almost the whole spark may be inside this recombination zone ; and as, under these conditions, the gas swept through the cathode by the water-vapour current will chiefly consist of that portion within the zone, an excess of oxygen should be found at the cathode, and a proportionate excess of hydrogen at the anode. When the spark is long, the greater portion of the electrolytic gas is produced outside the zone. The water-vapour enters at the centre of the spark; and if no recombination occurs near the cathode, equal quantities of oxygen will be swept towards each pole, and the hydrogen being uniformly distributed, pure electrolytic gas would be collected at both anode and cathode.

But recombination is taking place near the cathode, and consequently some of the electrolytic gas is removed there, so that a smaller quantity of oxygen is swept out at that pole than at the anode. The hydrogen, however, still tends to become distributed uniformly throughout the apparatus, so that it now appears in excess at the cathode.

The experiments described in this paper lead us to the conclusion that when electric sparks pass through a compound gas such as water-vapour or carbon dioxide, the separation and arrangement of the decomposition products is not an electrical phenomenon, but results from gaseous diffusion. The hypothesis of electrolysis in liquids is therefore inapplicable.

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VI. *Interaction of Dynamical Systems.*

By R. Hargreaves[*].

If there are two groups of coordinates q and χ with corresponding velocities $\dot{q}$ and $\dot{\chi}$, the kinetic energy of a system embracing both groups generally contains terms which are products of $\dot{q}$ and $\dot{\chi}$, as well as functions quadratic in the velocities of the separate groups; and the product-terms give a mutual or composite action of the groups in an explicit way. This is also the case when the kinetic energy is expressed in terms of the momenta. But if the velocities of one group and the momenta of the other are used, it is characteristic that the energy shall appear as a sum of detached quadratics, and all trace of composite action is lost.

It is proposed to deal with this and other cases where a mutual action is concealed. For the case stated a kinetic potential of mixed type is introduced, *i. e.* one involving the velocities of one group and the momenta of the other. It is clear that when coordinates of the second group are absent and the momenta invariable, we have the problem of ignored coordinates, which therefore appears as a special case.

§ 1. Potential energy in the form of a function of coordinates only may be omitted, as its presence or absence does not affect the questions considered. A kinetic energy

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[*] Communicated by the Author.

expressed in terms of velocities only is denoted by $Q(\dot{q})$; from it are derived

$$\text{momentum } p_r = \frac{\partial Q}{\partial \dot{q}_r}, \text{ and force } = \dot{p}_r - \frac{\partial Q}{\partial q_r} . \quad . \quad \text{(i)}$$

A kinetic energy expressed in terms of momenta only is denoted by $P(p)$; from it are derived

$$\text{velocity } \dot{q}_r = \frac{\partial P}{\partial p_r}, \text{ and force } = \dot{p}_r + \frac{\partial P}{\partial p_r} . \quad . \quad . \quad \text{(ii)}$$

It will then be shown that a composite system for which the kinetic energy is *given* in the form

$$E = Q(\dot{q}) + P(\varpi), \quad . \quad . \quad . \quad . \quad . \quad \text{(iii } a)$$

may be treated with the aid of a kinetic potential of mixed type, viz.:—

$$L = Q(\dot{q}) - P(\varpi) + I(\dot{q}, \varpi) \quad . \quad . \quad . \quad . \quad . \quad \text{(iii } b)$$

where I is a bilinear function of $\dot{q}$ and ϖ with coefficients dependent, like those of P and Q, on the coordinates q and χ. *In this mixed form* L *is to be taken as a function of type* (i) *for the coordinates* q, *and* $-$L *as a function of type* (ii) *for the variables* χ. From (iii b) are derived in this way

$$\text{momentum } p_r = \frac{\partial L}{\partial \dot{q}_r} = \frac{\partial Q}{\partial \dot{q}_r} + \frac{\partial I}{\partial \dot{q}}, \quad . \quad . \quad . \quad \text{(iii } c)$$

$$\text{velocity} \quad \dot{\chi}_s = \frac{\partial}{\partial \varpi_s}(-L) = \frac{\partial P}{\partial \varpi_s} - \frac{\partial I}{\partial \varpi_s}; \quad . \quad \text{(iii } d)$$

$$\text{and forces} \quad \dot{p}_r - \frac{\partial L}{\partial q_r}, \quad \dot{\varpi}_s + \frac{\partial}{\partial \chi_s}(-L)$$

$$\text{or} \quad \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_r} - \frac{\partial L}{\partial q_r}, \quad \dot{\varpi}_s - \frac{\partial L}{\partial \chi_s} . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii } e)$$

Since I is a bilinear function of $(\dot{q}, \varpi)$, we have at once

$$\sum_r p_r \dot{q}_r = 2Q + I, \text{ and } \sum_s \varpi_s \dot{\chi}_s = 2Q - I; \text{ so that}$$

$$\left.\begin{aligned} &\sum_r \tfrac{1}{2} p_r \dot{q}_r + \sum_s \tfrac{1}{2} \varpi_s \dot{\chi}_s = Q + P = E, \\ \text{and} \quad &\sum_r \tfrac{1}{2} p_r \dot{q}_r - \sum_s \tfrac{1}{2} \varpi_s \dot{\chi}_s = Q - P + I = L. \end{aligned}\right\} . \quad . \quad . \quad (1)$$

The latter equation gives the reason for the use of $-$L in the case of the variables χ.

Now E can be made homogeneous in two ways, (a) as a function of velocities by eliminating ϖ through the linear system (iii *d*), and (*b*) as a function of momenta by eliminating $\dot{q}$ through (iii *c*). I take it to be the criterion of regularity in the above system, that it should show the same dynamical quantities as the methods of (i) or (ii) when applied to the homogeneous forms of E. The requisite analysis is furnished by the lemma relating to transformation to be given in the next section. This is an extension of the usual theorem of reciprocity, and for convenience of general reference it will be given in an independent algebraical notation.

§ 2. Lemma.—Let Z be a quadratic function of n variables z, and J a bilinear function of z and of m other variables x, *i.e.*

$$J = \sum_{r=1}^{m} \sum_{s=1}^{n} c_{rs} x_r z_s. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Z can be expressed as a quadratic function of x and of n new variables y, specially correlated with z, by means of the n linear equations

$$\frac{\partial Z}{\partial z_s} \text{ (say } \zeta_s) = y_s + \frac{\partial J}{\partial z_s} = y_s + \sum_r c_{rs} x_r. \quad . \quad . \quad . \quad (3)$$

Calling this expression $Z(x,y)$, we prove

$$\frac{\partial Z(x,y)}{\partial x_r} = \frac{\partial J}{\partial x_r}, \quad \frac{\partial Z(x,y)}{\partial y_s} = z_s. \quad . \quad . \quad . \quad (A)$$

For the first,

$$\frac{\partial Z(x,y)}{\partial x} = \sum_s \zeta_s \frac{\partial z_s}{\partial x_r} = \frac{\partial}{\partial x_r} \sum_s \zeta_s z - \sum_s z_s \frac{\partial \zeta_s}{\partial x_r}$$

$$= 2\frac{\partial Z(x,y)}{\partial x_r} - \sum_s c_{rs} z_s, \quad \text{by (3)};$$

that is

$$\frac{\partial Z(x,y)}{\partial x_r} = \sum_s c_{rs} z_s = \frac{\partial J}{\partial x_r}.$$

For the second,

$$\frac{\partial Z(x,y)}{\partial y_s} = \frac{\partial}{\partial y_s} \sum_t \zeta_t z_t - \sum_t z_t \frac{\partial \zeta_t}{\partial y_s}$$

$$= 2\frac{\partial Z(x,y)}{\partial y_s} - z_s, \quad \text{by (3)};$$

or $$\frac{\partial Z(x,y)}{\partial y_s} = z_s.$$

We then prove that if the coefficients in Z and J depend on any parameter θ,

$$\frac{\partial Z(x,y)}{\partial \theta} = \frac{\partial J}{\partial \theta} - \frac{\partial Z}{\partial \theta}, \quad . \quad . \quad . \quad . \quad (B)$$

where in $Z(x,y)$ the coefficients of x^2, xy ... are differentiated, in Z the coefficients of z_s^2..., and in J those of $x_r z_s$. Thus $Z(x,y)$ depends on θ directly through the coefficients of $Z(z)$, and in an implicit way because z as expressed in terms of xy is also a function of θ through the coefficients. Hence

$$\frac{\partial Z(x,y)}{\partial\theta}=\frac{\partial Z}{\partial\theta}+\sum_s\zeta_s\frac{\partial z_s}{\partial\theta}=\frac{\partial Z}{\partial\theta}+\frac{\partial}{\partial\theta}\sum_s\zeta_s z_s-\sum_s z_s\frac{\partial\zeta}{\partial\theta}$$

$$=\frac{\partial Z}{\partial\theta}+2\frac{\partial Z(x,y)}{\partial\theta}-\sum_s z_s\frac{\partial}{\partial z_s}\frac{\partial J}{\partial\theta},\text{ by (3).}$$

But $\frac{\partial J}{\partial\theta}$ is a linear function of z, viz., it is J with $\frac{\partial c_{rs}}{\partial\theta}$ written for c_{rs}, and therefore

$$\sum_s z_s\frac{\partial}{\partial z_s}\frac{\partial J}{\partial\theta}=\frac{\partial J}{\partial\theta},\text{ and so }\frac{\partial Z(xy)}{\partial\theta}+\frac{\partial Z}{\partial\theta}=\frac{\partial J}{\partial\theta}.$$

In the usual theorem of reciprocity, the letters x and the function J do not occur.

§ 3. To express E or $Q(\dot q)+P(\varpi)$ in terms of velocities only, we make use of

$$\frac{\partial P}{\partial\varpi_s}=\dot\chi_s+\frac{\partial I}{\partial\varpi_s}\quad(i.e.\text{ iii }d),$$

to eliminate ϖ; consequently $(ZJzyx)$ of the lemma are replaced by $(PI\varpi\dot\chi\,\dot q)$. Hence

$$\left.\begin{aligned}&\text{by (A)}\qquad\frac{\partial P(\dot q,\dot\chi)}{\partial\dot q_r}=\frac{\partial I}{\partial\dot q_r},\quad\frac{\partial P(\dot q,\dot\chi)}{\partial\dot\chi_s}=\varpi_s,\\&\text{and by (B)}\quad\frac{\partial P(\dot q,\dot\chi)}{\partial\theta}=\frac{\partial I}{\partial\theta}-\frac{\partial P}{\partial\theta},\end{aligned}\right\}\quad.\quad(4)$$

θ being one of the coordinates q or χ, or indeed any other parameter involved in the coefficients of P Q and I. Thus

$$\left.\begin{aligned}&\frac{\partial E(\dot q,\dot\chi)}{\partial\dot q_r}=\frac{\partial Q}{\partial\dot q_r}+\frac{\partial I}{\partial\dot q_r}=p_r,\quad\frac{\partial E(\dot q,\dot\chi)}{\partial\dot\chi_s}=\frac{\partial Q}{\partial\dot\chi_s}+\varpi_s=\varpi_s,\\&\text{and}\\&\frac{\partial E(\dot q,\dot\chi)}{\partial\theta}=\frac{\partial Q}{\partial\theta}+\frac{\partial I}{\partial\theta}-\frac{\partial P}{\partial\theta}=\frac{\partial L}{\partial\theta}.\end{aligned}\right\}(5)$$

Thus the criterion, stated in § 1, for the normal character of the system derived from the use of the mixed kinetic potential L, is satisfied. Here L is a general quadratic function of $\dot{q}$ and ϖ having the part quadratic in $\dot{q}$ only essentially positive, that in ϖ only essentially negative; these conditions secure the positive character of E. The latter is derived from L by the formulæ

$$\left.\begin{aligned} &\mathrm{E}=\sum_r \dot{q}_r\frac{\partial \mathrm{L}}{\partial \dot{q}_r}-\mathrm{L}, \text{ or } \mathrm{E}=\sum_s \varpi_s\frac{\partial(-\mathrm{L})}{\partial \varpi_s}-(-\mathrm{L})=\mathrm{L}-\sum_s \varpi_s\frac{\partial \mathrm{L}}{\partial \varpi_s}, \\ \text{and}\qquad &2\mathrm{E}=\sum_r \dot{q}_r\frac{\partial \mathrm{L}}{\partial \dot{q}_r}-\sum_s \varpi_s\frac{\partial \mathrm{L}}{\partial \varpi_s}. \end{aligned}\right\} \quad (6)$$

The alternative transformation is to make use of (iii c) to eliminate $\dot{q}$ and express E as $\mathrm{E}(p,\varpi)$; as the latter is the reciprocal of $\mathrm{E}(\dot{q},\dot{\chi})$ it is not necessary to give details. It is also possible to use (iii c) and (iii d) in conjunction to effect a transformation from $\dot{q}$ and ϖ to p and $\dot{\chi}$, these being $m+n$ linear equations. It will be sufficient to state that $\mathrm{L}(p,\dot{\chi})$ is the reciprocal of $\mathrm{L}(\dot{q},\varpi)$, *i. e.* $\mathrm{L}(p,\dot{\chi})$ is a kinetic potential of type (ii) for the variables q, and $-\mathrm{L}(p,\dot{\chi})$ is a kinetic potential of type (i) for the variables χ. Thus

$$\dot{q}_r=\frac{\partial \mathrm{L}(p,\dot{\chi})}{\partial p_r}, \quad \varpi_s=-\frac{\partial \mathrm{L}(p,\dot{\chi})}{\partial \dot{\chi}_s}; \quad \text{and } \frac{\partial \mathrm{L}(p,\dot{\chi})}{\partial \theta}+\frac{\partial \mathrm{L}(\dot{q},\varpi)}{\partial \theta}=0$$

is true for coordinates of either type.

§ 4. The force corresponding to the coordinate q_r is, by (iii e),

$$\frac{d}{dt}\frac{\partial \mathrm{Q}}{\partial \dot{q}_r}-\frac{\partial \mathrm{Q}}{\partial q_r}+\frac{\partial \mathrm{P}}{\partial q_r}+\frac{d}{dt}\frac{\partial \mathrm{I}}{\partial \dot{q}_r}-\frac{\partial \mathrm{I}}{\partial \dot{q}_r}. \quad . \quad . \quad (7)$$

If I is taken to be

$$\sum_{r,s} c_{rs}\,\dot{q}_r\varpi_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the terms due to the function of interaction are

$$\begin{aligned} &\frac{d}{dt}\frac{\partial \mathrm{I}}{\partial \dot{q}_r}-\frac{\partial \mathrm{I}}{\partial q_r} \\ &=\sum_s c_{rs}\dot{\varpi}_s+\sum_{n,s}\frac{\partial c_{rs}}{\partial \chi_n}\dot{\chi}_n\varpi_s+\sum_{m,s}\left(\frac{\partial c_{rs}}{\partial q_m}-\frac{\partial c_{ms}}{\partial q_r}\right)\dot{q}_m\varpi_s. \quad (9) \end{aligned}$$

The force corresponding to the coordinate χ_s is

$$\dot{\varpi}_s+\frac{\partial \mathrm{P}}{\partial \chi_s}-\frac{\partial \mathrm{Q}}{\partial \chi_s}-\frac{\partial \mathrm{I}}{\partial \chi_s},$$

or

$$\dot{\varpi}_s+\frac{\partial \mathrm{P}}{\partial \chi_s}-\frac{\partial \mathrm{Q}}{\partial \chi_s}-\sum_{n,r}\frac{\partial c_{rn}}{\partial \chi_s}\dot{q}_r\varpi_n. \quad . \quad . \quad . \quad (10)$$

If no coordinates χ appear in the coefficients of PQI, and there is no external force tending to alter ϖ, the outcome of the second group of dynamical equations is that each ϖ is constant. P then becomes a function of coordinates q, and behaves as a potential energy, *cf.* (7). In (9) the effect of the function of interaction is reduced to the last term, viz.:

$$\sum_{m,s}\left(\frac{\partial c_{rs}}{\partial q_m}-\frac{\partial c_{ms}}{\partial q_r}\right)\dot{q}_m\varpi_s. \quad . \quad . \quad . \quad . \quad (9\,b)$$

§ 5. If the value of L is given as a difference of like expressions $\mathrm{Q}(\dot{q})-\mathrm{Q}'(\dot{\chi})$ or $\mathrm{P}(p)-\mathrm{P}'(\varpi)$, we have counterparts of the original case. Thus if

$$\mathrm{L}=\mathrm{Q}(\dot{q})-\mathrm{Q}'(\dot{\chi}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we form momenta from

$$\mathrm{E}=\mathrm{Q}(q)+\mathrm{Q}'(\dot{\chi})+\mathrm{I}(\dot{q},\dot{x}), \quad . \quad . \quad . \quad . \quad (12)$$

which being homogeneous is a kinetic potential of type (i). The equation

$$\varpi_s=\frac{\partial \mathrm{E}}{\partial\dot{\chi}_s}=\frac{\partial \mathrm{Q}'}{\partial\dot{\chi}_s}+\frac{\partial \mathrm{I}}{\partial\dot{\chi}_s}, \quad . \quad . \quad . \quad . \quad (13)$$

may be used to eliminate $\dot{\chi}$ from (11) and so express L in terms of $\dot{q}$ and ϖ. Here (ZJzyx) in the lemma are replaced by $(\mathrm{Q}', -\mathrm{I}, \dot{\chi}, \varpi, \dot{q})$, and

$$\text{(A) gives } \frac{\partial \mathrm{Q}'(\dot{q},\varpi)}{\partial\dot{q}_r}=-\frac{\partial \mathrm{I}}{\partial\dot{q}_r}, \quad \frac{\partial \mathrm{Q}'(\dot{q},\varpi)}{\partial\varpi_s}=\dot{\chi}_s,$$

$$\text{(B) gives } \frac{\partial \mathrm{Q}'(\dot{q},\varpi)}{\partial\theta}=-\frac{\partial \mathrm{I}}{\partial\theta}-\frac{\partial \mathrm{Q}'}{\partial\theta};$$

and therefore

$$\left.\begin{aligned}
&\frac{\partial \mathrm{L}(\dot{q},\varpi)}{\partial\dot{q}_r}=\frac{\partial \mathrm{Q}}{\partial\dot{q}_r}+\frac{\partial \mathrm{I}}{\partial\dot{q}_r}=\frac{\partial \mathrm{E}}{\partial\dot{q}_r}, \quad -\frac{\partial \mathrm{L}(\dot{q},\varpi)}{\partial\varpi_s}=-\frac{\partial \mathrm{Q}}{\partial\varpi_s}+\dot{\chi}_s=\dot{\chi}_s\\
&\quad\text{and}\\
&\frac{\partial \mathrm{L}(\dot{q},\varpi)}{\partial\theta}=\frac{\partial \mathrm{Q}}{\partial\theta}+\frac{\partial \mathrm{Q}'}{\partial\theta}+\frac{\partial \mathrm{I}}{\partial\theta}=\frac{\partial \mathrm{E}}{\partial\theta}.
\end{aligned}\right\}\ (14)$$

The transformed value of L is therefore a kinetic potential of mixed type. The treatment of the case $\mathrm{L}=\mathrm{P}(p)-\mathrm{P}'(\varpi)$ is similar. I is here subject to the limitation that E must be essentially positive.

§ 6. Some light is thrown on both cases by considering the contrary process, the passage from a homogeneous to a heterogeneous expression for energy. Here we suppose E given as

$$Q_{11}(\dot{q})+Q_{12}(\dot{q},\dot{\chi})+Q_{22}(\dot{\chi}), \quad . \quad . \quad . \quad . \quad (15)$$

and that $\dot{\chi}$ is to be replaced by ϖ, through the equation

$$\varpi_s=\frac{\partial E}{\partial \dot{\chi}_s}=\frac{\partial Q_{12}}{\partial \dot{\chi}}+\frac{\partial Q_{22}}{\partial \dot{\chi}_s}=\kappa_s+\frac{\partial Q_{22}}{\partial \dot{\chi}_s} \text{ say, } . \quad (16)$$

Q_{12} being the bilinear section so that κ_s , a linear function of $\dot{q}$. The actual transformation needs minor lemma. *If* $Q(x)$ *is a quadratic function of* x, *and* $K(y)$ *its reciprocal*, i. e. *the function obtained by transforming to variables* y, *where* $y_s=\frac{\partial Q}{\partial x_s}$; *then the transformation of* $\sum_s \kappa_s x_s+Q(x)$ *by means of*

$$y_s=\kappa_s+\frac{\partial Q}{\partial x_s}, \text{ or its equivalent } x_s=\frac{\partial}{\partial y_s}K(y-\kappa) \quad . \quad (17)$$

$$\textit{makes} \qquad \sum_s \kappa_s x_s+Q(x)=K(y)-K(\kappa). \quad . \quad (18)$$

For $\sum_s \kappa_s x_s=\sum_s \kappa_s \frac{\partial}{\partial y_s}K(y-\kappa)=\sum_s \kappa_s \left\{\frac{\partial K(y)}{\partial y_s}-\frac{\partial K(\kappa)}{\partial \kappa_s}\right\}$

$$=\sum_s \kappa_s \frac{\partial K(y)}{\partial y_s}-2K(\kappa) \quad . \quad (19\,a)$$

and $Q(x)=K(y-\kappa)=K(y)+K(\kappa)-\sum_s \kappa_s \frac{\partial K(y)}{\partial y_s}$; $\quad . \quad (19\,b)$

and (18) follows by addition.

Using K now for the reciprocal of Q_{22}, we have

$$E(\dot{q},\varpi)=\{Q_{11}(\dot{q})-K(\kappa)\}+K(\varpi)=T(\dot{q})+K(\varpi) \text{ say. } (20)$$

At the same time L, defined as $\sum_r \tfrac{1}{2}p_r\dot{q}_r-\sum_s \tfrac{1}{2}\varpi_s\dot{\chi}_s$, is equal to $Q_{11}(\dot{q})-Q_{22}(\dot{\chi})$; and this expressed in terms of $\dot{q}\varpi$ is

$$L(\dot{q},\varpi)=Q_{11}(\dot{q})-K(\varpi-\kappa)$$

$$=T(\dot{q})-K(\varpi)+\sum_s \kappa_s \frac{\partial K(\varpi)}{\partial \varpi_s}. \quad . \quad . \quad . \quad (21)$$

Thus in (20) we do in fact reach the energy-form treated in § 1, and $L(\dot{q},\varpi)$ is the difference of the quadratics in (20) with a bilinear function of $\dot{q}$ and ϖ added.

§ 7. The mutual action of the two systems in § 1 appears in the facts that p_r contains terms linear in ϖ, and $\dot{\chi}$ contains terms linear in $\dot{q}$. The coefficients of either set of terms are the coefficients in the function of interaction, which therefore expresses the mutual action directly. Suppose the coordinates χ absent, the momenta ϖ constant, and the energy given as $Q(\dot{q})+P(\varpi)$, and that the only object of referring to a homogeneous expression for energy is to ensure the regularity of the composite system; then the method of § 3 gives that assurance without calculating $E(\dot{q}, \dot{\chi})$. If the method of § 6 is applied, then T and K in (20) are given forms and (15) a presumed original. Q_{22} can be constructed at once, but not Q_{11} without a knowledge of the coefficients of κ_s the linear function of $\dot{q}$. These are the coefficients of Q_{12}, equal in number to those of $I(\dot{q}, \varpi)$, but they are not immediately connected with any information we may possess as to the mutual action. In this case therefore the method of § 6 is indirect and laborious in comparison with that of § 1 and § 3.

But if (15) is an original form which is to be reduced in virtue of the absence of χ and constancy of ϖ, then T and K in (20) are derived forms and are the Q and P of (iii). The bilinear section is in a different form from that of (iii *b*), but may be connected with it. For if

$$\left.\begin{aligned}
&Q_{12}=\sum_{m,s}\gamma_{ms}\dot{q}_m\dot{\chi}_s, \quad \text{and } K(\varpi)=\sum_{r,s}\beta_{rs}\varpi_r\varpi_s,\\
&\text{so that}\\
&\kappa_s=\sum_{m}\gamma_{ms}\dot{q}_m, \quad \text{and } \frac{\partial K(\varpi)}{\partial\varpi_s}=\sum_{r}\beta_{rs}\varpi_r;\\
&\text{then}\\
&\sum_{s}\kappa_s\frac{\partial K(\varpi)}{\partial\varpi_s}=\sum_{m,r}\varpi_r\dot{q}_m\sum_{s}\beta_{rs}\gamma_{ms}
\end{aligned}\right\} \quad . \quad (22)$$

and the bilinear forms in (21) and (iii *b*) are identified by writing

$$c_{mr}=\sum_{s}\beta_{rs}\gamma_{ms}. \quad \ldots\ldots \quad (23)$$

If the reader compares this with the work in Thomson & Tait's 'Natural Philosophy' (p. 323, § 319 F′), he will find that the coefficients c correspond to M, N,...; and the transfer to this final form is in fact essential to a compact statement of the result. Or, in other words, the problem for the remaining coordinates is conveniently restated in the form (iii), after finding T and K as in (20), and c_{mr} as in (23).

§ 8. A brief summary of the position may be given. We have just shown that the appearance of E as the sum of detached energy-forms of unlike type, viz.:

$$E=Q(\dot{q})+P(\varpi) \quad \ldots\ldots \quad (\text{iii } a)$$

is consistent with a mutual action. That action is expressed in a general way by the use of a mixed kinetic potential,

$$L = Q(\dot{q}) - P(\varpi) + I(\dot{q}, \varpi). \quad . \quad . \quad . \qquad (\text{iii}\,b)$$

On the other hand, L may appear as the difference of two detached energy-forms of like type, viz. :—

$$L = Q(\dot{q}) - Q'(\dot{\chi}) \quad . \quad . \quad . \quad . \quad . \qquad (\text{iv}\,a)$$

or

$$L = P(p) - P'(\varpi). \quad . \quad . \quad . \quad . \quad . \qquad (\text{v}\,a)$$

This is consistent with a mutual action expressed by the use of

$$E = Q(\dot{q}) + Q'(\dot{\chi}) + I(\dot{q}, \dot{\chi}) \quad . \quad . \quad . \qquad (\text{iv}\,b)$$

or

$$E = P(p) + P'(\varpi) + I(p, \varpi) \quad . \quad . \quad . \qquad (\text{v}\,b)$$

respectively, as energy-forms and at the same time kinetic potentials of types (i) and (ii). But here I must be such as to make E essentially positive.

In relation to the product-forms $\frac{1}{2}\sum_r p_r \dot{q}_r$ and $\frac{1}{2}\sum_s \varpi_s \dot{\chi}_s$, E is in all cases the sum, and L the difference. E is a kinetic potential when its expression is homogeneous, L is a kinetic potential when its expression is heterogeneous. When E is expressed as a sum of unlike forms, or L as a difference of like forms, all mutual action of the groups or systems is concealed, and these forms are unsuited for use as kinetic potentials.

§ 9. As an example of the method we take the problem of a perforated solid moving in a perfect liquid. Kirchoff wrote a potential ψ of acyclic motion in the form

$$\psi = u\psi_1 + \ldots + r\psi_6,$$

and obtained an energy function T quadratic in $u \ldots r$. Here $(u v w)$ is translation, $(p q r)$ rotation ; in some respects it is more convenient to use $u_1 \ldots u_6$, and then to write $\xi_1 \ldots \xi_6$ for components of momentum linear and angular, *i. e.* for $\frac{\partial T}{\partial u_1}, \ldots$. Kelvin added a cyclic potential $\omega = \kappa_1\omega_1 + \kappa_2\omega_2 + \ldots$, and obtained an energy-function K quadratic in κ. The energy of the whole motion is $T + K$, involving no products of u and κ, and there are reasons for assigning to κ the character of a momentum. Now when the momenta of the liquid motion are found by evaluating

$$\iiint \rho u \, dx \, dy \, dz, \quad \iiint \rho \, (xv - yu) dx \, dy \, dz \ldots,$$

the resulting values are given by

$$\xi_1 = \frac{\partial T}{\partial u_1} + c_{11}\kappa_1 + c_{12}\kappa_2 + \ldots, \ldots$$

where

$$\left.\begin{aligned} c_{11} &= \iint\left(l - \frac{\partial\psi_1}{\partial\nu}\right)d\sigma_1, \quad c_{12} = \iint\left(l - \frac{\partial\psi_1}{\partial\nu}\right)d\sigma_2, \ldots \\ c_{21} &= \iint\left(m - \frac{\partial\psi_2}{\partial\nu}\right)d\sigma_1, \quad c_{41} = \iint\left(ny - mz - \frac{\partial\psi_4}{\partial\nu}\right)d\sigma_1 \ldots \end{aligned}\right\} \quad (24)$$

Here $\sigma_1\ \sigma_2\ldots$ refer to the surfaces of barriers, (lmn) are direction-cosines of the normal to a barrier, and $d\nu$ an element of this normal. The second suffix in c refers to the barrier, the first to the velocities $u_{1\ldots6}$ in order. If we write the bilinear function $I = \sum_{a,b} c_{ab}\, u_a\, \kappa_b$, the momenta are given by

$$\xi_a = \frac{\partial P}{\partial u_a} + \frac{\partial I}{\partial u_a}, \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Also if we set down the value of I having regard to the meanings of c in (24), we find

$$I = \sum_b \iint\left(lU + mV + nW - \frac{\partial\psi}{\partial\nu}\right)_b \kappa_b d\sigma_b, \quad . \quad . \quad (26)$$

where $U = u + qz - ry \ldots$, *i.e.* (UVW) represents the velocity of a point of a barrier supposed to be in rigid connexion with the solid.

Now taking κ to correspond to ϖ of the general method, if there were no motion other than cyclic we should have

$$\dot{\chi}_b = \frac{\partial K}{\partial \kappa_b} = \iint \frac{\partial \omega}{\partial \nu} d\sigma_b,$$

or $\dot{\chi}_b$ would mean the flux through the barrier due to the cyclic motion. The condition that the composite dynamical scheme shall be regular requires a modification to

$$\dot{\chi}_b = \frac{\partial}{\partial k_b}(K - I) \qquad \textit{cf.}\ (\text{iii}\ d).$$

Thus

$$\dot{\chi}_b = \iint\left(\frac{\partial\psi}{\partial\nu} + \frac{\partial\omega}{\partial\nu} - lU - mV - nW\right)_b d\sigma_b, \quad . \quad (27)$$

or it is the flux *relative to the moving barrier*, due to the whole motion cyclic and acyclic. Momenta and fluxes are then derived from a kinetic potential of mixed type, viz. :—

$$\left.\begin{aligned} &L = T - K + I \\ &\xi_a = \frac{\partial L}{\partial u_a},\ \dot{\chi}_b = -\frac{\partial L}{\partial \kappa_b} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

in precise correspondence with the general scheme.

In the above statement of the case, the evidence of interaction is supposed to be first noticed in connexion with the value of momentum: the modification of flux obtained by assuming the regularity of the dynamical system then takes an entirely convincing form. If the modifications are taken concurrently, the proof of regularity is given by the coexistence of

$$\xi = \frac{\partial T}{\partial u} + \frac{\partial I}{\partial u},\ \text{and}\ \dot{\chi} = \frac{\partial K}{\partial \kappa} - \frac{\partial I}{\partial \kappa},$$

I being a bilinear function of u and κ. The whole forms an excellent example of the mode in which the coefficients of I are determined in a special problem. As the expression for I in (26) is an interpretable quantity, its treatment in the further development for several bodies and general coordinates offers no difficulties which do not also appear in treating T and K.

The conception of correlated expressions for energy is not confined to mechanics, and the generalized theorem of reciprocity in the lemma is applicable in all cases. Maxwell gave two such expressions for the energy of a system of insulated conductors, one a quadratic function of charges, the other a quadratic function of potentials. The former has a close analogy with the function of constants of circulation appearing in Kelvin's problem. In each case we have in the character of momentum a quantity unalterable so long as the degrees of freedom of the system are maintained, a quantity which is virtually a constant of integration in one group of the equations. It may be well to bear in mind, in dealing with different branches of physics, that the existence of a total energy in the form of detached expressions does not exclude interaction between the separate forms of energy.

VII. *Condensation of the Actinium and Thorium Emanations.*

By S. Kinoshita *.

IN their well-known experiment, Rutherford and Soddy † have shown that the radium emanation begins to condense at −150° C., and that there is only a slight difference between the temperatures of complete volatilization and of complete condensation. They also showed that the emanation of thorium behaved in a very different manner. The emanation began to condense at −120° C., but a much lower temperature, viz. about −150° C., was required in order to completely condense it. The temperature, at which the same number of particles of the emanation remained uncondensed, was different when different gases were employed to convey the emanation. Thus the temperature was higher for hydrogen than for oxygen, but the difference was not more than 3 degrees for the half value. A greater proportion was found to condense when the emanation was left for 90 seconds in the spiral than for 30 seconds. The different behaviour of the two emanations was ascribed by them to the great difference in the number of particles of emanation present.

Goldstein ‡ made some experiments on the condensation of the actinium emanation by a different method, using a preparation of the "Emanationskörper" of Giesel, now known as actinium. An exhausted glass tube was taken, at one end of which was placed the actinium preparation, and at the other a zinc-sulphide screen. The emanation diffused along the tube and produced phosphorescence on the screen. The luminosity was found to decrease when a glass tube, cooled by liquid air, was placed between the actinium and the screen, showing that some of the emanation was condensed on the walls of the tube. This experiment, which was made in the early stage of the enquiry, lacks quantitative precision.

The determination of the temperatures of condensation and volatilization of actinium emanation has been carried out by the writer, using the electrical method which has been adopted by Rutherford and Soddy for thorium and radium emanations.

A gas conveying a definite amount of the emanation is led directly into a partially exhausted copper spiral, the temperature of which, while rising slowly from that of liquid air,

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

† Phil. Mag. vol. v. p. 361 (1903).

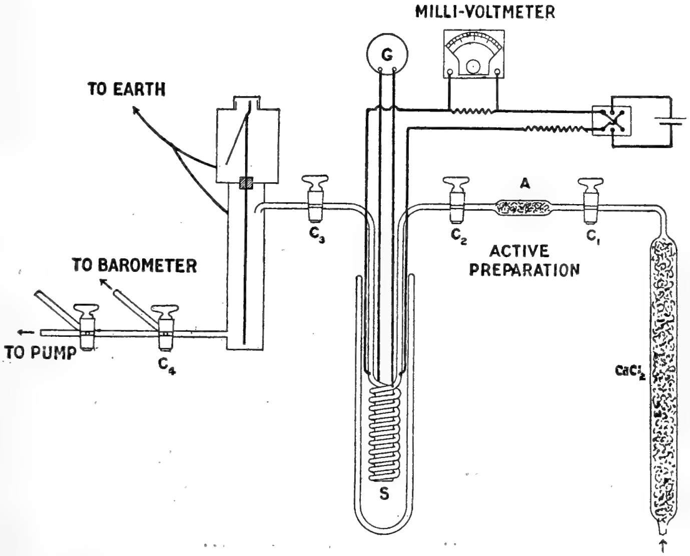
‡ *Berichte d. deutsch. phys. Gesellschaft*, p. 393 (1903).

can be measured. After leaving it for a certain time in this spiral to attain its temperature, and to let the emanation condense on the walls of the spiral, the gas is quickly led into a partially evacuated emanation electroscope, by means of which the activity of the emanation, escaping uncondensed along with the gas, can be measured.

The actinium emanation loses its activity very rapidly, its period being only 3·9 seconds, so that the activity decreases to 7 per cent. of its initial value after 15 seconds, and to 0·5 per cent. after 30 seconds. To get measurable effects it was, therefore, practically impossible to leave the emanation for more than 30 seconds to cool, although 1·5 grammes of actinium preparation had been taken, the activity of which was about 6000 times that of uranium oxide. It was, however, found experimentally that the proportion of uncondensed emanation at a given temperature is the same whether the emanation is left in the spiral for 15 or 24 seconds, provided the pressure is the same in both cases. Consequently 15 seconds seems sufficient time to allow for condensation in the spiral employed. At a temperature a few degrees below that of complete condensation, the emanation only took two or three seconds to condense. The rapidity of decay of activity of the emanation makes the experiment extremely difficult. An error of one-fifth of a second in the time during which the emanation is left in the spiral to condense causes an error of 3·5 per cent. in the final result, and one of 0·5 second, of 8·5 per cent.

The spiral was made of copper tubing, 127 cm. long, 3 mm. in internal diameter, and 1 mm. thick. This was wound into a double spiral of 11 turns, 8 cm. long, the mean diameter of the outer one being 2·5 cm., and of the inner 1·3 cm. One end of the spiral was connected by means of a rubber tube, 14 cm. long, with a glass tube A (fig. 1), in which the active preparation was kept. The other end was similarly connected with the emanation electroscope, a stopcock interposing in each case, so that both the tube A and the electroscope could be shut off from the spiral when necessary. The copper spiral itself was used as a thermometer, a constant current of 0·24 amp. being sent through it, while the change of resistance was measured by the fall of potential between two fixed points on the spiral by means of a D'Arsonval galvanometer (G). The current was adjusted by means of a sliding resistance, so as to keep the potential difference constant between two other points in the circuit, which were at the ordinary temperature, the potential difference being read by a Weston's milli-voltmeter. The reading of the galvanometer was proportional to the difference of potential. The heating effect of the circuit through the spiral was found to be negligible. The thermometer was calibrated from three different temperature readings, viz. 0° C.; the freezing-point of ethyl bromide, −125°·5 C.; and the temperature of liquid air, which had been determined by the aid of a hydrogen thermometer just before calibration. Subjoined are the results :—

Fig. 1.



Temperature.	Galvanometer reading.
0° C.	66·6
−125°·5 C.	41·2
−193°·6 C.	24·3

When plotted, these points do not lie on a straight line; but since the deviations therefrom are very small, intermediate temperatures can be determined by interpolation.

Now, if the emanation for initial activity I_0 is led into an electroscope after being left for T seconds in the spiral, its activity will be $I_0 e^{-\lambda T}$, if no condensation takes place. And the rate of fall of the gold leaf is proportional to $I_T e^{-\lambda t}$; thus

$$I_t = k\frac{ds}{dt} = I_T e^{-\lambda t},$$

where k is a constant, s the reading of the gold-leaf at time t,

λ being the radioactive constant of the emanation. Let s_τ and s_0 be the values of s at $t=\tau$ and $t=0$ respectively, then by integration

$$k(s_\tau-s_0)=\frac{\mathrm{I_T}}{\lambda}(1-e^{-\lambda\tau}),$$

or

$$\mathrm{I_T}=\frac{k\lambda(s_\tau-s_0)}{1-e^{-\lambda\tau}}.$$

The experiment therefore simply consists in measuring the number of scale-divisions passed over in a constant interval of time τ. This number is proportional to the activity, *i. e.*, to the amount of emanation escaping with the gas. A correction must be applied for the active deposit which is formed from the emanation.

As a verification of the method, the radioactive constant of the actinium emanation was determined by measuring $s_\tau-s_0$ for T = 25 and 20 seconds. The results are as follows:—

	T=25 seconds.	T=20 seconds.
$s_\tau-s_0$......	3·6	8·7
	3·6	8·73
	3·6	8·64
	...	8·75
Mean...	3·6	8·705

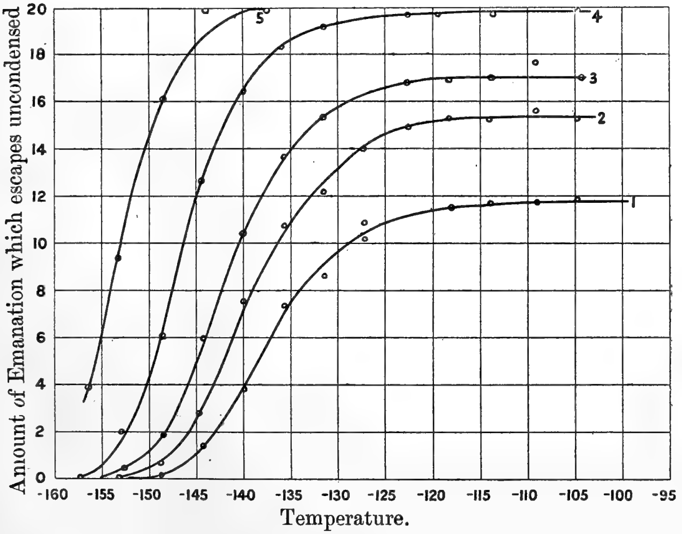
This gives $\lambda=\frac{1}{5}\log_e\frac{8\cdot705}{3\cdot6}=0\cdot176$ or period $=3\cdot92$ seconds, which agrees very well with previous determinations.

Experiment with Actinium Emanation.

The copper spiral was immersed in a Dewar's vessel, the mouth of which was closed with cotton-wool, and when the spiral had cooled down, all the liquid air was removed by inverting the vessel, after which the temperature was allowed to rise. The rate of rise of temperature was about 1°·1 to 1°·3 per minute. The electroscope and the spiral were evacuated by a water-pump to a pressure of 10 mm. of mercury, then all the stopcocks C_1, C_2, C_3, and C_4 were closed, A being at atmospheric pressure. C_2 was then opened, the gas in A which conveyed the emanation rushed into the spiral; and after a few seconds C_2 was again closed. Seventeen seconds after C_2 had been opened, the stopcock C_3 was turned, when the gas rushed into the electroscope, and the gold-leaf began suddenly to fall. Two readings s_0 and s_τ were taken, the former just before opening C_3 and the latter after 20 seconds. Act. A was deposited rapidly on the inner surface of the electroscope, but the correction due to this cause could be easily made by measuring the activity after 50 or 60 seconds, when all the emanation had practically died away. At the same time the galvanometer reading was taken to obtain the temperature of the spiral. The position of the zero point of the galvanometer was verified between each pair of readings. The process was repeated about every 5 degrees. It was found that the actinium emanation began to condense at about −120° C., and, just as in the case of the thorium emanation, some remained uncondensed below that temperature, The behaviour was the same whether the emanation was conveyed by air or by hydrogen within the limits of error of observation, but it varied largely according to the pressure at which the condensation took place.

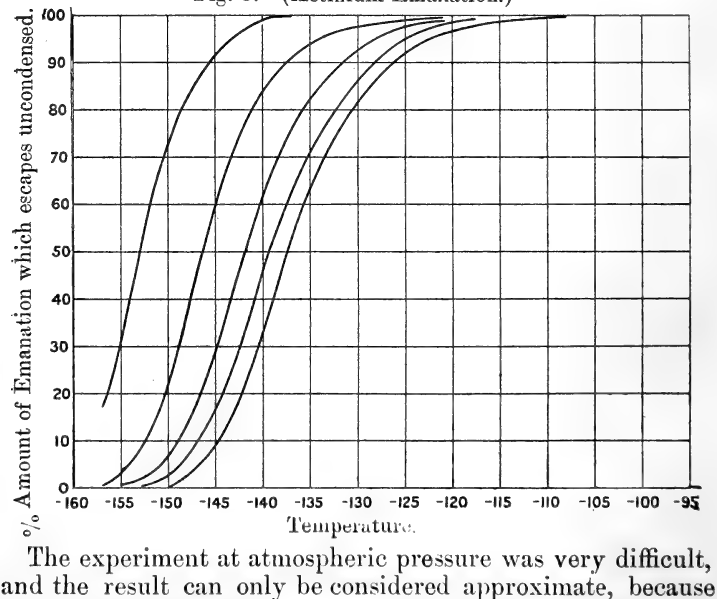
To test the nature of this variation, glass tubes varying in volume were inserted between A and the stopcock C. The results are shown in fig. 2, in which the abscissa represents

Fig. 2. (Actinium Emanation).



the temperature, and the ordinate $s_T - s_0$, which is proportional to the amount of emanation escaping uncondensed. Curve (1) is the experiment without any glass tube, (2) with a glass tube about 2·5 mm. in diameter and 6 cm. long, (3) with one of 18 cm., (4) with one of 24 cm., and (5) at atmospheric pressure. The scale of (5) is slightly reduced in the diagram. Each curve is obtained from two or three experiments under the same conditions. The pressure in the spiral at which the emanation condensed was calculated from that in the spiral itself, and from the ratio of the volume of the spiral to that of A (the portion between C_1 and C_2), allowance being made for the difference in temperature between the two systems. The difference in the final values of the ordinates of these curves is due to the fact that, when a glass tube is inserted, more emanation goes into the electroscope. Theoretically the curves should attain maximum values at certain temperatures and then decrease, because the higher the temperature of the spiral, the less emanation passes into it. But, on the other hand, when the spiral is cooler, it retains more emanation when the stopcock C_3 is opened. The magnitude of this last correction was determined, but found to be smaller than the experimental error.

Fig. 3. (Actinium Emanation.)



The experiment at atmospheric pressure was very difficult, and the result can only be considered approximate, because when the spiral was at atmospheric pressure and the stopcock C_3 was opened, the gold-leaf fell a few divisions, even if no emanation were present. The cause of this is not very evident, but is possibly due to electrification of the gas, rushing rapidly through the rubber tube. If the electroscope were evacuated at a pressure much higher than 10 mm.. viz. 200 or 400 mm., in order to admit a smaller quantity of gas into the electroscope, the discharging power due to the active deposit increased very greatly, and exact measurements could not be taken.

It is difficult to fix the exact points at which the curves in fig. 2 attain maximum values. However, the temperature at which a fixed amount of emanation escapes at different pressures can be found with more accuracy by reducing these curves to the same scale, as shown in fig. 3. The temperatures for 5 per cent. and 95 per cent. of emanation remaining uncondensed can be seen from the second and last columns of the table (p. 129). These are the inside limits of temperatures of initial and of complete condensation.

Experiment with Thorium Emanation.

Since the thorium emanation had been investigated by Rutherford and Soddy, its determination was made only under the same conditions as actinium emanation; so that we can compare the behaviour of both more closely. The emanation was left for 17 seconds in the spiral, and the same glass tubes were inserted between A and C_1, to vary the pressure. The fall of the gold-leaf was, in this case, measured for 60 seconds. The activity due to the active deposit of thorium was negligible. Consecutive readings as temperature rose could not be taken so rapidly as in the previous experiments. An interval of 6 or 7 minutes was therefore allowed between two readings (corresponding to 7° or 8° C. rise in temperature of the spiral). The amount of thorium emanation in A had then reached about 99 per cent. of its equilibrium value. Fig. 4 shows the direct results and

Fig. 4. (Thorium Emanation.)

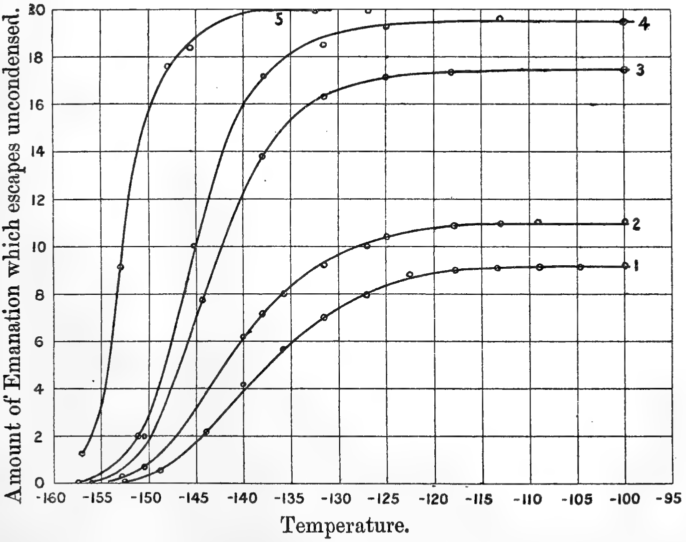
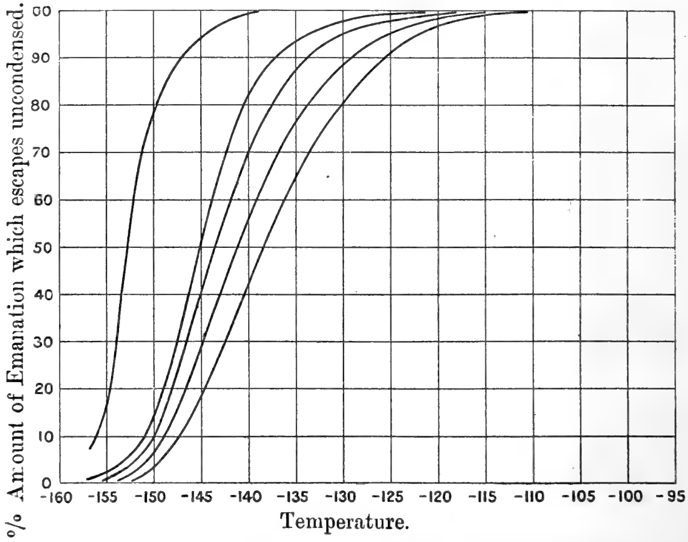


fig. 5 is reduced to the same scale as for the actinium emanation. The temperatures at which 5 and 95 per cent. of the emanation remains uncondensed are similarly given in the table (p. 129).

Fig. 5. (Thorium Emanation.)

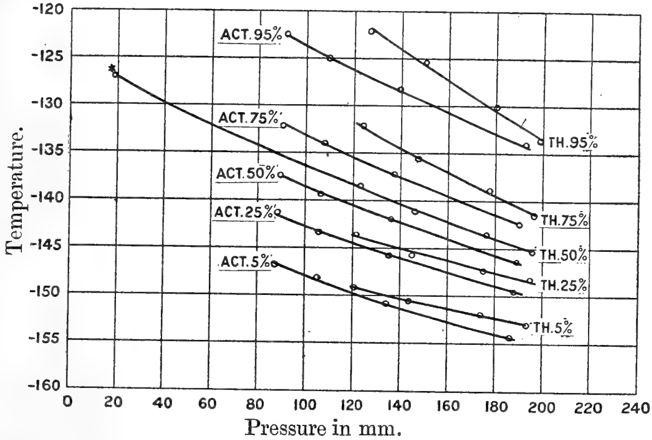


It was not thought necessary in these experiments to use a bath of liquid to keep the temperature of the copper spiral constant. The liquid air vessel extended a considerable distance above and below the spiral, and the slow rise of temperature observed (about 1° per minute) allows time for temperature-conduction to become steady. In any case, the reading of the galvanometer gives the average temperature of the spiral. As an indication of the accuracy of the temperature readings, it may be noted that the temperature of initial condensation of the thorium emanation obtained under these conditions was close to that found by Rutherford and Soddy, who used a copper spiral immersed in a bath of ethylene kept well stirred.

Comparison of the Condensation and Volatilization Temperature of the Thorium and Actinium Emanations.

The experiment brings out the very striking fact that both emanations are so similar with regard to condensation and volatilization, that we can hardly distinguish one from the other. Curves representing the temperature at which certain proportions of the emanation remain uncondensed at different pressures can be derived from those in figs. 3 and 5, and are

Fig. 6.



shown in fig. 6 for 5, 25, 50, 75, and 95 per cent. A point marked with (*) was taken from the paper of Rutherford and Soddy †. From these we get :—

Percentage remaining uncondensed.	5 per cent.		25 per cent.		50 per cent.		75 per cent.		95 per cent.	
Pressure in mm.	Act.	Th.	Act.	Th.	Act.	Th.	Act.	Th.	Act.	Th.
90.........	−147·0	......	−141·8	......	−137·5	−135·3	−132·0	......	−122·2	......
100.........	−148·0	......	−142·7	......	−138·5	−136·4	−133·1	......	−123·7	......
120.........	−149·8	−149·1	−144·5	−143·7	−140·5	−138·3	−135·5	−131·7	−126·2	−120·5
140.........	−151·4	−150·3	−146·0	−145·0	−142·2	−140·5	−137·5	−134·5	−128·5	−124·0
160.........	−152·7	−151·4	−147·5	−146·2	−144·0	−142·2	−139·5	−137·0	−130·8	−127·7
180	−154·0	−152·3	−148·9	−147·5	−145·8	−144·0	−141·4	−139·5	−133·0	−130·5
190	−154·5	−152·8	−149·6	−148·1	−146·5	−144·8	−142·5	−140·5	−134·0	−132·0
760...	......	......	−155·8	−154·2	−153·0	−152·8	−149·6	−150·5	−143·2	−144·3

Thus emanations remain partially uncondensed below the temperature of the initial condensation over a range of 20° C. or 30° C., according to the pressure. The temperature at

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† *Loc. cit.*

which a certain proportion of the emanations remains uncondensed depends largely on the pressure, especially when this is low. But the variation becomes less when the pressure increases. Thus the temperature, at which 50 per cent. of the actinium emanation remains uncondensed, varies from −137°·4 C. to −146°·5 C. as the pressure varies from 90 to 190 mm., *i. e.* 9° C. for a difference of 100 mm. in pressure, but only 6°·5 C. from 190 mm. to atmospheric pressure, *i. e.* for 570 mm. difference. The thorium emanation is similar to the above, but condenses at a temperature 2 or 3 degrees higher than the actinium emanation at the low pressure. The difference is not sensible at atmospheric pressure. The variation in the amount of condensation of the emanation at different pressures is probably connected with the greater rapidity of diffusion of the emanation at low pressures.

It remains to compare the number of particles of the thorium and actinium emanations which entered the spiral in the experiments described above. Let N and N′ be the respective numbers which are present in the spiral at the end of the time during which each is left in it, when neither condenses. Then, assuming that the α particles from both emanations are similar, and possess the same ionizing power upon the gas under the same conditions, we have from the equation obtained before

$$\frac{N'}{N}=\frac{I_T'}{I_T}\frac{\lambda}{\lambda'}=\frac{s_\tau'-s_0'}{s_\tau-s_0}\cdot\frac{1-e^{-\lambda\tau}}{1-e^{-\lambda'\tau'}},$$

for given pressures, where I′, λ', and s' are values for the actinium emanation. By substitution of the experimental values in this equation $\frac{N'}{N}$ is found to be nearly $\frac{1}{2}$. But since the rate of decay is different for the two emanations, the number of particles of actinium emanation, on entry into the spiral, must have been $\frac{1}{2}\cdot\frac{\lambda'}{\lambda}$, or about 7 times more numerous than those of the thorium emanation. Still, these numbers are of the same order of magnitude, and the experiments were thus made as nearly as possible under identical conditions.

When this work was finished a paper was published in *Le Radium*, by Henriot[*], who applied the method used by Goldstein to find the temperature of condensation of the

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[*] *Le Radium*, tom. v. No. 2. p. 41 (1908).

actinium emanation. He placed half a gramme of an actinium salt, of activity of about 4000, in a glass tube. This tube was connected through a series of U-tubes to another, in which a screen of zinc sulphide was enclosed. By exhausting the tubes to a high vacuum, the actinium emanation diffused rapidly through them, and the scintillations on the screen were observed through a microscope. The U-tubes were cooled in petroleum ether to —170° C. in a Dewar's vessel, and the temperature was allowed to rise slowly. A thermo-couple, inserted in the vessel, was used to measure the temperature. In this way, he observed that the scintillation began at about −143° C., this being the mean of four experiments giving values of −149° C., −140° C., —143° C., and −140° C. The scintillation attained a maximum intensity in the neighbourhood of −100° C. These two temperatures of complete and initial condensation are not widely different from those found by the writer, but the method is merely qualitative in character. In the present research a quantitative comparison of the condensation phenomena of the emanation of thorium and actinium has been made by the electrical method, under varying conditions of pressure and temperature, similar in general character to that made by Rutherford and Soddy for the emanations of thorium and radium.

Summary of Results.

The actinium emanation begins to condense at about −120° C., and some of the emanation remains uncondensed below that temperature. At about −150° C. it condenses as a whole. These, and the intermediate temperatures, at which a certain proportion of the emanation condenses, vary with the pressure, but the variation becomes less when the pressure increases. Experiments on similar lines with thorium emanation show that it condenses at about 2° or 3° C. higher temperature than the actinium emanation, the dependence of their condensation-points upon pressure being very similar.

In conclusion I wish to thank Prof. Rutherford for suggesting the experiment, and for his continual interest and advice during the progress of this research.

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VIII. *Notes on the Plug Permeameter.*

By CHARLES V. DRYSDALE, *D.Sc.*[*]

[Plates II. & III.]

IN 1901 the writer described a permeameter[†], devised with the object of enabling permeability-tests to be made on castings and forgings for dynamo-work. The apparatus consisted of a special drill, which could be employed to bore a hole in the casting or forging, leaving, however, a small piece of the metal in the form of a rod or pin standing in the centre of the hole. A split iron plug, arranged to fit both the conical sides of the hole and over the pin, was employed to complete the magnetic circuit; and this plug carried a bobbin wound with magnetizing and search coils. A special portable testing set was also designed with the object of making permeability-tests by direct reading of H and B.

It was noticed at the time that the magnetization-curves obtained by this method fell below those obtained by measurements on a long bar of the same material. This would naturally be attributed to a bad magnetic joint between the pin and plug; but experiments made at the time seemed to point rather to the effect being due to the reluctance of the return path at the point of entrance of the flux, due to the concentration of the lines of force at these points. This seemed probable from the fact that the readings were remarkably consistent when the plug was removed and replaced.

This hypothesis rendered it probable that there might be a more or less definite relation between the value of the true magnetizing-force H in the specimen, and the apparent magnetizing-force $H' = \frac{4\pi}{10}\frac{Cn}{l}$; and arrangements were made to test this relation. The most perfect method was suggested by the double-yoke method of Prof. Ewing. It consisted in finding the relation of the induction density and the magnetizing current for the ordinary drilled specimen, and afterwards when the length of the specimen was doubled by drilling to a greater depth with a second drill. The increase of the magnetizing current for the same induction should give the true H. A large number of tests were made in this manner, but proved of little value, as, although the first drilling presented no difficulties, it was found impossible to perform the second drilling accurately enough to preserve parallelism of the pin.

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[*] Communicated by the Physical Society: read March 27, 1908.

[†] Proc Inst. Electr. Eng. vol. xxxi. p. 283.

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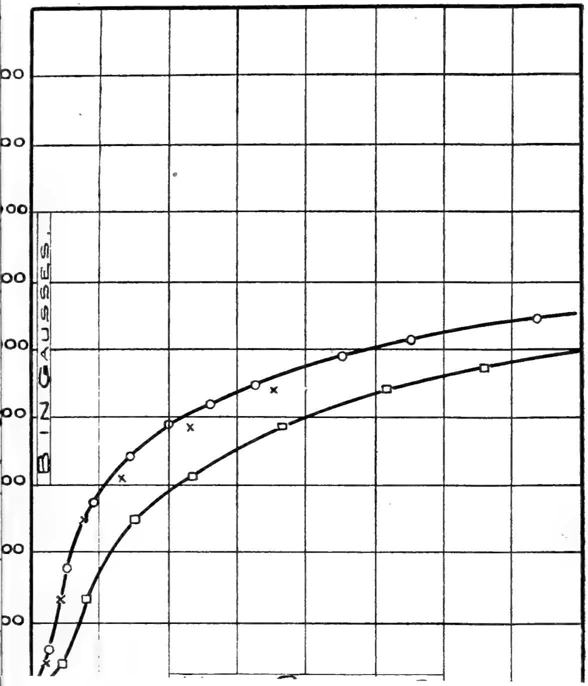
FIG. 3.—ORDI

FIG. 5.—SPECIAL CAST IRON NO. 2.



COMPARISON OF RING AND PLUG TESTS.

Fig. 2.—Ordinary Cast Iron No. 1.

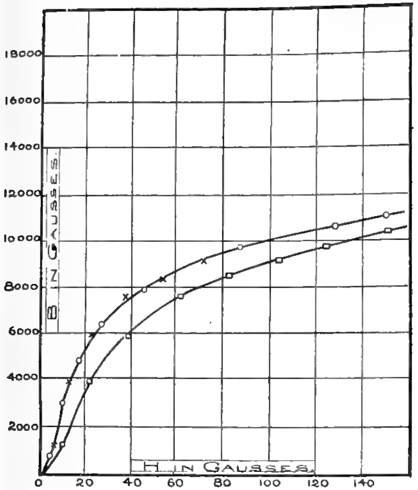


Fig. 3.—Ordinary Cast Iron No. 2.

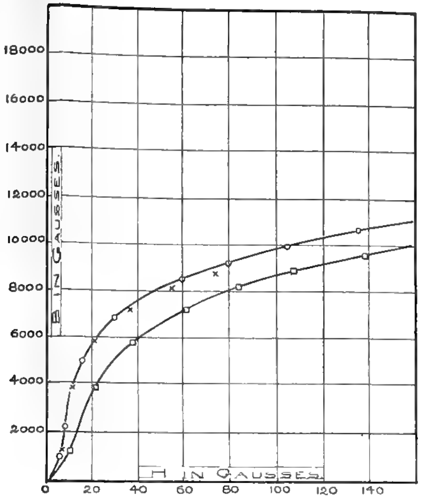


Fig. 4.—Special Cast Iron No. 1.

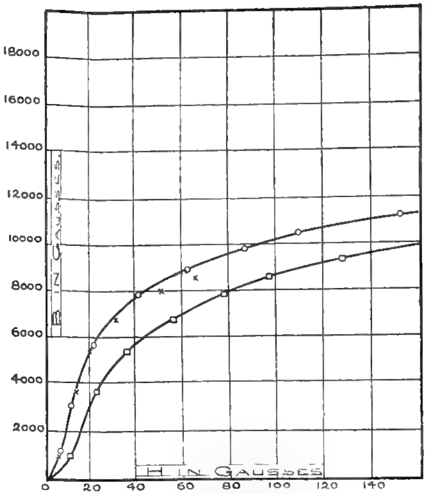


Fig. 5.—Special Cast Iron No. 2.

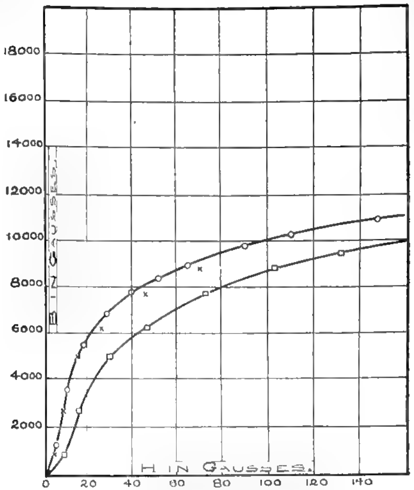


Fig. 6.—Wrought Iron No. 1.

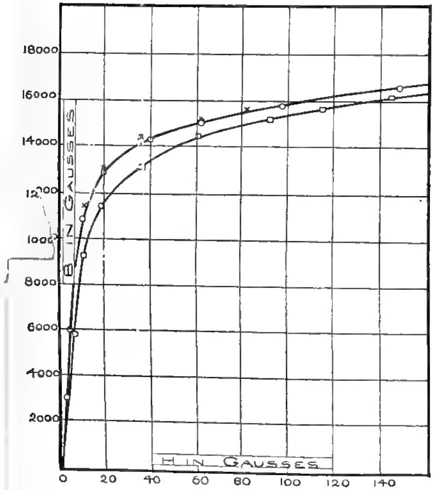


Fig. 7. Wrought Iron No. 2.

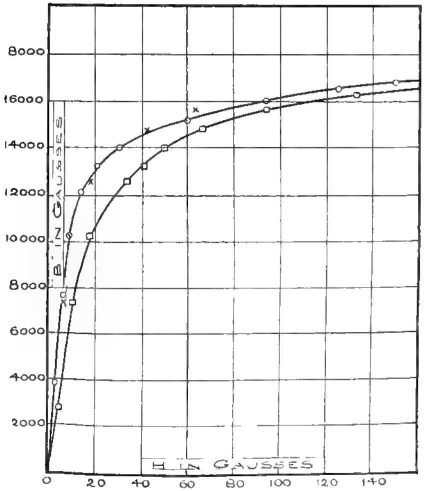


Fig. 8.—Mild Steel No. 1.

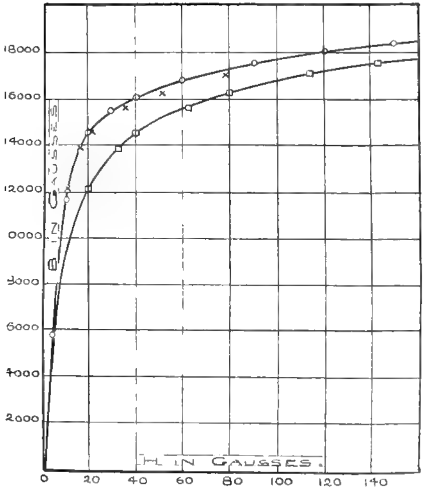
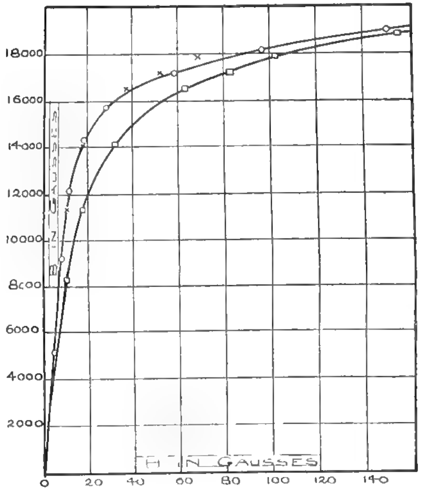
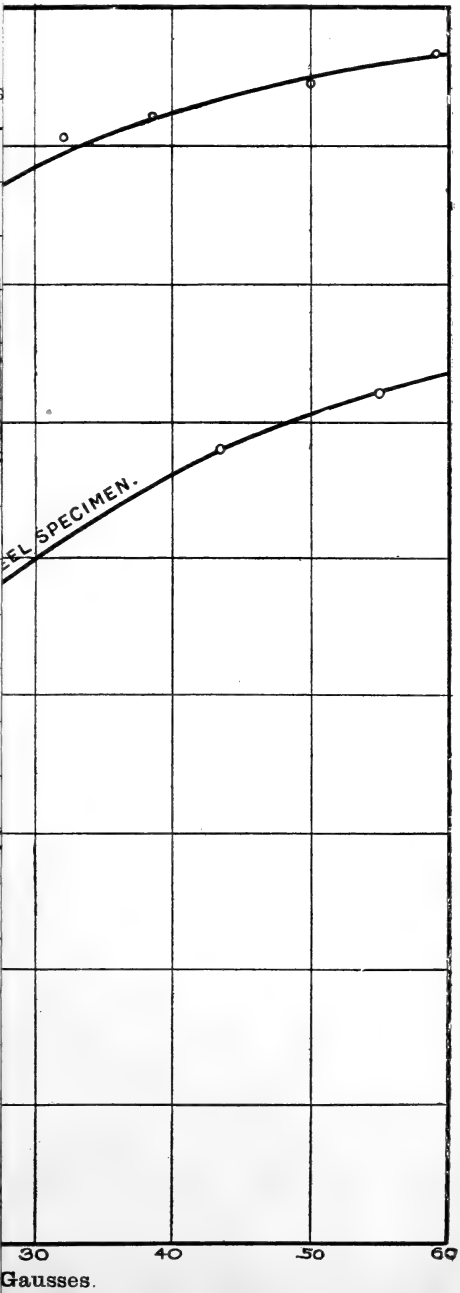


Fig. 9. —Mild Steel No. 2.



IG. 12.



Fig

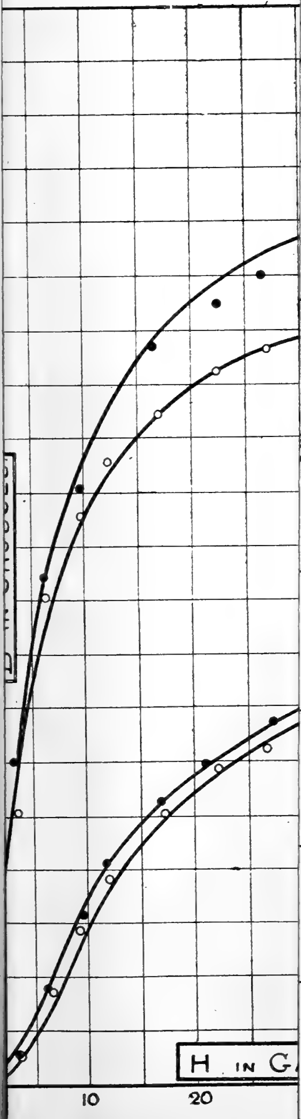


Fig. 10.

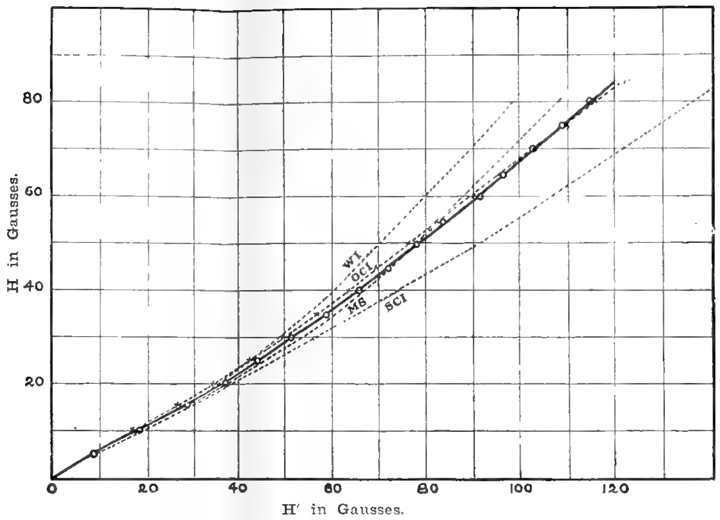


Fig. 11.

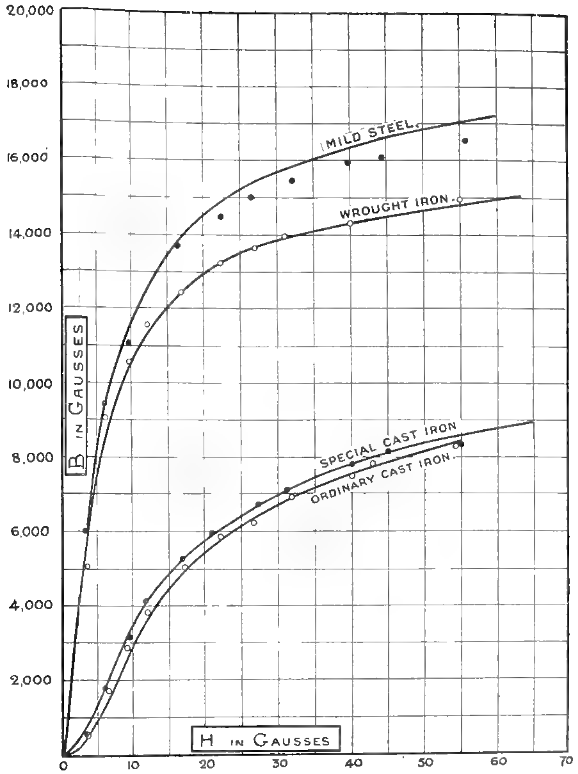
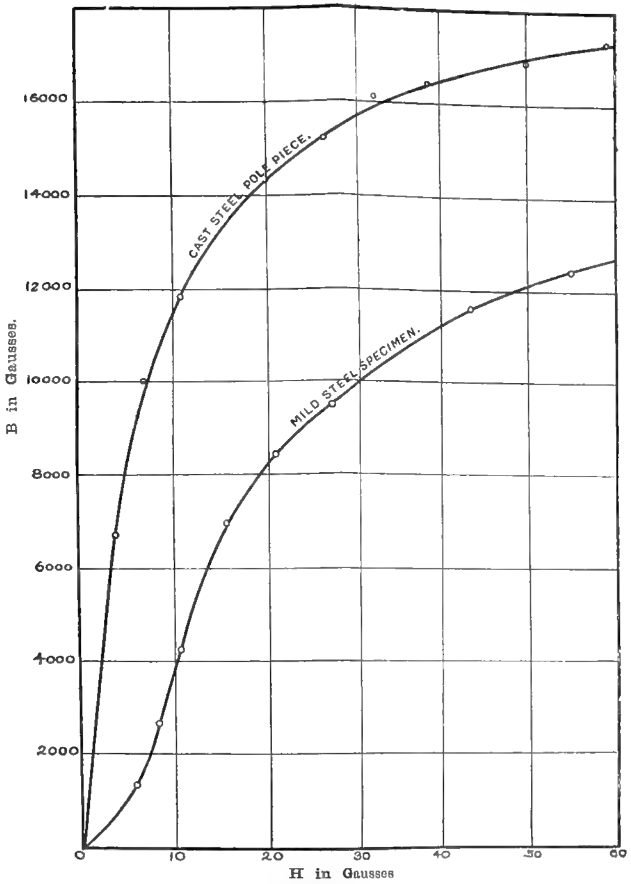


Fig. 12.



Recourse was therefore had to the more simple device of obtaining some specimens of cast and wrought iron and steel, in the form of rings; testing them by the ordinary ring method, and afterwards cutting them up and drilling, for tests by the plug. Rings of this kind were made for us by Messrs. G. Wailes of Euston Road, and were of ordinary cast iron (O.C.I.), special cast iron (S.C.I.), wrought iron (W.I.), and mild steel (M.S.). Two rings of each material were tested, and each ring was cut into four quadrants. Each of these quadrants was drilled in both ends, so that eight drillings were made in each ring. Readings of B were then made with the plug method, at nominal values of H of 30 and 100 on the eight drillings, and the drilling selected for final test, the readings on which corresponded to the mean of the eight. It may be mentioned that the whole of the 64 drillings on the eight rings were made with the same drill, which was none the worse after. None of the drillings gave a bad fit with the plug. Fig. 1 shows the form and mode of cutting and drilling the ring, which was 5 in. external diameter and 1 in. square in section; while Table I. shows an example of the readings on the various drillings of one ring, and the amount of variation usually found. It should be specially noted that these variations are not apparently due to variation in the fit of the plug, but rather to actual differences in the magnetic quality of the iron.

Fig. 1.

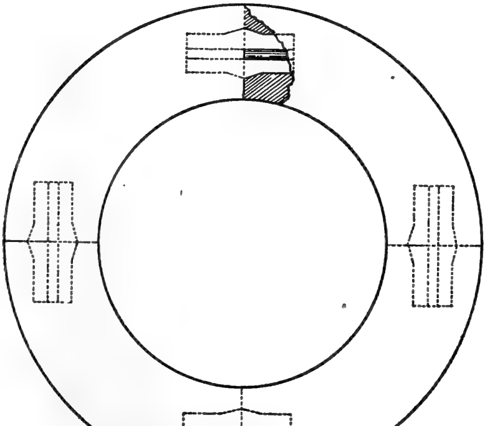


Table I.

Readings on Wrought Iron Ring.

Hole No.	Fit.	H=30. B.	H=100. B.
1 ……	Fair.	13,140	15,600
2 ……	Moderate.	12,880	15,820
3 ……	Good.	12,400	15,130
4 ……	Good.	12,040	14.550
5 ……	Fair.	11,730	14,550
6 ……	Good.	12,930	15,080
7 ……	Good.	11,200	14,190
8 ……	Fair.	11,670	14,550
1 (Check-reading) ……		……	15,600
Mean …… …………..		12,250	14,900

Figs. 2–9, Pl. II., show magnetization-curves taken on the ring and by the plug on the mean drilling for each specimen. It will be noted that the curve obtained by the plug lies below that for the ring in every case ; but there is no evidence to show that this is due to an air-gap. If such a gap were present, of approximately equal amount in each of the specimens, the shearing-over of the curves of the wrought-iron and mild-steel specimens would be much more marked in comparison to those of the cast-iron specimens, owing to the much greater permeability and induction-density in the former.

Table II. is obtained from the curves by finding the value of H′, the nominal magnetizing force in the case of the plug-test, for each value of H from the ring-test, for a given induction-density; and fig. 10, Pl. II., gives curves showing the relation of H′ to H for each of the materials and for the mean of all. It will be observed that although there are considerable differences between the values in the various columns, they appear to have no relation to the permeability of the specimen, and must therefore be regarded as accidental. In fact, the difference between H and H′ is greater in the case of the special cast-iron than for either the wrought-iron or mild-steel specimens, which is exactly contrary to the effect which would be produced by an air-gap. The difference must consequently be attributed to the shortness of the specimen ; and the results therefore may have some general value in indicating the amount of the end effect in the case of yoke-permeameters, in which the specimen is only five diameters long.

TABLE II.

Relation of H to H′.

H.	Mean H′ for O.C.I.	Mean H′ for S.C.I.	Mean H′ for W.I.	Mean H′ for M.S.	Mean.
0 ……	0	0	0	0	0
5 ……	8·5	9·7	8·5	8·0	8·7
10 ……	17·2	19·2	18·75	18·5	18·4
15 ……	26·2	29·4	28·2	29·0	28·2
20 ……	34·0	39·0	35·7	37·7	36·6
25 ……	42·2	47·7	42·2	46·5	44·7
30 ……	49·5	56·0	48·0	54·2	51·5
35 ……	57·0	65·25	54·0	61·0	59·3
40 ……	63·5	73·75	60·5	66·5	66·0
45 ……	69·5	81·75	64·5	72·2	71·9
50 ……	76·5	90·75	69·7	77·5	78·5
55 ……	83·5	98·25	75·0	82·0	84·7
60 ……	90·0	106·0	79·5	88·5	91·0
65 ……	96·5	114·0	83·7	93·2	96·9
70 ……	103·0	121·5	89·0	97·5	102·8
75 ……	109·2	129·0	94·2	102·2	108·6
80 ……	115·0	135·7	99·0	108·5	114·6

In order to show the result of correcting the indications of the instrument, the curves figs. 2–9 have points marked by crosses, in which the readings of the plug-permeameter are shifted backwards along the H axis by amounts corresponding to the mean curve in fig. 10. The agreement with the ring-tests then becomes fairly good. Fig. 11, Pl. III., shows readings taken by one of the portable testing sets, in which the H scale has been marked off in this way. The curves are those given by the ring method, while the points are taken by the testing set. The agreement is as good as in most of the recognized permeameters.

Fig. 12, Pl. III., shows two curves taken by the plug permeameter: one on a cast-steel pole-piece for a large generator, which was sent us by the dynamo-builders under the impression that it was of poor magnetic quality. The test shows the permeability to be very good. The other curve is for another specimen of steel, and indicates the remarkable variations of quality which are found in practice.

It should be mentioned that when the plug used in these tests was replaced by a second one, the results agreed within an accuracy of $1\frac{1}{2}$ per cent.

The general conclusion to be drawn from these experiments is that the plug permeameter, in reasonably careful hands, gives as good results as any other method of iron testing, so far as permeability tests are concerned. In a recent paper by Mr. Murdoch[*] this permeameter was criticized as employing a very small specimen; but this is precisely what has been aimed at in its design. It appears to be of great importance that permeameters for castings or forgings should be capable of being employed on the bulk of the metal itself, without extra machined specimens, and up to the present no other instrument has been devised which meets this requirement.

The writer's hearty thanks are due to Mr. A. C. Jolley for the considerable amount of work involved in carrying out the tests. Mr. C. M. Dowse has also rendered considerable assistance in the later tests.

IX. *The Use of Shunts and Transformers with Alternate Current Measuring Instruments.* *By* CHARLES V. DRYSDALE, *D.Sc.*[†]

[Plate IV.]

THE growing demand for instruments for alternate-current measurement, of considerable range and accuracy, has called attention to some of the difficulties attending their production, especially to their limited range. As alternate-current instruments measure the root-mean-square values of the P.D. or current, it necessarily follows that the deflecting torque falls very rapidly as the P.D. or current is decreased, For most commercial instruments, it may be taken that a tenfold range of torque is the utmost possible for accurate reading, so that when the deflexion is proportional to the torque the range of an A.C. instrument can only be of the order of 3 to 1 except by the employment of double coils or auxiliary devices. The auxiliary devices which may be employed are transformers for electromagnetic ammeters, voltmeters, and wattmeters; shunts for ammeters and wattmeters, series resistances for electromagnetic voltmeters, and condensers and split resistances for electromagnetic voltmeters. Of these, the use of shunts and transformers may give rise to serious errors, and it is proposed here to investigate the amount of these errors and the conditions for their elimination.

In dealing with any shunting or transforming device we must bear in mind that it may cause errors in two ways:—(*a*) by the multiplying power of the shunt or the ratio of the transformer being affected by frequency, &c.; and (*b*) by a phase displacement being introduced between the current or P.D.

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[*] Electrician, vol. lx. p. 245.

[†] Communicated by the Physical Society: read March 27, 1908.

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ent Transformers.

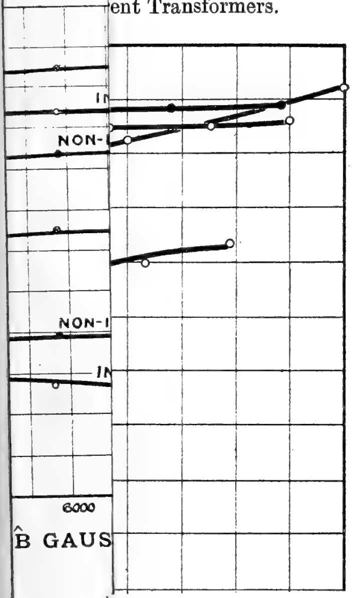


Fig. 7.—Ratio Tests on Current Transformer.

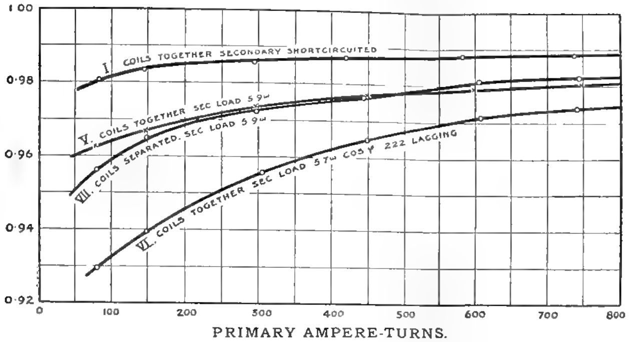


Fig. 8.—Phase Displacement on Current Transformer.

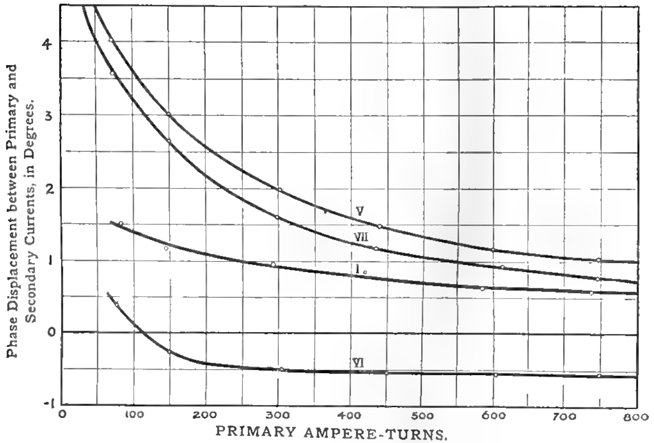


Fig. 9.—Ratio Tests on Voltage Transformer.

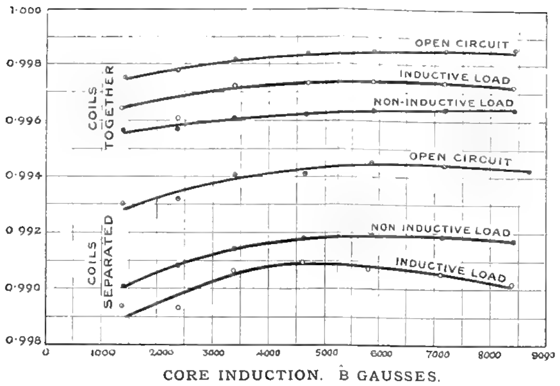


Fig. 10.—Displacement Tests on Voltage Transformer.

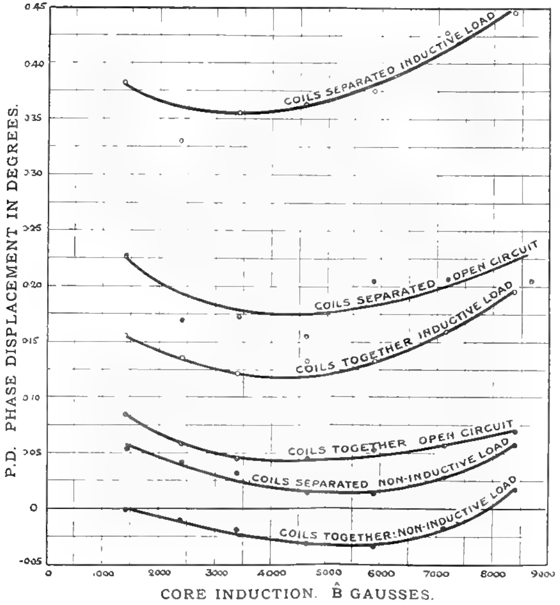


Fig. 11.—Relation between Core Loss and Magnetizing Current.

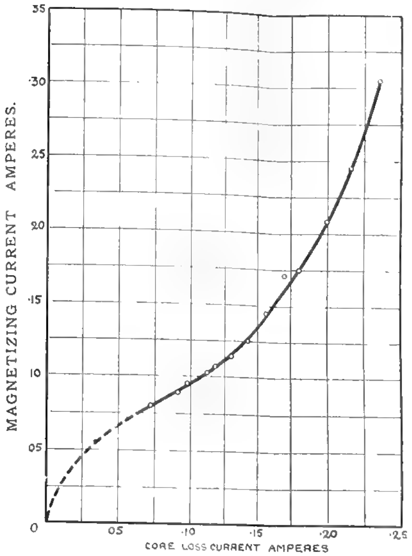


Fig. 12.—Relation between $\frac{A_c}{B}$ and $\frac{A_m}{B}$.

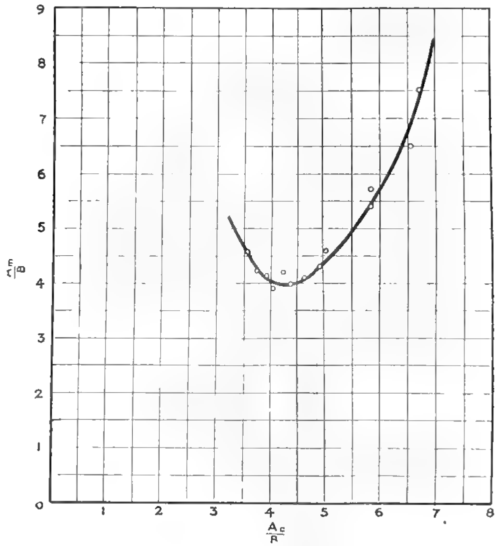


Fig. 13.—Ratio Tests on Current Transformers.

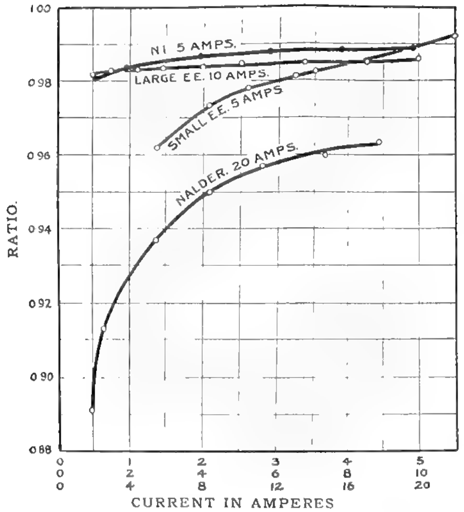
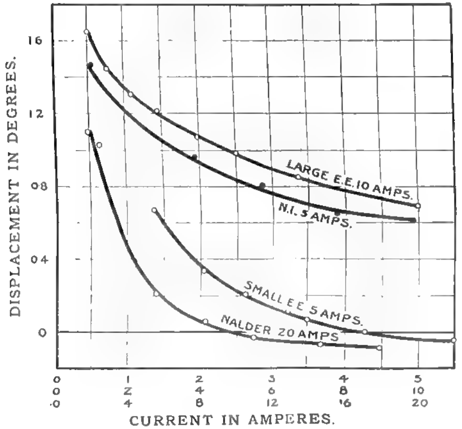


Fig. 14.—Displacement Tests on Current Transformers.

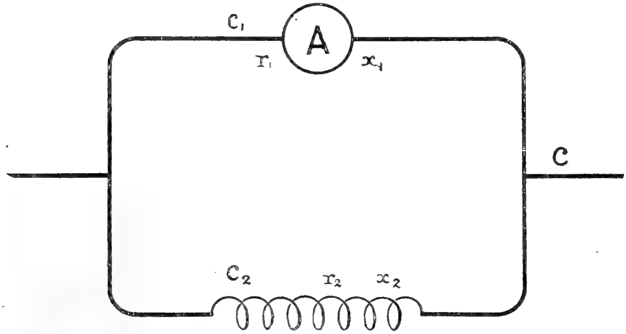


on the instrument and the main current or voltage. Ammeters and voltmeters are of course only affected by the first error, but the phase-displacement may be of much greater importance in wattmeters.

SHUNTS.

Multiplying Power.—In fig. 1, we have an instrument or

Fig. 1.



resistance r_1 and reactance x_1 shunted by a circuit of resistance r_2 and reactance x_2. Then, if V is the P.D. between the terminals, and C_1 and C_2 are the currents in the instrument and shunt respectively, we have

$$C_1 = \frac{V}{I_1} = \frac{V}{r_1 - jx_1} \quad \text{and} \quad C_2 = \frac{V}{I_2} = \frac{V}{r_2 - jx_2}.$$

Hence the total current in the circuit $C = C_1 + C_2$

$$= V\left\{\frac{1}{r_1 - jx_1} + \frac{1}{r_2 - jx_2}\right\} = V\frac{r_1 + r_2 - j(x_1 + x_2)}{(r_1 - jx_1)(r_2 - jx_2)}, \quad (1)$$

and the virtual current $\overline{C} = \overline{V}\frac{I}{I_1 I_2}$, where I is the impedance of the whole circuit formed by the instrument and shunt *in series*, and I_1 and I_2 are the impedances of the instrument and shunt respectively.

Consequently, since $\overline{C_1} = \frac{V}{I_1}$ the multiplying power of the shunt

$$M' = \frac{\overline{C}}{\overline{C_1}} = \frac{I}{I_2}. \quad (2)$$

Hence

$$M' = \sqrt{\frac{(r_1+r_2)^2+(x_1+x_2)^2}{r_2^{\,2}+x_2^{\,2}}} = \sqrt{\frac{\left(\frac{r_1+r_2}{r_2}\right)^2+\left(\frac{x_1+x_2}{r_2}\right)^2}{1+\left(\frac{x_2}{r_2}\right)^2}}$$

But the multiplying power of the shunt for direct currents $M = \frac{r_1+r_2}{r_2}$ from which $r_1=(M-1)r_2$. In addition $\frac{x_1}{r_1}=T_1p$, where T_1 is the time constant of the instrument and p is 2π times the frequency as usual. Similarly $\frac{x_2}{r_2}=T_2p$, where T_2 is the time constant of the shunt.

Putting these values in the expression above we have

$$M' = \sqrt{\frac{M^2+\{(M-1)T_1+T_2\}^2p^2}{1+T_2^{\,2}p^2}},$$

which after a little further simplification reduces to

$$M' = M\sqrt{1+\frac{M-1}{M^2}\,\frac{(M-1)T_1+(M+1)T_2}{1+T_2^{\,2}p^2}(T_1-T_2)p^2}. \quad (3)$$

This formula at once shows that if $T_1=T_2$ the shunt has the same multiplying power for both direct and alternate currents, as is well known. It further shows that if

$$(M-1)T_1+(M+1)T_2=0 \qquad \text{or} \qquad \frac{T_2}{T_1}=-\frac{M-1}{M+1}$$

the shunt is again correct. This would be the case if the instrument is shunted with a resistance r_2 and capacity K such that $Kr_2=\frac{M-1}{M+1}T_1$*.

If the instrument is inductive, and is shunted with a non-inductive resistance, $T_2=0$ and the formula reduces to

$$M' = M\sqrt{1+\left(\frac{M-1}{M}\right)^2T_1^{\,2}p^2}. \quad . \quad . \quad . \quad (4)$$

As an example, a Kelvin centiampere balance was found on test to have a resistance of 62·4 ohms and an inductance (by secohmmeter) of 161 millihenrys. The time constant of this instrument was therefore ·00258 second. The instrument

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* Mr. Alexander Russell has cast doubts on this formula, and I have found that it is only true in special cases. It was based on the assumption that a shunted condenser could be treated as an impedance with negative time constant, which is not strictly true.

was then shunted with a non-inductive resistance, and it was found that a current of ·878 amp. gave a reading of ·17 amp. on the balance with direct current, thus giving a multiplying power M of 5·16. Hence at 50 periods, which is the usual frequency of the supply, M′ should be

$$5{\cdot}16\sqrt{1+\frac{4{\cdot}16^2\times{\cdot}00258^2\times314^2}{5{\cdot}16^2}}=6{\cdot}17;$$

while on testing a current of ·927 amp. gave a reading of ·15 amp. or a multiplying power of 6·18. It should be noticed that the formula may be expressed in the form $T_1=\frac{\sqrt{M'^2-M^2}}{(M-1)p}$, which gives us a convenient method of testing the inductances of ammeters, &c.

For commercial work, therefore, we see that the only legitimate method of employing shunts is to make the time constants of the instruments and shunts either negligible or approximately equal. If T_1 and T_2 are nearly equal since $\sqrt{1+h}=1+\frac{h}{2}$ nearly when h is small,

$$M'=M\left\{1+\frac{M-1}{2M^2}\frac{(M-1)T_1+(M+1)T_2}{1+T_2{}^2p^2}(T_1-T_2)p^2\right\}.\quad(5)$$

It will be noticed that for a given difference in the time constants the correcting term is greater the greater the value of M and the less that of T_2. Consequently, if we take in our formula M so large that M, (M+1) and (M−1) may be regarded as equal and at the same time neglect T_2p in comparison with unity, we have:

$$M'=M\left\{1+\frac{T_1+T_2}{2}(T_1-T_2)p^2\right\}=M\{1+(T_1-T_2)Tp^2\},\quad(6)$$

where T is the average value of the two time constants T_1 and T_2.

This may be written in the form $\frac{\Delta M}{M}=T\,.\,\Delta T\,.\,p^2$, and finally

$$\frac{\Delta M}{M}=T^2p^2\frac{\Delta T}{T}.\quad\ldots\ldots\quad(7)$$

Consequently, to ensure that the ratio M shall not be altered by more than x per cent. with alternating current of given frequency, the time constants must be adjusted to equality within $\frac{x}{T^2p^2}$ per cent.

In the case of the Kelvin centiampere balance before mentioned, $T = {\cdot}00258$ at a frequency of 50, therefore $Tp = 314 \times {\cdot}00258 = {\cdot}810$ and $T^2 p^2 = {\cdot}655$. Consequently the time constant or the self-induction of the shunt must be adjusted to $\frac{1}{\cdot 655} = 1{\cdot}53$ per cent. for an accuracy of 1 per cent. in the multiplying power. The simplest method of adjusting or checking the shunt is of course to test the ratio with both D.C. and A.C. or with A.C. of two different frequencies.

Phase Displacement.—Returning to formula (1) and rationalizing the denominator, we get

$$C = \frac{V}{I_1^2 I_2^2}\{(r_1+r_2) - j(x_1+x_2)\}(r_1+jx_1)(r_2+jx_2)$$

$$= \frac{V}{I_1^2 I_2^2}\{(r_1+r_2)(r_1r_2 - x_1x_2) + (x_1+x_2)(r_1x_2+r_2x_1)$$
$$+ j[(r_1+r_2)(r_1x_2+r_2x_1) - (x_1+x_2)(r_1r_2-x_1x_2)]\},$$

and consequently

$$\tan\phi = \frac{(r_1+r_2)(r_1x_2+r_2x_1) - (x_1+x_2)(r_1r_2-x_1x_2)}{(r_1+r_2)(r_1r_2-x_1x_2) + (x_1+x_2)(r_1x_2+r_2x_1)}$$

where ϕ is the angle of lag of the main current behind V.

Inserting the values of M, T_1, and T_2 as before, we get

$$\tan\phi = \frac{T_1 + (M-1)T_2 + \{(M-1)T_1 + T_2\}T_1T_2p^2}{M + \{(M-1)T_1^2 + T_2^2\}p^2}\,p.$$

Similarly $\tan\phi_1 = T_1 p$ where ϕ_1 is the lag in the instrument. Hence

$$\tan(\phi_1 - \phi) = \frac{\tan\phi_1 - \tan\phi}{1 + \tan\phi_1 \tan\phi}$$

is the tangent of the angle of lag of the current in the instrument behind the main current. Putting in the values of $\tan\phi_1$ and $\tan\phi$ and simplifying, we have as the result

$$\tan\psi = \tan(\phi_1 - \phi)$$
$$= (M-1)(T_1-T_2)p\,\frac{1+T_1^2p^2}{M + \{MT_1^2 + (M-1)T_1T_2 + T_2^2\}p^2 + \{(M-1)T_1+T_2\}T_1^2T_2p^4}$$
$$= \frac{M-1}{M}(T_1-T_2)p\left\{1 - \frac{(1+T_1^2p^2)\{(M-1)T_1+T_2\}T_2p^2}{M + \{MT_1^2 + (M-1)T_1T_2 + T_2^2\}p^2 + \{(M-1)T_1+T_2\}T_1^2T_2p^4}\right\} \quad (8)$$

The phase-displacement is consequently zero for either $M=1$ or $T_1 = T_2$ as is obvious, and also for $1 + T_1^2p^2 = 0$, which is impossible. If the shunt is non-inductive $T_2=0$ and $\tan\psi=\frac{M-1}{M}T_1p$; while if the instrument is non-inductive and the shunt inductive,

$$\tan\psi=-\frac{M-1}{M+T_2^2p^2}T_2p.$$

Again, if both T_1p and T_2p are small compared with unity, the expression for $\tan\psi$ reduces to $\frac{M-1}{M}(T_1-T_2)p$. This of course means that the tangent of the phase-displacement between the instrument and mains is the fraction $\frac{M-1}{M}$ of that between the instrument and shunt, as is obvious geometrically. Finally, if T_1 and T_2 are nearly equal,

$$\tan\psi=\psi=\frac{M-1}{M(1+T^2p^2)}(T_1-T_2)p \quad . \quad . \quad . \quad (9)$$

where T is the mean time constant as before. When T is small this reduces to the last expression.

As an illustration of the error produced by shunting a wattmeter, we may assume a case where the time constant of the main circuit has a value of ·0025 as in the Kelvin balance above cited, and suppose that it is shunted with a non-inductive shunt of a nominal multiplying power of 10. We then have $M=10$, $T_2=0$, and T_1p at 50∼

$$=314\times{\cdot}0025={\cdot}785.$$

Hence

$$M'=M\sqrt{1+\left(\frac{M-1}{M}\right)^2T_1^2p^2}=10\sqrt{1+{\cdot}81\times{\cdot}785^2}=12{\cdot}25.$$

The phase-displacement is

$$\tan\psi_1=\frac{M-1}{M}T_1p=\frac{9}{10}\times{\cdot}785={\cdot}705\,;$$

so that the current in the wattmeter lags about 35° behind that in the main circuit. Hence the instrument would read 22·5 per cent. too low owing to the error in the ratio, while the phase-displacement would cause the power factor to be apparently about ·5 when actually zero.

This strikingly illustrates the enormous errors which may be produced by shunts in wattmeters. For any given small displacement ψ we have from (9)

$$\frac{T_1-T_2}{T}=\frac{\Delta T}{T}=\frac{M}{M-1}\left(\frac{1-T^2p^2}{Tp}\right)\psi \quad . \quad . \quad . \quad (10)$$

and ψ will then be the maximum error in the power factor for loads nearly in quadrature. Consequently, in the above case, if the error in the power factor is not to exceed ·01,

$$\frac{\Delta T}{T} = \frac{10}{9}\frac{(1-\cdot785^2)}{\cdot785} \times \cdot01 = \cdot00542 \quad \text{or} \quad \cdot54 \text{ per cent.};$$

and we saw before that for the ratio to be correct to 1 per cent.

$$\frac{\Delta T}{T} = 1\cdot53 \text{ per cent.}$$

TRANSFORMERS.

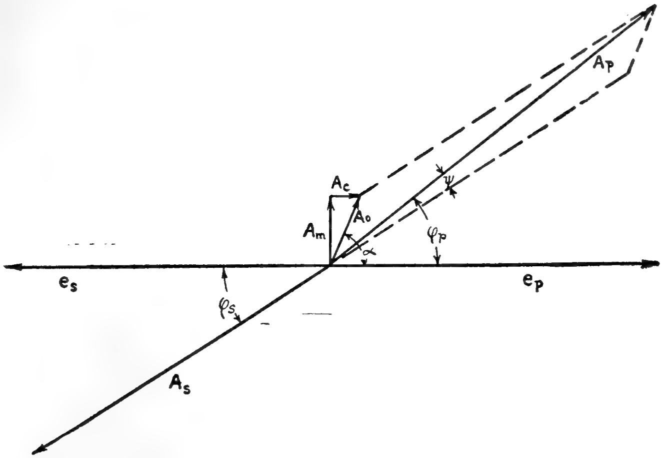
In dealing with the application of transformers to instruments, we shall have to consider separately their employment as "current transformers" or as "voltage transformers"; the former being employed in conjunction with ammeters for the purpose of utilizing instruments of convenient range, and to insulate the instrument from high voltage circuits; the latter with electromagnetic or hot-wire voltmeters to avoid undue waste of energy, and again as with ammeters to disconnect them from the high-pressure circuits. In wattmeters and energy-meters of the induction type, transformers are frequently employed in both the main and shunt circuits simultaneously.

The relations between the primary and secondary currents and voltages have been obtained by Steinmetz and others from the well-known vector diagram, but it will be well to treat the problem *ab initio* as we require the results to be exhibited in the most convenient form.

Current Transformers.—It is most convenient to deal at first with the magnitudes and phase relations of the currents, and we can afterwards apply the results to the investigation of the voltage relations.

Let A_p = primary ampere turns $= C_p n_p$.
A_s = secondary " " $= C\, n_s$.
A_m = magnetizing " " $= C_m n_p$.
A_c = core loss " " $= C_c n_p$.
A_0 = no load " " $= C_0 n_p$.
ϕ_p = lag of primary current behind core E.M.F.
ϕ_s = lag of secondary " " " "
α = lag of no load " " " "
ψ = phase displacement between primary and secondary currents.

Fig. 2.



Then we have

$$\hat{A}_p + \hat{A}_s = \hat{A}_0 \text{ vectorially ;}$$

or writing the currents in the Steinmetz notation,

$$\hat{A}_s = -A_s \cos\phi_s - jA_s \sin\phi_s \quad . \quad . \quad . \quad . \quad (11)$$

$$\hat{A}_0 = A_c + jA_m.$$

Hence

$$\hat{A}_p = A_0 - A_s = A_s \cos\phi_s + A_c + \quad (A_s \sin\phi_s + A_m) \quad . \quad (12)$$

and

$$\overline{A_p} = \sqrt{(A_s \cos\phi_s + A_c)^2 + (A_s \sin\phi_s + A_m)^2}$$
$$= \sqrt{A_s^2 + 2A_s(A_c \cos\phi_s + A_m \sin\phi_s) + A_0^2}.$$

If A_0 is small in comparison with A_s as it should always be in practice, we may write

$$\frac{A_p}{A_s} = 1 + \frac{A_c}{A_s} \cos\phi_s + \frac{A_m}{A_s} \sin\phi_s. \quad . \quad . \quad (13)$$

If R_c is the ratio of the primary to secondary currents, and R_t the ratio of secondary to primary turns, we have

$$R_c = R_t \left(1 + \frac{A_c}{A_s} \cos\phi_s + \frac{A_m}{A_s} \sin\phi_s\right). \quad . \quad . \quad (14)$$

Hence the ratio of the currents can only be equal to the transformation ratio if A_c and A_m are both zero or

$$\tan\phi_s = -\frac{A_c}{A_m} = -\cot\alpha.$$

This implies that the secondary current should be in quadrature with the no load current, as is geometrically obvious.

To test the constancy of transformation we have

$$\Delta R_c = R_t \left\{ \Delta\left(\frac{A_c}{A_s}\right)\cos\phi_s + \Delta\left(\frac{A_m}{A_s}\right)\sin\phi_s \right\}, \quad . \quad (15)$$

which shows that for constant ratio of transformation both A_c and A_m must be proportional to A_s or that

$$\tan\phi_s = -\frac{\Delta\left(\frac{A_c}{A_s}\right)}{\Delta\left(\frac{A_m}{A_s}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

For constant secondary impedance A_s is proportional to the core E.M.F. and hence to the induction density in the core, B. Hence the current vector should be perpendicular to the curve of which the ordinate is $\frac{A_m}{A_s}$, representing the reluctance of the circuit, and the abscissa is $\frac{A_c}{A_s}$ or the ratio of the core-loss current to B. It is obvious that this is when the secondary load is a leading one, and this result is contrary to the frequently quoted experiments of Mr. Campbell [*], who is claimed to have found experimentally that better constancy of ratio is obtained with an inductive instrument. In the case, however, where there is an air-gap in the transformer, the curve connecting $\frac{A_m}{A_s}$ with $\frac{A_c}{A_s}$ may be practically horizontal, and in this case the regulation will be worst on a non-inductive instrument, and better the greater is either the lag or lead of the secondary current. In estimating the value of Mr. Campbell's experiments it must not be forgotten that the two Kelvin balances employed by him must have been of very different impedance and consequently the core inductions would have been decidedly different. This of itself would probably have been sufficient to produce the effect found. Experimental evidence will be found below on this point.

Effect of variation of frequency.—Increase of frequency increases the impedance of the instrument if inductive, but at the same time increases the E.M.F. for the same core induction. With a fully inductive instrument, therefore, and if eddy currents are absent, variations in frequency should

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[*] Phil. Mag. vol. xlii. p. 271; Journal I. E. E. vol. xxxiii. p. 654.

have no effect upon the ratio. This agrees with Mr. Campbell's theoretical and experimental conclusions.

Phase Difference.—Reverting to equations (11) and (12), we have

$$\tan\phi_p = \frac{A_s \sin\phi_s + A_m}{A_s \cos\phi_s + A_c},$$

Hence

$$\tan\beta = \tan(\phi_p - \phi_s) = \frac{\frac{A_m}{A_s}\cos\phi_s - \frac{A_c}{A_s}\sin\phi_s}{1 + \frac{A_c}{A_s}\cos\phi_s + \frac{A_m}{A_s}\sin\phi_s} \quad . \quad (17)$$

which is zero for A_m and A_c both zero or for $\tan\phi_s = \frac{A_m}{A_c}$ as is obvious.

Hence for zero phase-displacement the instrument should be so inductive that the ratio of its reactance to resistance equals the ratio of the magnetizing to the core-loss currents of the transformer.

As the relation between $\frac{A_m}{A_s}$ and $\frac{A_c}{A_s}$ is not in general linear it follows that the phase-displacement cannot be constant, but it is fairly evident that the best constancy would be approximately obtained when the actual displacement is smallest, *i. e.* with an inductive instrument.

With variation of frequency it is again obvious that with a fully inductive instrument, without eddy currents in the transformer, the phase-displacement should be unaffected by frequency. The less inductive the instrument the more rapidly should the phase-displacement decrease with frequency, owing to the drop in the induction density.

P.D. Relations.—Writing the secondary current in the form $A_s(\cos\phi_s + j\sin\phi_s)$ and the primary

$$A_s\cos\phi_s + A_c + j(A_s\sin\phi_s + A_m),$$

let r_p and r_s be the primary and secondary resistances and x_p and x_s the primary and secondary reactances for coils of a single turn each.

Then

$$V_p = E + \{A_s\cos\phi_s + A_c + j(A_s\sin\varphi_s + A_m)\}(r_p - jx_p)$$

$$-V_s = E - A_s(\cos\phi_s + j\sin\phi_s)(r_s - jx_s),$$

from which

$$V_p = E + A_s \left\{ r_p\left(\cos\phi_s + \frac{A_c}{A_s}\right) + x_p\left(\sin\phi_s + \frac{A_m}{A_s}\right) - j\left[x_p\left(\cos\phi_s + \frac{A_c}{A_s}\right) - r_p\left(\sin\phi_s + \frac{A_m}{A_s}\right)\right]\right\} . \quad (18)$$

and

$$-V_s = E - A_s\{r_s\cos\phi_s + x_s\sin\phi_s - j(x_s\cos\phi_s - r_s\sin\phi_s)\} \quad (19)$$

Voltage Ratio.—Taking the ratio of $\frac{V_s}{V_p}$, simplifying, and neglecting squares of small quantities, we have

$$R_v = R_t\left\{ 1 - \frac{A_s}{E}\left[(r_p + r_s)\cos\phi_s + (x_p + x_s)\sin\phi_s\right] - \frac{A_c}{E}r_p - \frac{A_m}{E}x_p\right\},$$

which will be seen to be correct from the vector diagram.

Denoting $r_p + r_s$ by r the equivalent resistance,
$x_p + x_s$ by x ,, ,, reactance,
and $\sqrt{r^2 + x^2}$ by I ,, ,, impedance,

$$R_v = R_t\left\{1 - \frac{A_s}{E}(r\cos\phi_s + x\sin\phi_s) - \frac{A_c}{E}r_p - \frac{A_m}{E}x_p\right\}. \quad (20)$$

For an electrostatic or high-resistance voltmeter, $A_s = 0$ and we have

$$R_v = R_t\left\{1 - \frac{A_c r_p + A_m x_p}{E}\right\}. \quad . \quad . \quad . \quad (21)$$

For a hot-wire instrument $\phi = 0$ and

$$R_v = R_t\left\{1 - \frac{A_s r + A_c r_p + A_m x_p}{E}\right\}. \quad . \quad . \quad (22)$$

Returning to formula (20) we have

$$\frac{\Delta R_v}{R_v} = r_p\Delta\left(\frac{A_c}{E}\right) + x_p\Delta\left(\frac{A_m}{E}\right)$$

if the instrument and internal impedances are constant. This is independent of the phase of the secondary current and can only be zero if A_c and A_m are proportional to E, which is only the case for an air-core transformer. For an iron-core transformer the best constancy of ratio is thus obtained by making A_c and A_m and also r_p and x_p as low as possible, the core being of the best quality iron, and the coils subdivided and intercalated.

P.D. Phase Relations.—From equations (18) and (19) we obtain

$$\tan\psi_p = -\frac{x_p\left(\cos\phi_s+\frac{A_c}{A_s}\right)-r_p\left(\sin\phi_s+\frac{A_m}{A_s}\right)}{E+A_s\left\{r_p\left(\cos\phi_s+\frac{A_c}{A_s}\right)+x_p\left(\sin\phi_s+\frac{A_m}{A_s}\right)\right\}}A_s$$

$$\tan\psi_s = \frac{x_s\cos\phi_s-r_s\sin\phi_s}{E-A_s\{r_s\cos\phi_s+x_s\sin\phi_s\}}A_s.$$

If, as should be the case with voltage transformers, the resistance and inductive drop in the transformer are small compared with E, we have

$$\psi_p-\psi_s=\beta=-\frac{A_s(x\cos\phi_s-r\sin\phi_s)+A_cx_p-A_mr_p}{E} \quad . \quad (23)$$

as is geometrically obvious.

For the phase-difference to be zero it follows that either the resistance and inductance must be zero, or that

$$\tan\phi_s=\frac{A_s^2rx\pm(A_cx_p-A_mr_p)\sqrt{A_s^2(x^2+r^2)-(A_cx_p-A_mr_p)^2}}{A_sr^2-(A_cx_p-A_mr_p)^2} \ . \ (24)$$

In this expression if A_s is large compared with A_c or A_m $\tan\phi_s=\frac{x}{r}$, or the ratio of the reactance to the resistance of the instrument should be the same as for the transformer, and the instrument should therefore be fairly inductive.

With a non-inductive instrument

$$\beta=\frac{A_sx+A_cx_p-A_mr_p}{E}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and if the instrument takes no appreciable current compared with A_c or A_m,

$$\beta=\frac{A_cx_p-A_mr_p}{E}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

To find the variation of phase-displacement with voltage we have evidently from (23)

$$\Delta\beta=x_p\Delta\left(\frac{A_c}{E}\right)-r_p\Delta\left(\frac{A_m}{E}\right),$$

and this is evidently zero for an air-core transformer.

Relation between the Secondary Current and the Magnetizing and Core-Loss Currents.—If l is the length of the magnetic path, a its area of cross section, and I_s the total secondary impedance (reduced to 1 turn), we have

$$\text{Effective core E.M.F. } \bar{e} = \frac{a\bar{B}p}{10^8} = \frac{a\hat{B}p}{\sqrt{2}\times 10^8} \text{ volts per turn;}$$

$$\text{Secondary ampere turns } A_s = \frac{\bar{e}}{I_s} = \frac{a\hat{B}p}{\sqrt{2}\times 10^8 I_s},$$

from which

$$\hat{B} = \frac{\sqrt{2}\times 10^8 I_s A_s}{ap} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Assuming the core loss to be $\eta\hat{B}^c$ ergs per c.c. per cycle:—
Total core loss

$$w_m = \frac{\eta\hat{B}^c V_n}{10^7} \text{ watts,}$$

and the core-loss ampere turns

$$A_c = \frac{w_m}{\bar{e}} = \frac{5\sqrt{2}}{\pi}\eta l \left\{\frac{\sqrt{2}\times 10^8 I_s A_s}{ap}\right\}^{(c-1)} \quad . \quad . \quad (28)$$

For the magnetizing current

$$A_m = \frac{10}{4\pi}\frac{\bar{B}l}{\mu}$$

or

$$A_m = \frac{10^9}{4\pi}\frac{l}{\mu a p} I_s A_s. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

These relations are sufficient to enable the magnetizing and core-loss currents to be calculated when the total secondary impedance is known. The resistances are of course readily calculable, while the equivalent inductance of the whole transformer for a single primary and secondary winding may be calculated from the following formula, deduced from that given by Prof. Kapp :

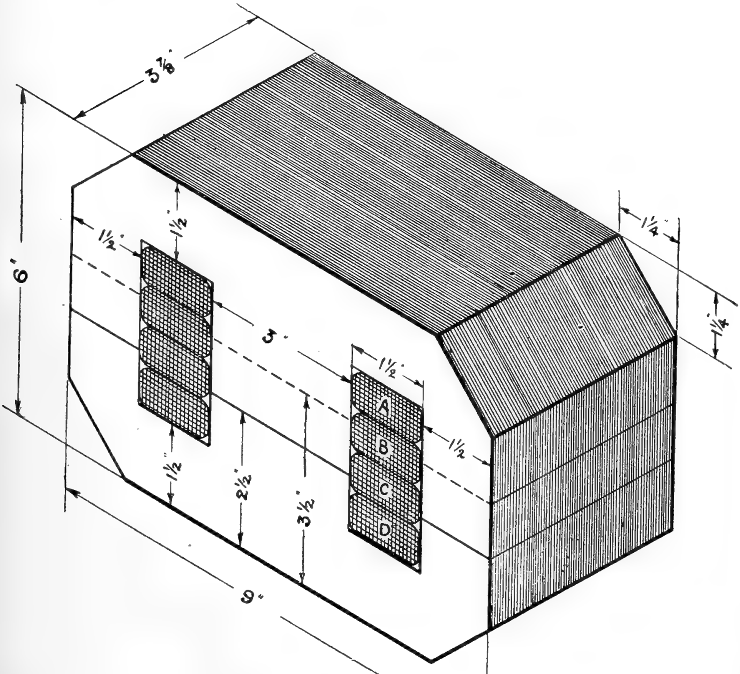
$$L = C\frac{\sqrt{2}}{10^{10}}\frac{P}{LK^2}(3KS+T) \quad . \quad . \quad . \quad . \quad . \quad (30)$$

P being the mean perimeter of the coils in inches,
L the length of gap from iron to iron, parallel to insulation between coils,
S the thickness of the insulation in inches,
K the number of sections per coil,
T the length of the winding space,
and C a constant given as 44 for core and 55 for shell type transformers.

From personal experiment, however, the author has found that the value 44 is more nearly correct for shell type transformers.

Experimental.—As some of the conclusions arrived at are of importance, and are somewhat at variance with existing ideas, some experimental evidence will be of value. A brief reference only will be necessary here as some of these tests have already been published *, together with a description of the methods by which the results were obtained.

Fig. 3.—Isometric view of Transformer Core.



The principal transformer tested was made for the tests, and was of the shell type ; the core having a magnetic path of 35·3 cm. and a sectional area of 71 sq. cm. Four independent coils, each of 150 turns of No. 18 D.C.C. copper wire, were wound side by side, the resistance of each coil being 1·2 ohms. Fig. 3 shows the core, and fig. 4 the

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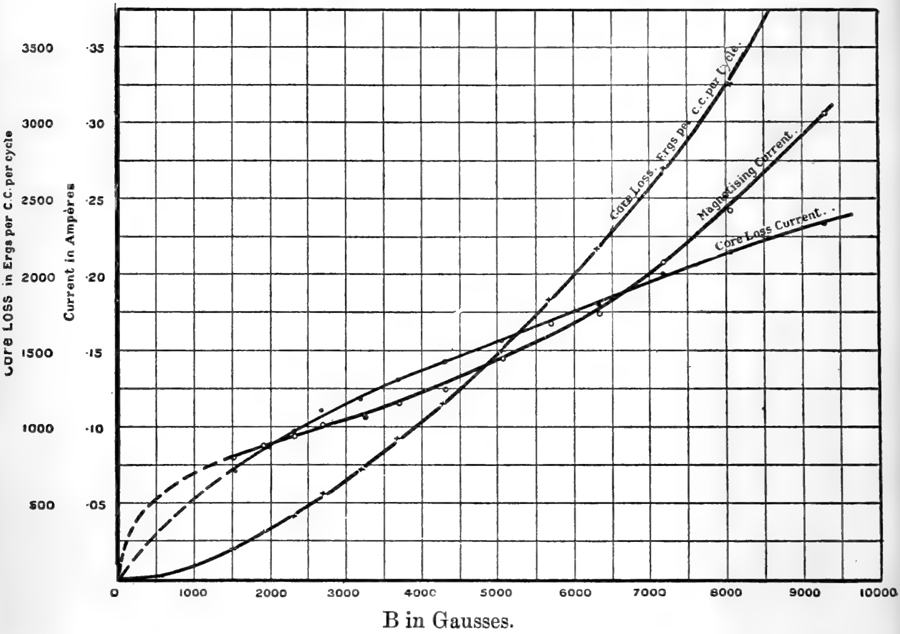
* "Phase Displacements in Resistances and Transformers," Electrician, No. lviii. p. 160.

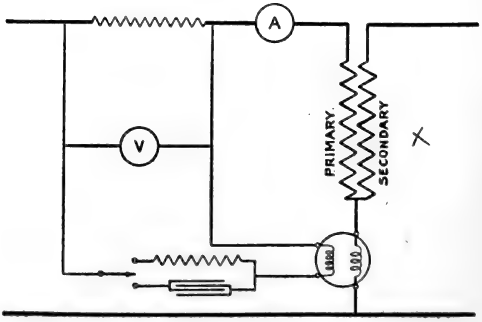
Fig. 4.—Relation of Magnetizing and Core-loss Currents to Induction.



relation of the magnetizing and core-loss currents to the core induction, determined experimentally.

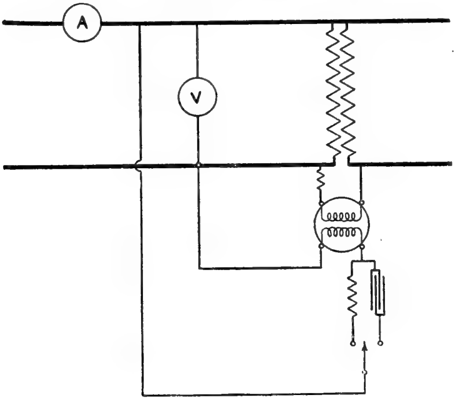
Figs. 5 and 6 show the connexions for determining the

Fig. 5.—Connexions for Current Test.



current and P.D. ratios and phase displacements. The current ratio is determined by an ordinary wattmeter instead of the differential wattmeter previously employed. Figs. 7 and 8 (Pl. IV.) show the current ratio and phase-displacements for this transformer, while figs. 9 and 10 give the P.D. relations

Fig. 6.—Connexions for P.D. Test.



which have been determined over a greater range of core induction than before.

As a test of formulæ 14 and 17 for the ratio and phase-displacement when used as a current transformer, we will take case VII., where the coils were separated and a secondary load of 5·9 ohms non-inductive was employed. The core induction was then found from the voltages in the unused coils and was taken at 1565 for a secondary load of 5 amps. On measuring the equivalent reactance of the transformer it came out at 5·12 ω or 2·56 ω for the secondary leakage reactance. From this we get a total secondary resistance of 7·1 ω, reactance of 2·56 ω, and impedance of 7·5 ω approx. $\cos\phi_s = \cdot 94$ and $\sin\phi_s = \cdot 34$.

Formula 14 gives us as the loss of ratio per cent.

$$100\frac{R_t-R_c}{R_t}=100\left\{\frac{A_c}{A_s}\cos\phi_s+\frac{A_m}{A_s}\sin\phi_s\right\},$$

which works out at 1·92 per cent., while the experimental value is 1·8 per cent.

The phase-displacement in the same case may be taken as

$$\frac{A_m}{A_s}\cos\phi_s-\frac{A_c}{A_s}\sin\phi_s,$$

which works out to ·58°, the experimental value being ·75°.

In the case of a lagging load as in curve VI. but with the coils close together, the calculated loss of ratio is 1·87 per cent. as against 2·7 per cent. by experiment, and the phase-displacement works out at ·57°* which agrees with the experimental value. The agreement between calculation and experiment is not always therefore very close, but this is probably due to the difficulty of determining the core induction. In a current transformer the magnetic leakage may be quite comparable with the main working flux, owing to the small value of the latter, and hence the distribution of flux in the core is very irregular. The mean value of the induction, however, as calculated by formula 27, agrees very fairly with the experimental value, being 1575 as against 1565 in case VII., and 1345 as against 1385 in case VI. Calculations have not been made in other cases, as the induction densities are too low.

The statement on p. 144 that a non-inductive secondary circuit should give a better ratio than an inductive one of the same impedance, is amply borne out by comparing curves V. and VI. The advantage of a low induction density is also manifest.

Calculations of P.D. ratio and phase-displacement show an agreement within ·1 per cent. in the ratio and ·01° in the displacement, which is sufficient for most purposes. The theory is in each case confirmed.

Tests made with instrument transformers of various makers have in no case shown anything like such good results, and the writer is of opinion that these results represent nearly the best that can be obtained without using some special alloy of low core-loss, and also of high permeability. In view of the importance which magnetic leakage assumes in current transformers, the secondary current nearly always lags 20° to 30°, and the magnetizing current is therefore nearly as important as the core loss-current.

Fig. 11 (Pl. IV.) gives the relation between A_c and A_m and is consequently the locus of the end of the no load vector A_0 for various inductions. This vector is therefore over a considerable part of the range, at about 45°, and consequently the best ratio should be obtained with a secondary circuit leading by about 45°. In fig. 12 a curve is given for the relation of $\frac{A_c}{B}$ to $\frac{A_m}{B}$ which is of use in working out the P.D. ratio and phase-displacement.

Figs. 13 and 14 show curves of ratio and phase-displacement for three current transformers made by Messrs. Everett &

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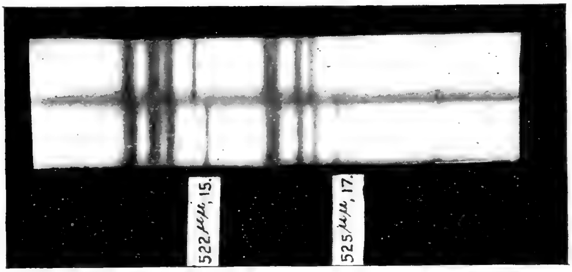
* The curves for current ratio and phase-displacement appeared in the 'Electrician' (*loc. cit.*), but in case VI. the phase-displacement was unfortunately given with reversed sign.

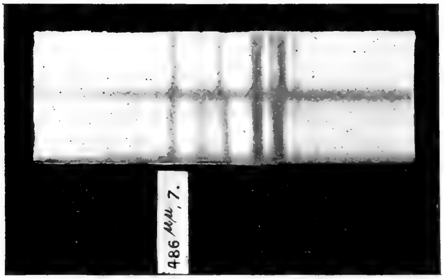
FIG. 1.



XENOTIME.

Spectra of two circular vibrations of different sense in a magnetic field of 12,000 gauss, at temperature of liquid air. Plate $0^{\mathrm{mm}}\cdot 80$ thick; green group. 2° sp. Rowland grating. Scale: $1^{\mathrm{mm}} = 0^{\mu\mu}\cdot 165$.

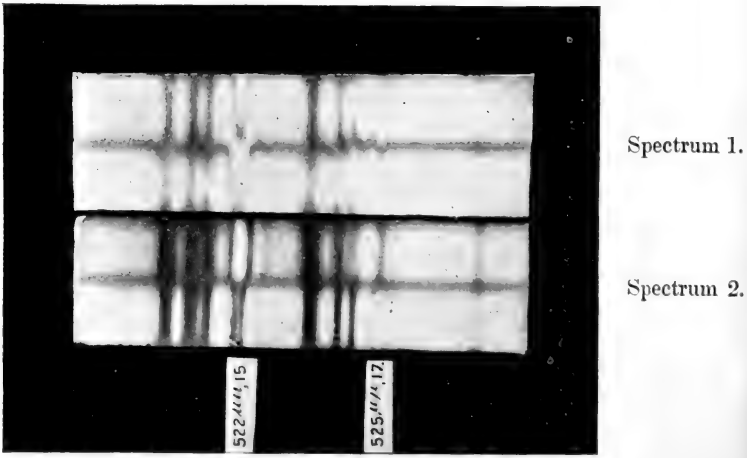
FIG. 2.



XENOTIME.

Spectra of two circular vibrations of different sense. Plate $0^{\mathrm{mm}}\cdot 80$ thick; 2° sp. Rowland grating. Blue-green group. Magnetic field 12,000 gauss, at temperature of liquid air. Scale: $1^{\mathrm{mm}} = 0^{\mu\mu}\cdot 165$.

FIG. 3.



XENOTIME.

Rotatory magnetic polarization at −188°. Magnetic field 12,300 gauss. Plate $0^{\mathrm{mm}}\cdot 80$ thick.

Edgcumbe and Messrs. Nalder Bros. & Thompson. In the former, the primary and secondary windings were close together, giving good ratio but large phase displacement; and it is noticeable that throughout lower phase-displacement is got by greater loss of ratio, as indicated in the tests on the experimental transformer. In the Nalder transformer, the primary and secondary coils are wound on thick porcelain bobbins side by side. The leakage is therefore somewhat large, producing a variation of ratio of about 8 per cent. between 2 and 18 amperes; but this is accompanied by a phase-displacement which is less than ·2° over the range from 6 to 18 amperes or the upper two-thirds of the range. Such a transformer therefore, if used with a wattmeter, *and calibrated with it*, should do fairly well for commercial testing.

In conclusion it should be noted that the tests on all four transformers give results which are not very widely different, and the results may therefore be taken as fairly representative of the behaviour of instrument transformers.

The writer wishes to express his thanks to his senior Demonstrator, Mr. A. C. Jolley, for great assistance in the experimental work, and to Mr. A. F. Burgess, B.Sc., for checking the calculations.

X. *On the Dispersion of Magnetic Rotatory Power in the neighbourhood of Bands of Absorption in the case of Rare Earths. Remarks on the subject of recent communications by Prof. R. W. Wood and Mr. G. J. Elias.* By JEAN BECQUEREL*.

[Plate V.]

THE question of the variation of magnetic rotatory power in the neighbourhood of bands of absorption has given rise to numerous researches and stimulated much controversy.

The various explanations of the phenomenon of magnetic rotatory polarization can be grouped into two principal theories†, which give results which are almost identical for the rotatory dispersion in transparent regions, but which are different for variations of the rotatory power near to and within an absorption-band.

According to "the molecular current theory" the rotation will be produced in opposite senses on the two sides of a band. On the contrary, according to the hypothesis based on the Hall effect, the rotations will be in the same sense on

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* Communicated by the Author.

† See Drude, *Lehrbuch der Optik*, 1906, p. 406.

each side of a band, and in the opposite sense in the interior of the band.

Experiments performed with vapours exhibiting the Zeeman effect gave results in entire agreement with the latter theory[*]. For solid bodies and solutions not merely the theories but the experiments themselves have been subject to much discussion. The results obtained by Schmausz[†] with solutions of colouring matters and with salts of didymium were in agreement with the molecular current theory; but according to Bates[‡] these experiments are not free from criticism. Moreover, R. W. Wood[§], in the chloride of praseodymium, found opposite rotations on the two sides of certain bands.

Until 1906 no observation with a solid body or a solution had confirmed the truth of the theory based on the Hall effect—the theory which at the same time represented the effects in vapours.

It seemed to me that magnetic rotatory polarization in solid bodies should result, at least in certain cases, as with vapours, in a modification of the bands of absorption under the influence of magnetism. I then endeavoured to observe directly whether or not the bands were displaced in a magnetic field.

My first experiments, carried out with solid bodies possessing the finest possible bands, viz. with xenotime (phosphate of yttrium and erbium) gave me extremely definite results, which I have since been able to extend to all crystals and to those solutions which possess bands sufficiently narrow. The phenomenon observed with crystals is of the same nature as the effect discovered by Zeeman in the spectra of vapours, but presenting fundamental differences from the Zeeman phenomenon of which the two following are the most important:—

(1) The order of magnitude of the displacements for many of the bands of crystals is notably greater than for the effects observed with vapours. The separation of the components of some doublets produced by the magnetic field surpasses in fact 1 $\mu\mu$ in a field of 30,000 gauss. This is the case for the bands of wave-lengths 642·27 and 643·45 $\mu\mu$ of xenotime.

(2) When the optic axis of a uniaxal crystal is oriented

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[*] Macaluso and Corbino, *Comptes Rendus*, 127. p. 548 (1898). Henri Becquerel, *Comptes Rendus*, 125. p. 679 (1897). and 127. p. 899 (1898); P. Zeeman, *Arch. néerlandaises*, vii. p. 465 (1902).

[†] A. Schmausz, *Ann. der Phys.* ii. p. 280 (1900); viii. p. 842 (1902). x. p. 853 (1903).

[‡] Bates, *Ann. der Phys.* xii. p. 1080 (1903).

[§] R. W. Wood, *Phys. Zeitschr.* vi. p. 416 (1905).

parallel to the lines of force of the magnetic field and the direction of propagation of the light is the same, the bands corresponding to the absorption of the circular components of given sense are not all displaced in the same direction in the spectrum.

The most probable explanation of this behaviour appears to me to be that amongst the various bands some are due to vibrations of negative electrons (as in the phenomenon of Zeeman), but that others are produced by *positive electrons which thus appear for the first time in optical phenomena.*

These results can be seen very definitely in figs. 1 & 2 (Pl. V.) which represent for two groups of xenotime the spectra of the two circular components in a field of about 12,000 gauss. The crystal was immersed in liquid air with the object of obtaining, as we shall see later, the most definite and sharpest bands. These figures are a reproduction (magnified 3·7 times) of negatives obtained with a Rowland-grating spectrograph.

In this note I shall content myself with enumerating those new phenomena which are related to magnetic rotatory polarization alone, asking the reader to refer for the description of the experiments and the detailed results to the publications made by me 26th March, 1906 to 30th March, 1908 *.

Placing the optic axis of a crystal of xenotime parallel to the lines of magnetic force and to the direction of propagation of the light, I showed that the bands, which are variable under the influence of the field, give, when the components corresponding to the two circular components of opposite senses have appreciably the same intensity, the same effects as for rays through vapour; *we observe, consequently, a magnetic rotatory power of the same sense on each side of a band and of the opposite sense inside the band. The direction of the rotation depends upon the direction of the displacement of the absorption bands of the circular components.* The variation of the rotatory power is positive outside and negative inside the band if this arises from negative electrons. The opposite takes place if the band arises from positive electrons.

These are the first results in agreement with the theory

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* Jean Becquerel, *Comptes Rendus*:—1906, 26 March, 9 April, 21 May, 19 Nov., 3 Dec., 10 Dec.; 1907, 21 Jan., 25 Feb., 25 March, 13 May, 17 June, 19 Aug., 11 Nov., 25 Nov., 9 Dec., 30 Dec.; 1908, 30 March.—*Le Radium,* iv. No. 2. p. 49, No. 3. p. 107, No. 9. p. 328, No. 11. p. 385 (1907); v. No. 1. p. 5 (1908).—*Physik. Zeitschr.* viii. No. 19. p. 632, No. 25. p. 929 (1907); ix. No. 3. p. 94 (1908).

Jean Becquerel and Kamerlingh Onnes, *K. Akad. v. Weten. te Amsterdam,* 29 Feb. 1908; *Comptes Rendus,* 23 March, 1908.

based on the Hall effect ever observed in the case of a solid body. A crystal of xenotime behaves, therefore, from the magneto-optic point of view, like a vapour exhibiting the Zeeman effect. Moreover, one obtains *experimentally* this new and supremely important result: the effect of an absorption band depends, assuming the existence of electrons of two signs, upon the sign of the charge of the electrons producing the particular band under consideration.

Fig. 3 represents the variations of the magnetic rotatory power of xenotime, at the temperature of liquid air, in the neighbourhood of the bands shown in the group in fig. 1. The spectrum (1) of fig. 3 shows the dislocation of the black fringes obtained in the spectrum by placing against the slit of the spectrograph a Babinet compensator placed between two crossed Nicol's prisms in such a manner that the central fringe is normal to the slit, and preceded by a quarter-wave plate which transforms the two circular components of opposite senses into two rectilinear vibrations parallel to the two principal directions of the compensator. The displacements of the fringe measure the rotatory power. The fringe and the components of the band 522·15 $\mu\mu$ form a very remarkable V-shaped curve.

The spectrum 2 of fig. 3 was obtained by polarizing, at 45° to the horizontal, the light which falls on the crystal, and placing in front of the slit of the spectrograph a rhombohedron of Iceland spar which gives two images polarized horizontally and vertically respectively. The two contiguous images are identical if the field is not excited; but when the crystal is submitted to a magnetic field, a rotation of the plane of polarization of the incident vibration corresponds to an increase in the luminous intensity in one of the images and a decrease of that of the other. For the components of the bands 522·15 and 525·17 $\mu\mu$ the phenomenon is exceedingly definite.

Identical results were obtained with all crystals or solutions of salts which produce bands responsive to a magnetic field.

Some months after my first experiments on the magnetic rotatory polarization in xenotime*, Elias† obtained quite similar effects with a solution of chloride of erbium which he recalls in a recent communication‡.

On each side of a broad band of a solution of chloride of erbium (about 520 $\mu\mu$) the rotation is negative, whilst it is positive in the midst of the band. The experiments of Elias,

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* Jean Becquerel, *Comptes Rendus*, 21 May, 1906.

† G. J. Elias, *Physik. Zeitschr.* vii. p. 931, 15 Dec. 1906.

‡ Phil. Mag. [6] vol. xv. p. 538, April 1908.

made by a method having great precision, permit one to follow the details of the variation of rotatory power in the neighbourhood and in the interior of the band, and it is manifest, from the numerous irregularities of the curve, that the band is complex, *i. e.* it is formed by the superposition of several components. It is quite impossible to deduce from these results any certain conclusion relative to the effect of a *simple* band.

On the contrary, with crystals which exhibit fine bands, such as xenotime, tysonite, porisite, apatite ; and especially if we study the absorption at a very low temperature (as we shall show later on), we have the advantage of being able to observe simple bands ; and we then see the connexion which exists between magnetic rotatory dispersion and the modification which each band undergoes. The variation of the magnetic rotatory powers appears indubitably as the consequence of the simultaneous effect of anomalous dispersion and of the separation, under the influence of the magnetic field, of bands into two components absorbing circular vibrations.

In tysonite, after having studied, at ordinary temperatures and at the temperature of liquid air, the variations of the index of refraction in the neighbourhood of one of the bands ($523{\cdot}5\ \mu\mu$) and measured the separation of the components in a magnetic field, I was able to predict from the formula given by Voigt, what the magnitude of the rotation should be in the interior of a band, at 20° C. and −188° C. The calculated and observed numbers are in as satisfactory agreement with one another as possible [*].

R. W. Wood, in a note [†] published in the month of February last, shows that very complex effects occur in the neighbourhood of a group of bands of nitrate of neodymium. In crystals, I have for a long time observed and pointed out the existence of phenomena near certain bands which do not possess the simplicity of those which I have just described ; in particular, a strong band of tysonite ($577\ \mu\mu$) gives a negative rotation on the side of smaller wave-length and a positive rotation on the side of greater wave-length. This result appears at first to be in agreement with the molecular current theory ; but, before coming to any conclusion, it is important to learn whether one has to deal with a simple band, or if, on the contrary, the band is a complex group. It is evident that a combination of bands of negative and

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[*] Jean Becquerel, *Comptes Rendus*, 11 & 12 Nov., 1967 ; *Le Radium*, v. No. 1. p. 11 (1908).

[†] R. W. Wood, Phil. Mag. [6] vol. xv. p. 270, Feb. 1908.

positive electrons, of various degrees of responsiveness and whose effects are superposed, may give rise to phenomena possessing very great complications. It is effects of this nature, I think, which were observed in nitrate of neodymium by Professor Wood.

The only means of elucidating this question consists in separating complex groups into their components: and I have shown that we may in a number of cases succeed in doing this by studying the absorption at very low temperatures.

Having been led to investigate whether or not changes of period produced by a magnetic field depend upon temperature, I observed a new phenomenon*. *Under the influence of a lowering of temperature* (in the absence of any action of a magnetic field) *the absorption bands of solids and solutions become much finer*; so much so indeed that at the temperature of liquid air the salts of rare earths, either crystallized or in frozen solution, exhibit absorption spectra having very remarkable sharpness.

Measurements made upon several bands of tysonite showed that, down to the temperature of liquid air, the breadth of these bands varies proportionately to the square root of the absolute temperature. Besides this†, at −190° C. the bands have an intensity which is in general much greater than at ordinary temperatures; not only because they are more constricted, but also as I have established, because the quantity of energy absorbed increases in the case of nearly all bands.

These researches have just been pushed to the lowest temperatures at present realizable. In the cryogenic laboratory in the University of Leyden, Professor Kamerlingh Onnes and myself‡ have been able to study absorption and magneto-optic phenomena in crystals at temperatures down to that of the solidification of hydrogen (−259° C.).

We observed that the majority of bands continue to narrow down, but in general at a less rate than according to the law which was proved to be valid down to the temperature of liquid air.

We have shown, moreover, that *for each band a temperature exists for which the absorption passes through a maximum.* Certain bands which, on cooling to −190° C., became extremely intense, diminished afterwards till they became

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* *Comptes Rendus*, 25 Feb., 13 May, 17 June, 1907.

† *Comptes Rendus*, 11 & 25 Nov., 1907; *Le Radium*, iv. No. 11. p. 385 (1907); *Physik. Zeitschr.* ix. No. 3. p. 94 (1908).

‡ *K. Akad. Amsterdam*, 29 Feb., 1908; *Comptes Rendus*, 23 March, 1908.

invisible at −259° C. Some bands which made their first appearance at low temperatures still continue to increase in intensity at −259° C.; we think they all should possess a maximum, but at a temperature which we have not yet attained.

The study of magneto-optic phenomena at very low temperatures has considerably extended the field of research and has led to new results of very great interest. In the first place, the separation between bands of absorption of the two circular components, that is to say, *the changes of period of oscillating systems under the influence of an external magnetic field are independent of the temperature. Even in paramagnetic bodies these changes of period constitute phenomena which are connected with diamagnetism**.

Moreover, at very low temperatures, an unforeseen effect is observed. *The bands which correspond to the absorption of the opposite circular components are very often of unequal intensity.* At temperatures of −253° and −259° the components which the magnetic field displaces towards the blue increases at the expense of the other component. The dissymmetry is greater to such an extent as the field is more intense and the temperature is lower.

An example of this dissymmetry is visible on fig. 1 for the band 525·17 $\mu\mu$ of xenotime at −188°. We clearly see that in one of the two spectra of the circular components the band 525 which is displaced by the field towards the violet side is more intense than the band corresponding to the other spectrum.

To return to the question with which this note is specially concerned: the variations in the intensity of the bands and their magnetic components draw in their train, as we might expect, modifications in the magnetic rotatory dispersion. The magnitude of the effects produced for each band depends upon the intensity of absorption and on the breadth of the band. When a band becomes finer and more intense the variations of rotatory power increase at the same time; moreover, the dissymmetry of intensity for the two magnetic components is accompanied by a dissymmetry in the rotation produced by the band. I have indicated on fig. 1 the inequality of the circular components of the band 525·17 $\mu\mu$ of xenotime; in fig. 3 it is seen that, on the edges of the band, the two maxima of positive rotation are unequal; the more intense are on the violet side because the circular component displaced towards the violet is more intense than the other

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* Jean Becquerel, *Le Radium*, v. No. 1. p. 5 (1908); Jean Becquerel and Kamerlingh Onnes, *loc. cit.*

component. The inequality of these two maxima of rotation enables us even to measure the dissymmetry in the intensity of the two components.

At the temperature of liquid or solid hydrogen the dissymmetry is sometimes such that the direction of the phenomenon is the same as if there existed only one of the circular components, corresponding to vibrations in one direction alone ; *we then obtain rotations in opposite senses at the two edges of the band.* This result again is a consequence of the simultaneous effects of anomalous dispersion and of the modifications undergone by the band under the influence of the field : it is in good agreement with the theory based on the Hall effect; but we must take into account the new fact that no theory can yet explain the dissymmetry of intensity of the two components corresponding to opposite circular vibrations.

Lastly, in a general manner, the constriction of the bands which takes place under the influence of cooling enables us to separate many complex groups into their elements and to explain certain effects. Thus, to return to an example cited above, the band 577 $\mu\mu$ of tysonite, which gives opposite rotations at the two edges, appears double at very low temperatures ; and it is constituted of a band of positive and one of negative electrons in juxtaposition ; the effects of these are superposed.

The variation of magnetic rotatory power near an absorption-band seems then to be related to the hypothesis of the Hall effect, according to which they are a consequence of the simultaneous action of anomalous dispersion and of the change of period of the absorbing electrons in a magnetic field.

It is not proved as a matter of fact that a simple band in any case gives rise to the phenomena indicated by the molecular current theory.

The single effect which it might perhaps be possible to bring into relation with the latter theory is the increase of the magnetic rotatory power of paramagnetic crystals when we lower the temperature*.

I found that this rotatory power is very nearly in inverse proportion to the absolute temperature. But one is not concerned in this phenomenon with the perturbations produced by bands of absorption.

In conclusion, I will add a few remarks relative to *biaxial*

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* *Comptes Rendus*, 23 May, 1907 ; *Le Radium*, v. No. 1. p. 12 (1908). Jean Becquerel and Kamerlingh Onnes, *loc. cit.*

crystals. Certain crystals, such as the sulphates of neodymium and praseodymium, possess at the temperatures of liquid or solid hydrogen true rays of absorption of a fineness as great as the rays of metallic vapours. The rays which correspond in the three principal spectra are very sensibly of the same wave-length, but differ in breadth and intensity.

Let us denote by 1, 2, 3 the three principal directions of absorption relative to one of these rays. We shall transmit the light along the direction of the magnetic field. We can, in succession, align the directions 1, 2, 3 parallel to the light and to the field; the two vibrations simultaneously observed being normal to this direction are then respectively parallel to 2 and 3, 1 and 3, 1 and 2. When the rays are very fine and occupy exactly the same position in both spectra, experiment proves* that in the first case the vibrations 2 and 3 are connected together by the fact of the field which is perpendicular to them giving magnetic doublets having the same separation; in the second case the vibrations 1 and 3 also give rise to a doublet, *but this doublet is different from the first*; lastly, in the third case, the vibrations 1 and 2 give rise to a third doublet which differs from both the others.

These results can be interpreted, according to the theory of a quasi-elastic force, by the existence of three principal electromagnetic magnitudes for the absorbing electrons in biaxial crystals.

This phenomenon must be considered as the generalization of phenomena which, in isotropic bodies or in uniaxial crystals, are connected with magnetic rotatory polarization; for it proves *experimentally* in the more complex case of biaxial crystals, that the magnetic field produces a connexion between the two principal vibrations which are perpendicular to it.

April 23, 1908.

XI. *On Cathode and Canal Rays from Hollow Cathodes.*

By Jakob Kunz, *Dr. phil., Privatdozent für Physik am eidg. Polytechnikum, Zürich*†.

IN his paper, "Ueber die Canalstrahlengruppe," *Verhandlungen der deutschen physikalischen Gesellschaft* im Jahre 1902, p. 228, E. Goldstein describes canal-rays starting from cathodes made of two separated parallel metal plates of different shape. The nature of these rays not being fully determined, the following experiments were made.

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* J. Becquerel and Kamerlingh Onnes, *loc. cit.*

† Communicated by the Author.

Fig. 1.

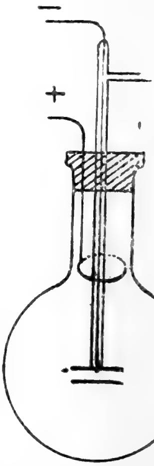
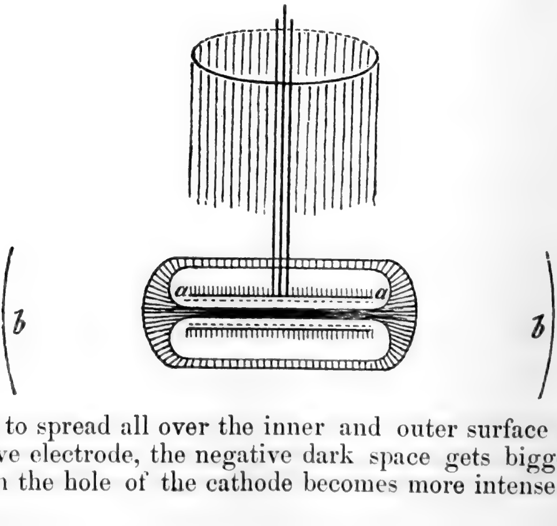


Fig. 2.

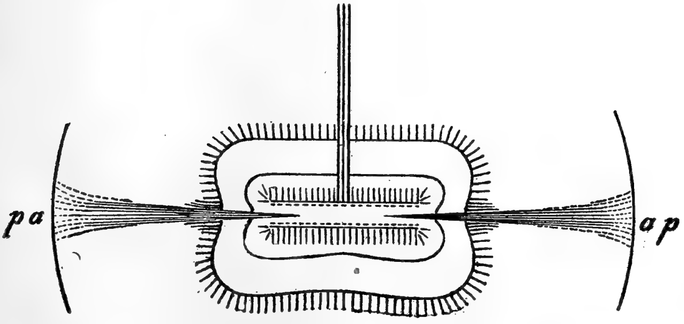


Experiment 1.—The vacuum was made by means of a mercury-pump in a bulb of the form shown in fig. 1. The cathode is a cylindrical tube of brass, 2·4 cm. long, 0·4 cm. in diameter. The anode is a ring of aluminium. The wires in the tube are insulated from one another by glass tubes, and the bulb is sealed up with ebonite and sealing-wax. If now the air is gradually pumped out, at a certain stage the cathode is found to be surrounded by a comparatively dark space, called Crookes's. Beyond this dark space and enveloping it, there is a very bright luminous ring, called the negative glow. This ring passes through the hole of the cathode and emits a very vivid violet light Beyond the luminous region there is another comparatively dark space—Faraday's dark space—of a very variable length even at constant pressure. Between this dark space and the anode there is a luminous column, called the positive column, which, when the current and pressure are within certain limits, exhibits the well-known alternations of dark and bright spaces—the striations. If now the pressure is diminished, a thin layer of yellow luminosity begins to spread all over the inner and outer surface of the negative electrode, the negative dark space gets bigger, the light in the hole of the cathode becomes more intense ; it is also very bright just at the points *a*, and two spots of green phosphorescence appear at *b*, where the prolonged axis of the tube cuts the glass bulb (fig. 2).

On the outside of the cathode, the boundary of the dark space is approximately the surface traced out by normals of constant length drawn to the surface of the cathode ; in the tube itself, however, the width of the dark space is much smaller than outside.

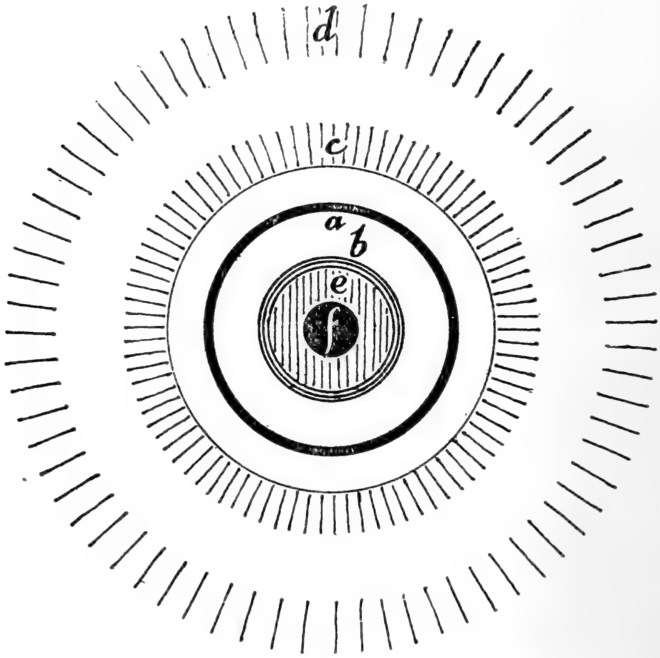
As the pressure is decreased, there appear two beautiful well-defined rays of bright blue light starting from both ends of the cathode, spreading out as they approach the wall of the tube, and producing the yellow-green phosphorescence due to cathode rays. The rays start from a short distance within either end of the tube, the centre appearing quite empty except for a faint yellow light enveloping the cathode inside and out. The very sharply defined bright central beam of blue light is deflected by a magnet in the same way as ordinary cathode rays. Under the given pressure, a pale bluish misty luminosity fills the whole tube, due to secondary cathode rays produced by the ionization of the gas by the primary rays. At the same time, a band of weak phosphorescence appears round about the meridian of the bulb, if we consider the axis of the cathode-tube as polar axis of the sphere. This phosphorescence is produced by cathode rays, which are invisible in the gas and which start nearly at right angles from the outer surface of the cylindrical cathode.

Fig. 3.



When the vacuum advances, all the phosphorescent spots on the glass wall become brighter ; the general dim bluish luminosity gradually disappears. The bright blue polar cathode rays remain visible for a long time, but get very much fainter when the vacuum is the best possible, becoming prolonged through the centre of the cathode; so that the middle of this tube is found to be filled with bright bluish light. The phosphorescent spots at the poles in fig. 3 become surrounded by a system of circular phosphorescent rings, separated from one another by almost dark intervals. The limits of these rings are sharply defined: the ring which appears first is the ring *a* in fig. 4, being separated from the central spot by a dark band with limits of geometrical distinctness. With decreasing pressure, a fresh ring (*b*) appears, followed by the two broad faint rings *c* and *d*; and finally the central spot is contracted into a small circle distinctly separated from a ring *e* which seems much fainter than the ring *b*. The limits of ring *d* are far from being as sharp as those of the other rings.

Fig. 4.

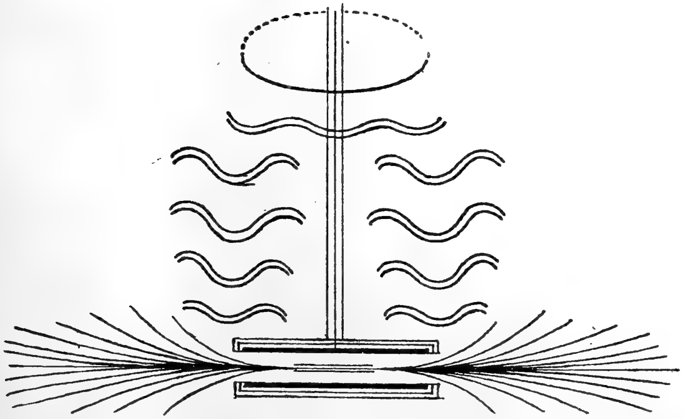


At the most complete vacuum, the yellowish light surrounding the cathode nearly disappears; but there is to be found a very thin layer of red light quite close to the cylinder visible only when looked at in a direction parallel to the axis of the tube. The inner edge of both ends of the cathodic cylinder glows also with a dim red light.

The question now arises as to what is the origin of the blue polar beam, and how the various rings are brought into existence.

Experiment 2.—If the outside of the cylindrical tube and the edge at either end are covered with ebonite, so that only the inner metal surface is free, the same succession of phenomena occurs as in experiment 1, except that the two faint rings *c* and *d* and the three layers round the outer surface do not appear. Neither are they to be found when only the outer edge of both ends is covered with a ring of ebonite. These rings *c* and *d* take their origin, therefore, at the end of the tube on the outer surface of the cylinder. They might be considered as belonging to the meridian band of phosphorescence, with which they have the same connexion as have the two rings *a* and *b* with the central spot in fig. 4. If the whole tube is insulated except for the inner surface, the blue polar rays are very bright, spreading out wider than in the first experiment and producing rings of variable diameter. In this case, at a certain not-too-low pressure, beautiful striations of red positive light were found to reach the region of the blue cathode light, as a rule only in the beginning of a new discharge and going back to the anode without change of pressure. This aspect is given in fig. 5.

Fig. 5.



Experiment 3.—A glass tube is introduced into the cathodic tube so that the inner coating of the cylinder is perfectly insulated, the outer coating being free. The negative glow now never enters the tube, no blue beams of cathode rays appear, neither the rings *a*, *b*, *c* of fig. 4. At the lowest pressure, however, a faint small spot of phosphorescence appears at the poles of the bulb, flitting hither and thither in a very unsettled fashion. Small sparks move round about the edges of the tube, giving rise to irreglar cathode-rays. The rings *c* and *d* of fig. 4 are found to be indistinct. At the most complete vacuum, a small amount of yellowish-white light is to be seen in the centre of the glass tube of the cathode.

If two short glass tubes about 4 mm. long are introduced into the metal tube from both ends, so that only the inner edges are covered, the phenomena in the beginning of the exhaustion are different from those just described in so far as the negative glow enters into the tube from both ends without going through the whole tube, and as the blue central cathode rays just appear at the ends of the tube producing a spot of weak phosphorescence at the poles of the glass bulb. As the air is pumped out, this blue light disappears again ; but the polar spots in front of the openings of the cylinder are much brighter and more fixed than in the previous experiment, much as in the first experiment. The inner edges of the glass tubes exhibit a red glow, as if due to the impact of positive rays. As in the case of small glass tubes put at the inner ends of the tube, the blue central beam and the rings *a* and *b* of fig. 4 do not appear, we see that these phenomena take their origin from the inner edges of the metallic tube. The bright central spots *f* of fig. 4 are due to rays starting from the central parts of the tube. The difference in the appearance in the case of one glass tube filling the whole metallic cylinder, and of two short glass tubes at the ends of the cathode for a certain not too low pressure, is illustrated in fig. 6. If the pressure becomes lower, the central blue light of fig. 6 *b* disappears, the polar spots *p* get fainter, and the first, second, and third layers in fig. 6 *b* give the same aspect as those in fig. 6 *a*. The polar spots of phosphorescence *p* in fig. 6 *b* become very bright again with still decreasing pressure, while the corresponding spots in the case of the long glass tube filling the whole cathode are found to be very dim and unsettled.

If a short glass tube is introduced into the cathode so that at either end about 2 mm. of the inner surface of the metal cylinder is free, we should expect from the last experiment the same succession of phenomena as those observed in the first experiment, and that is indeed what happens. With increasing vacuum, the central blue beams and the spots of yellow-green phosphorescence surrounded by a bright ring on

Fig. 6 *a*.

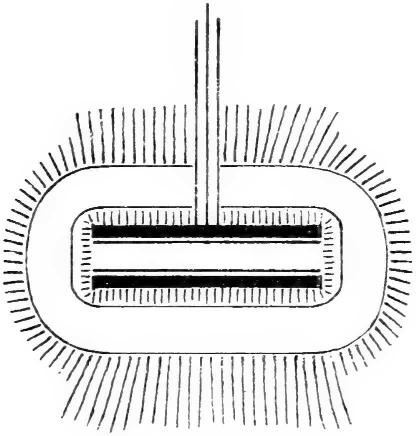
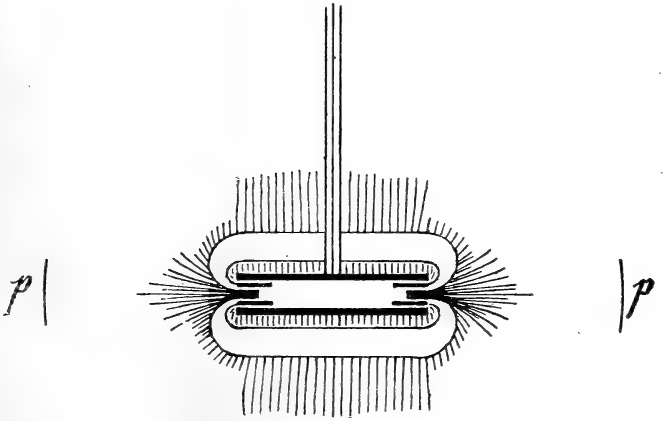
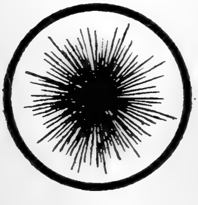


Fig. 6 *b*.



the glass wall gradually appear. The blue polar beam and the central spot are, however, not so intense as in the first experiment, owing to the fact that the rays starting from the central parts of the tube are cut off by the glass tube. The ring *b* of fig. 4 does not appear until we reduce the length of the glass tube to about half that of the cathodic cylinder and introduce it into the middle of the cathode.

Fig. 7.



In the last two cases the glass tube glows at low pressure with an intense orange light, which might be brought about by the impact of positive particles. After the experiment a brown deposit was found on the inner surface of this glass tube. This experiment tells us again that the rays producing the ring *a* of fig. 4 start from the inner edge of the cathodic cylinder, the ring *b* from a part nearer to the centre, and the central spot *f* from the middle of the hollow cathode.

The blue cathode rays propagating in the direction of the axis arise from the edges of the cathode, as will be seen directly from fig. 3.

The phenomena observed on each side of the cathodic cylinder seem to be independent of one another. If, for instance, a short glass tube is introduced covering the inner end of the metallic tube, or if this end is closed by a short metal bar, the phenomena observed on the other side of the tube coincide with those observed in experiment 1.

If at one end of the cathode a metal wire or a small piece of ebonite is pushed over the inner and outer edge of the tube, the disturbance of the picture produced by the cathode rays will be found to be at a place opposite to the obstacle in the tube, showing that the rays giving rise to the ring *a* of fig. 4 cross one another. With decreasing pressure, the rings of phosphorescence illustrated in fig. 4 appear in the order *a*, *b*, *e*, *f*. It is also worth mentioning that the diameters of the rings depend on the pressure. With decreasing pressure the diameters of the rings become smaller. A reduction of 5·4 cm. to 5·0 cm. was observed in the diameter of the ring *a*, and of 3·8 cm. to 2·9 cm. in ring *b*.

We shall now proceed to explain the appearance of the rings quite distinctly separated from one another, as indicated in fig. 4. The cathode rays are deflected in an electric field, which is very intense in the Crookes's dark space. When the pressure is not very low, the field close to the cathode is more intense than that at some distance away from it. The corpuscles being still close to the cathode, will acquire so much kinetic energy that they will not be much deflected from the path along the normals of the surface; they will, however, soon be absorbed and ionize the air in the opening of the tube of the cathode to a very great extent. This ionization is accompanied by a very bright luminosity of the gas column inside the tube. The component of the electric force acting parallel to the axis of the tube, will move the ions parallel to this axis. Thus the rays shown in fig. 2 may be produced. If now the pressure decreases, the dark space gets bigger and fills the whole metallic tube. The ionization taking place mostly outside the cathode, penetrates the tube for only a short distance; and the negative corpuscles driven by the electric field in the direction of the axis constitute the blue beam represented in fig. 3.

According to this view, the intense blue beams are to be considered as the negative glow of the inner surface of the tube. The negative glow belonging to the outer surface gets fainter and more uniformly blue as it recedes from the outer surface. The total amount of ionization taking place all over the region of the negative glow, however, may remain nearly constant with decreasing pressure. The narrow region in which the central blue beam occurs is a place of strong ionization and weak electric field. The ionization is due to corpuscles moving from the inner surface of the metal.

The faint blue luminosity filling almost the whole glass bulb, and produced by cathode rays starting from the outer surface, is as it were concentrated for the inner surface into a sharp beam whose colour is found to coincide with that of the misty luminosity. In pure air the blue colour is predominant; in damp air a change into a reddish colour takes place; while in the presence of mercury vapour the rays appear to be of a bluish-white colour. The polar visible beams, being a continuation of the negative glow of the inner surface of the cylinder, appear in the same interval of pressure as that faint misty luminosity due to secondary cathode rays. As the bright central beam and the faint luminosity of the negative glow of the outer surface die away together with decreasing pressure, the yellow phosphorescence caused by the primary cathode rays gets brighter. The fact that with decreasing pressure the blue central beams enter deeper into the hole of the cathode, is connected with the change in direction of the lines of electric force and with the appearance of the bright rings of phosphorescence on the glass wall.

The positive ions are mostly attracted by the negative metal cylinder just in the inner edge of the cylinder, giving rise to primary cathode rays which get more and more deflected as the pressure decreases and the length of the dark space becomes greater. Since the strength of the field only changes slowly as we recede from the cathode, the velocity acquired by the corpuscles will be smaller than at higher pressure. In addition, the deflecting electric force will be greater at a greater distance from the cathode. For both reasons, the cathode rays get more and more deflected from the path perpendicular to the inner surface of the cathode.

At a certain stage of pressure these primary rays start between the normals of the surface and the electric force and produce phosphorescence around a circular ring on the glass wall.

Fig. 8.

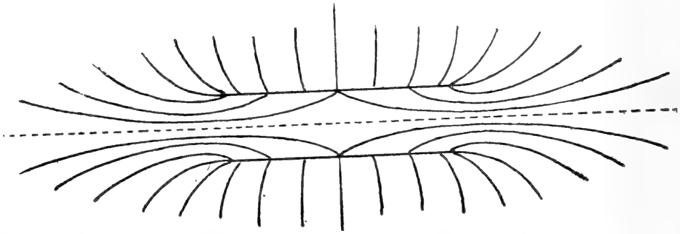
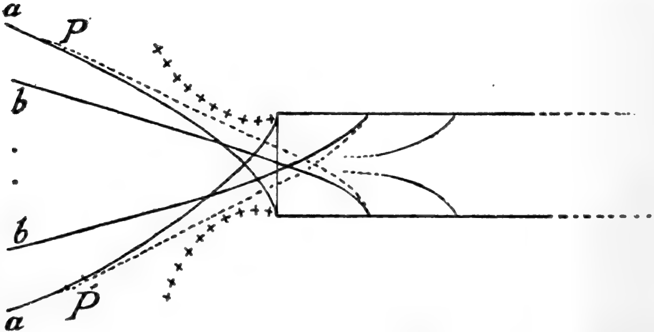


Fig. 8 will give an idea of the distribution of the electric force round the cathode at the low pressure. The cathode rays begin to ionize the gas at the boundary of Crookes's dark space and the negative glow. If now the path of the cathode rays is curved, and if the positive ion is produced at P (fig. 9), then, in consequence of the difference in mass between the positive and negative ions, the former will not follow the path of the negative corpuscles up to the cathode. They will take another way and strike against the inner surface of the cylinder along a circle distant a certain length from the end of the tube.

Fig. 9.



++++ line of electric force.
—— path of negative ions.
- - - - path of positive ions.

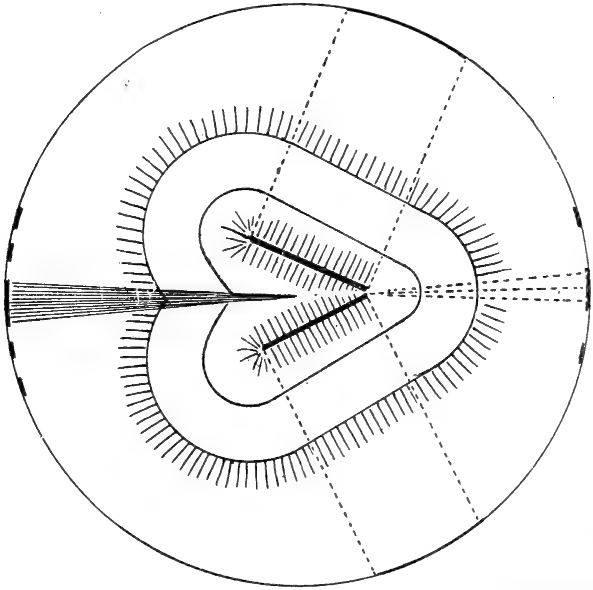
Along this circle there is a new source of cathode rays starting in a smaller electric field than those at the end of the tube and in a direction between the normal and the electric force, but more parallel to the axis than the rays considered just before. Leaving the hole of the cathode, they come into a stronger electric field by which they are necessarily more deflected than those producing the ring *a* of fig. 4. As they pass through a longer interval of air than the latter ones, their ring *b* of phosphorescence will only appear at a pressure a little lower than those of the ring *a*. The same consideration applies to the rays of the ring *b* as well as to those of ring *a* of fig. 4, and shows us that at a still lower pressure we should expect a further dark ring inside the ring *b*, and afterwards a central bright spot of phosphorescence: and that indeed happens.

This explanation seems to account for all the phenomena observed, and recalls the distribution of the phosphorescent patch observed by Campbell Swinton.

The positive particles playing an important part in this interpretation, we might expect to find the same outside the hollow cathode as within. Positive rays have not been directly observed so far in the above experiments. An interesting observation, however, wants mentioning. If the discharges take place at a high degree of exhaustion, the brass cathode will be disintegrated to a large amount and a brown deposit will spread over the glass bulb with a uniform thickness except at the poles. If now the cylindrical cathode is turned, say, 60° about the supporting axis, a small circular part of the deposit will be found to get swept out at the new poles of the bulb under the action of the discharges. This effect may be due to canal-rays. E. Goldstein showed, indeed, that the positive rays have the property of sweeping away metallic deposits. If a conical hollow cathode was used, rays different in colour and magnetic deflexion were found to start from the narrower end at a very low pressure; the yellowish-white colour and the absence of magnetic deflexion of one part of these rays seem to indicate that we are dealing with a mixture of positive and negative rays. The blue beam starting from the wider end goes deeper back to the point of the cone with decreasing pressure, and is continued by a faint yellowish ray. The central patch of phosphorescence due to the blue beam is surrounded by two bright rings, whereas at the opposite pole of the glass bulb we find only a faint central spot surrounded by the outer ring. This is exactly what we should expect from the view given above, because the rays which would produce the inner ring cannot escape from the pointed end of the cone.

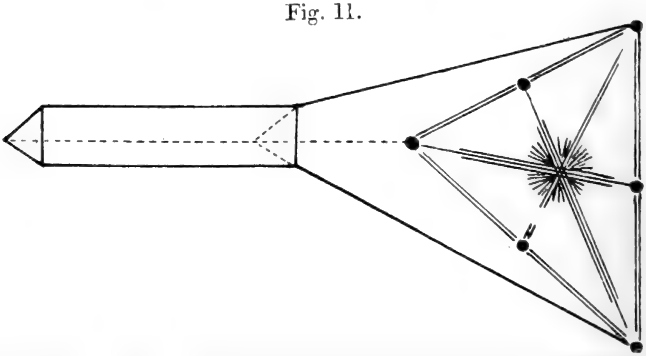
If we draw perpendicular lines from the coating of the cone outwards, a certain zone of the spherical bulb will be cast out, and this zone is found to glow in a dim phosphorescent light due to cathode rays. If the middle of the cylindrical tube used for the above experiments is surrounded by a metal wire, this meridional band will be divided into two parts separated by a dark space. On the side toward the poles of the bulb each part is accompanied by a small strip of phosphorescence.

Fig. 10.



Very beautiful geometrical figures of phosphorescence are obtained when the cross section of the hollow cathodic tube is not spherical but of any other shape. In the case of a triangular tube I found a central cross, a bright spot at each end and in the middle of each side, and a phosphorescent

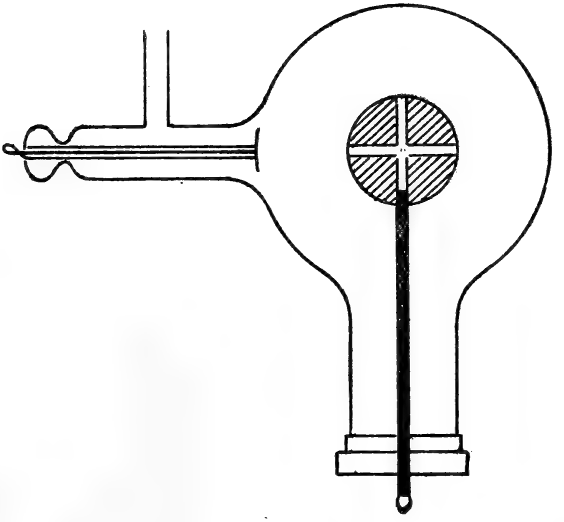
Fig. 11.



boundary of the triangle connecting with the cathode, as indicated in fig. 11.

Experiment 4.—A further series of experiments was undertaken in order to find out the conditions under which canal-rays occur outside the cathode. A tube shown in fig. 12 was employed. The anode is a disk of aluminium about 1 cm. in diameter. The cathode at first was a sphere of brass, perforated in three directions perpendicular to one another. A bar of brass surrounded by a glass tube was screwed into one of the six openings, the diameter of the opening being about 3 mm. The distribution of the first three layers next to the cathode changes in a very interesting way during the evacuation, as will be seen from the three following figures. One of the openings is directed towards the anode. The Crookes's dark space in fig. 13 is exceedingly small; the metallic sphere is enveloped by a spherical shell of red-violet light. This is the negative glow, and is pierced at the five openings by a red beam of the shape of a flat table-plate. The holes are filled with bright violet light; a column of faint red light goes up to the anode without striations. At this comparatively high pressure the surface of the glass bulb already begins to get fluorescent. As the vacuum increases the light flaming out of the openings assumes the shape of an open umbrella, Crookes's dark space becomes much larger, the velvet glow covers the surface of the sphere (fig. 14). At the following

Fig. 12.



stage of pressure (fig. 15) we observe five bright well-defined blue beams starting from the holes of the cathode and nearly reaching the surface of the glass bulb. These rays reach a maximum of luminosity and then get fainter with increasing

Fig. 13.

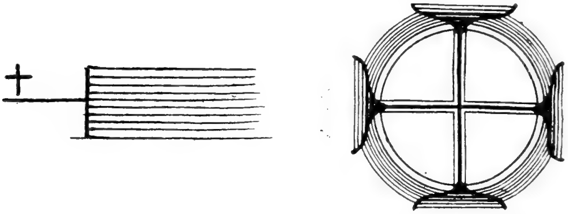
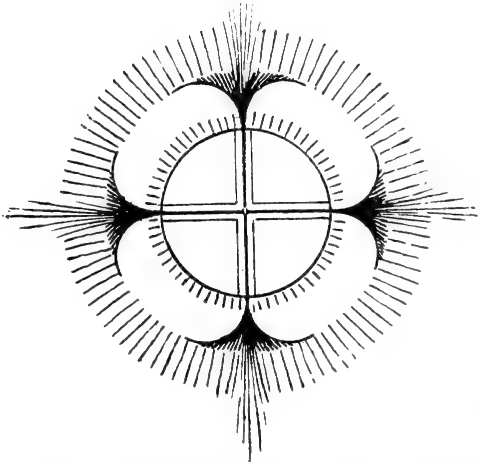


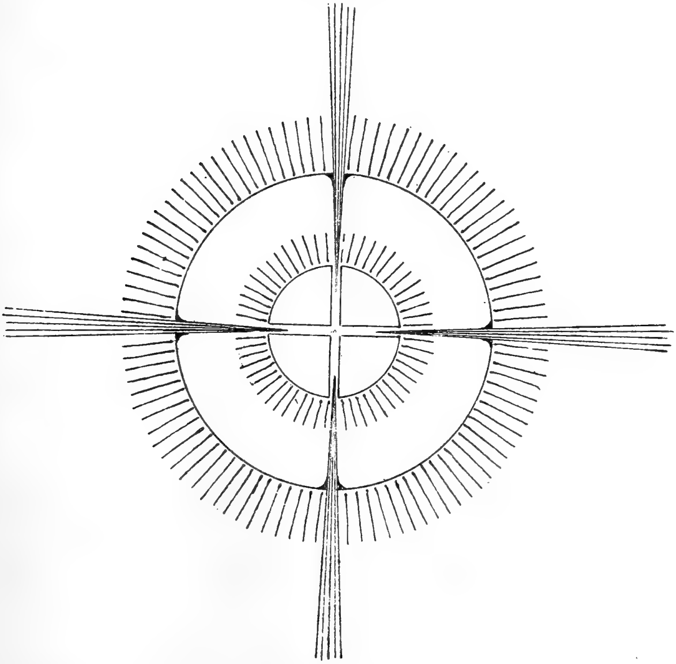
Fig. 14.



vacuum; while the phosphorescent spot on the glass wall, due to these blue beams, becomes surrounded by a dark ring which itself gets limited outwards by a new bright ring. At the lowest pressure obtained, the central circular spot is found to be surrounded by a ring of faint luminosity. This is followed by a dark ring, then a bright ring, continued by a general faint phosphorescence of the bulb due to cathode rays starting from the surface of the cathode.

At low pressure the phenomena observed coincide with those made with a cylindrical tube. The five holes of the spherical cathode give rise to the same kind of rays. The blue colour in the air, the yellow phosphorescence on the glass wall, and the amount of magnetic deflexion are the same for all the five beams. It is especially worth noting that the rays travelling from the cathode towards the anode appear to have the same properties as those going in the opposite direction, whereas in the ordinary tube used for canal-rays we find these positive rays starting from the cathode in a direction opposite to the cathode rays. In the present arrangement, however, no canal-rays were found at the surface of the glass wall; but a red light was observed not unlike the velvet glow along the surface of the holes. Nevertheless it is possible that some canal-rays escape from the openings without being capable of observation under the given circumstances.

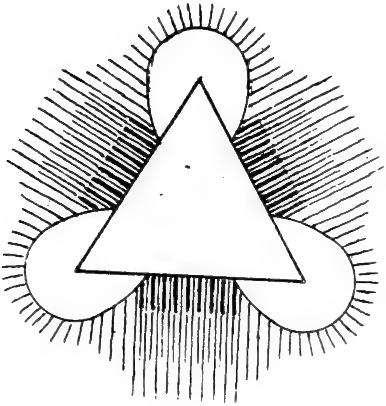
Fig. 15.



In the following experiment the metal sphere was surrounded by a sheet of sulphur 2 mm. thick, so that only the walls of the five holes and a part of the surface in front of the anode were free from insulation; so we might expect to get canal-rays in the opposite direction. Very bright blue beams start, however, from all the five holes having the same qualities in each direction; a red glow in the middle of the cathode may easily be observed, recalling the colour of positive rays. In hydrogen the phenomena at low pressure coincide with those observed in air.

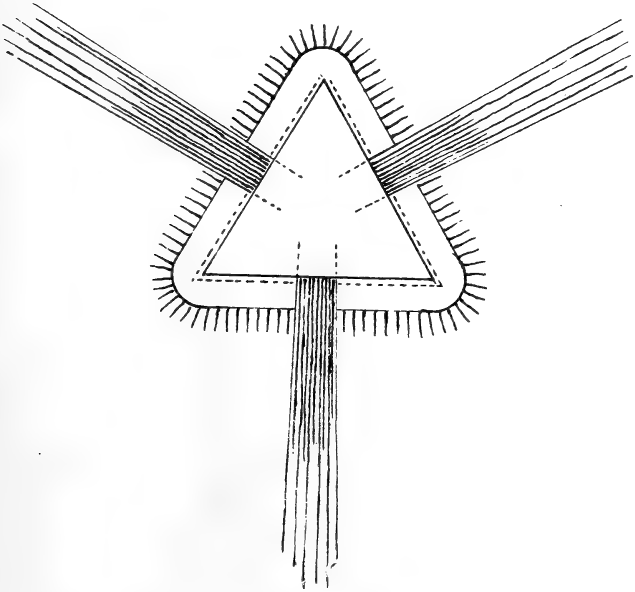
Experiment 5.—In place of the sphere used in the last experiment, the cathode consists of two parallel triangular plates 3 or 4 mm. apart held together by means of three thin pins and supported by a bar of brass entering into the middle of the plane of one of the plates. The triangular hollow space between the two plates lies in the same horizontal plane as the anode towards which a corner of the triangle is directed. At a comparatively high pressure we observe a narrow dark space surrounding each plate. Beyond this is the negative glow, and this is exceedingly bright between the two triangles. Three blue beams start from this central light, in a direction perpendicular to the sides of the triangle, giving the aspect shown in fig. 16 when looked at in a direction perpendicular to the plates. As the air is pumped out, the velvet glow appears, Crookes's dark space gets wider, the light between the plates disappears, the blue beams from the sides of the triangular hollow space contract into sharper beams spreading out over a longer distance than before, as will be seen from fig. 17.

Fig. 16.



At a still lower pressure the blue cathode rays **A** get very bright and distinct, causing quite distinct patches of phosphorescence, while from the corners of the triangle short red beams start into existence. The difference of colour between the two kinds of beams is most remarkable in hydrogen and helium. As we go on lowering the pressure the cathode rays A cease to be visible in the gas, while now the red rays B, of

Fig. 17.



figs. 18 and 19 (p. 178), pass through a maximum of brightness. The phosphorescence on the glass wall due to these rays is very faint. In one case only I was able to detect the sodium line in the spectrum of the same. The red rays travelling from the corners of the triangle seem not to be deflected by a magnetic field of moderate strength. Professor J. J. Thomson, who applied a very strong field to these rays, could find so far no deflexion at all. He found, moreover, that rays of this kind not only leave the triangle from the corners but also from the sides without being susceptible of magnetic deflexion. At a very low pressure the cathode rays also, though invisible in the gas, start nearly round about the triangle and produce along the meridian of the glass bulb a band of phosphorescence. This phosphorescence presents a maximum of luminosity at regions in front of the sides of the cathode. It is scarcely interrupted opposite the corners and is accompanied on either

Fig. 18.

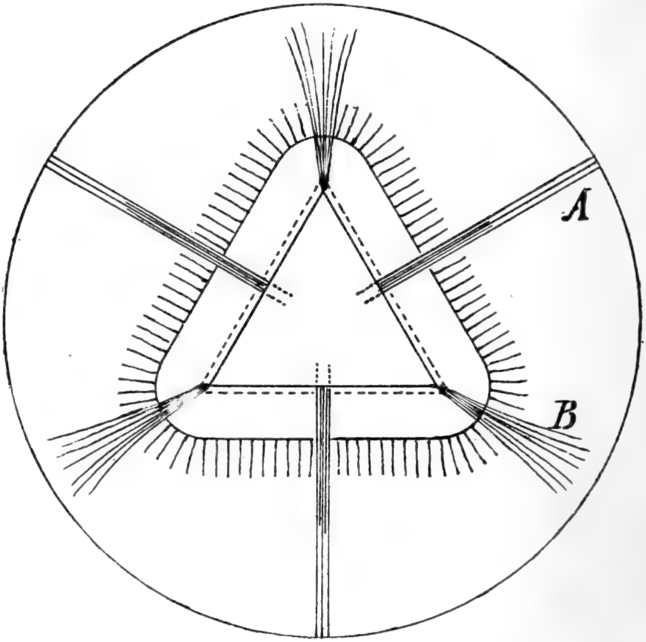
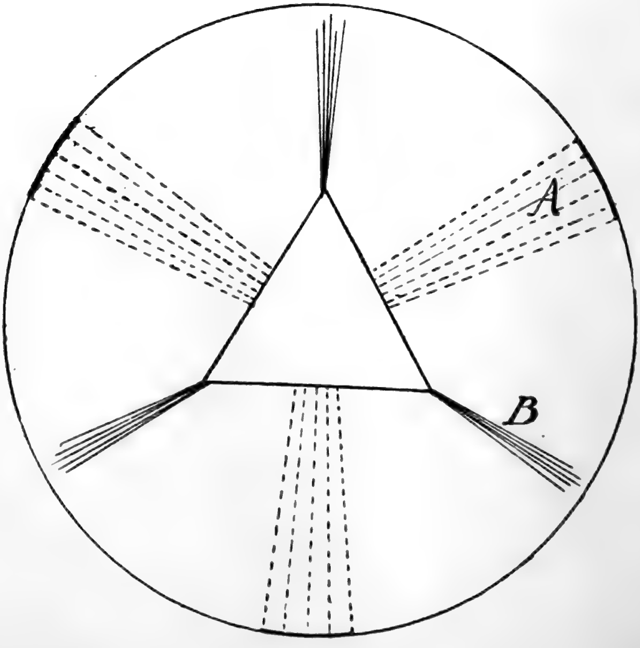
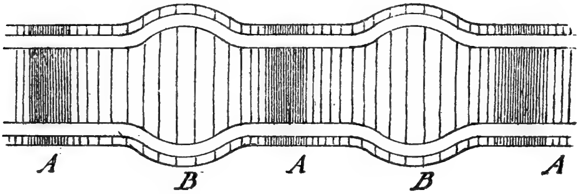


Fig. 19.



side by a narrow phosphorescent band. Its aspect is represented in fig. 20. The red rays B closely resemble the positive canal-rays. The facts, however, that their maximum of luminosity does not quite coincide with that of the cathode rays, that they are visible only for a short distance from the cathode and do not seem to be capable of magnetic deflexion, make further measurements necessary. The absence of magnetic deflexion may be explained by the assumption that the positive particles ionize the gas through which they pass, get neutralized by the impact of a corpuscle, and travel in the neutral state through the magnetic field.

Fig. 20.



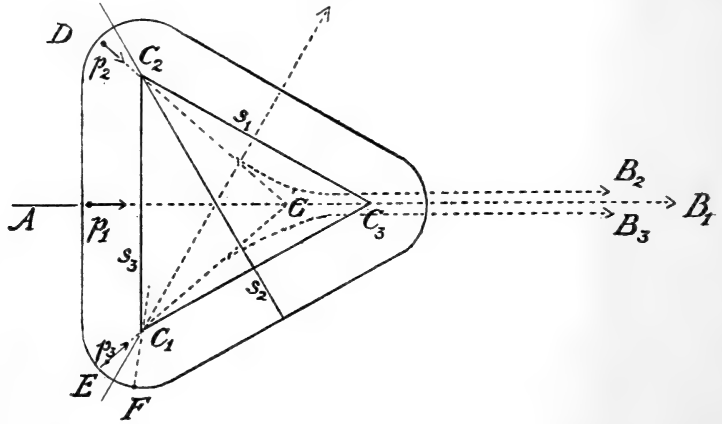
If the red rays prove to be positive rays, we have in the last experiment an interesting case in which positive particles travel against the field from the cathode up to the anode. The question arises how the current between the two electrodes is closed.

If we turn the cathode 60° round the supporting axis the distribution of blue and red rays remains unaltered, the red ones starting from the corners, the blue ones from the sides of the triangle. In this case, cathode rays form the bridge between the electrodes.

If we consider the red rays as positive rays corresponding to ordinary canal-rays, and if we take the well-known view of the origin of cathode rays as produced by the impact of positive particles which themselves are due to ionization by cathode rays, we should expect that by cutting off the negative rays at one side of the triangle, the red rays from the opposite corner would disappear. And that is what happens. If we, however, by an obstacle prevent the positive rays from escaping from one corner, the cathode rays starting from the opposite side of the triangle do not disappear. This fact also agrees well with the view of mutual dependence of the rays of opposite sign. Let us consider a positive particle p_1;

it will ionize the gas between the two plates and travel along the line AB_1.

Fig. 21.



A positive ion such as p_2, driving from the negative glow in the direction D G, will be deflected from its straight course, being attracted by the electricity stored up along the side s_1 and at the corner C_3. The path of p_2 will therefore be along the dotted line DB_2, while the path of p_3 will be along EB_3. All the positive particles attracted from the negative glow between D and E will leave the triangle in a narrow bundle from the opposite corner, whereas the beam of cathode rays will be much broader, and this in many cases has been observed (see figs. 17 and 19). The same considerations apply to the two other sides of the triangle. We see from fig. 21 also that there will be at each corner a small angular interval such as E F, from the negative glow of which the positive particles, few in number, are subject to the same force of attraction from the side s_2 as side s_3. These ions will leave the triangle from the opposite side s_1. As they pass through a field of strong negative electrification they are very likely to get neutralized.

It follows from this explanation that by closing the side E D between the two plates, both the blue beam perpendicular to this side and the red beam starting from the opposite corner should disappear, whereas by putting an obstacle between the two plates at the corner C_3 the red positive ray from this corner should disappear, while the cathode rays from the opposite side should not. Both deductions agree well with the facts observed.

The blue beam, the length of which is increasing with decreasing pressure, as will be seen from the figures 16 and 17, corresponds to the blue beams, starting from cylindrical tubes, indicated in the figures 3 and 10. We have seen that these blue beams begin to disappear while the rings of phosphorescence shown in fig. 4 gradually start into existence with decreasing pressure. Those rings are due to cathode rays produced by the impact of positive ions against the inner surface of the metal tube; the positive ions themselves are due to the ionization of the gas in the negative glow produced by the corpuscles. Just as in the case of a cylindrical cathode the rings appear gradually while the blue beams, different in origin from the primary cathode rays, disappear, so we are to expect from the view given that the maximum of luminosity of the blue cathode rays will appear at a higher pressure than the maximum of brightness of the positive rays. And that is exactly what happens.

A further argument in favour of the view developed is the appearance of the narrow strips of phosphorescence represented in fig. 20, which accompany the central band. They occur at the same stage of pressure at which the red positive rays get very bright. These narrow bands are obviously of the same origin as the ring *a* in fig. 4. Positive particles travelling inwards from the negative glow DE may either strike against the metal or pass through between the two plates. The former ones cause cathode rays which are indicated by the bright bands of phosphorescence; the latter constitute the red beams from the corners of the triangle.

We also understand that the three bands of phosphorescence along the meridian of the bulb are widening out at places in front of the corners and contracting before the sides of the triangle. If we consider a corpuscle just leaving one plate at a corner in the direction towards the other plate, it will be attracted by the stream of positive electricity, and its deflexion from the normal or polar direction will be less in the beginning of its career than when it starts from the middle of one side, in which case it will be driven away from the normal direction by the stream of negative electricity between the two plates. Thus corpuscles rising from the corners will move in a path further apart from the meridian plane lying parallel to the triangular plates, than will corpuscles which start from the middle of a side of the triangles.

From the theory illustrated in fig. 21 we draw the following conclusions :—

(1) If we compose a cathode of two circular plates instead of two triangular ones, we should expect starting from any point of the circumference of the free space between the

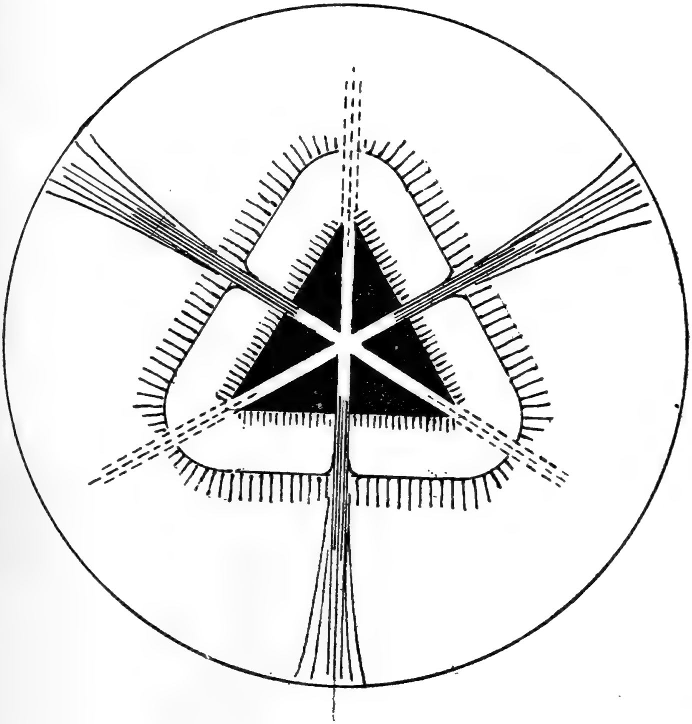
plates cathode rays as well as positive rays. The blue cathode rays reach a maximum of luminosity before the red positive rays. As the latter pass through a field of negative electrification, they will be neutral to a large extent and not much liable to magnetic deflexion.

(2) If we connect the two triangular plates not by means of thin pins but by larger masses of metal, so that the only free space between the plates is in the form of three rectangular ducts (see fig. 22) crossing one another, we should expect the six holes to behave in the same way at a certain comparatively high pressure, that is to say, we should expect them to emit bright blue beams corresponding to those observed in the case of perforated cylindrical and spherical cathodes. As the air gets exhausted, the visible cathode rays from the openings of the middle of the sides will still be bright, whereas the rays from the corners become nearly invisible. At a still lower pressure the difference in luminosity becomes smaller. Invisible cathode rays start from all the six holes, probably accompanied by a weak stream of positive ions and neutral molecules. The difference of appearance in the previous stage is due to the fact, that the negative glow before the sides of the triangle is very much stronger than before the corners, a phenomenon observed without exception in every case of cathodes having sharp corners. As there is no large open side from which the positive particles may be collected into a sharp beam, we cannot expect to find a distinct beam of canal-rays. The experiment has perfectly justified this inference from the theory. The state of things, in which the difference between the beams is most conspicuous, is represented in the figure 22, which shows also that the negative glow in front of the sides is more intense than before the corners of the triangle.

(3) If the cathode is made of two parallel square plates separated 3 mm. from one another and connected by thin pins, we should expect to find at a comparatively high pressure four blue broad bands starting perpendicularly from either side of the square. These rays will disappear with decreasing pressure and will be replaced by red beams accompanied by cathode rays, invisible in air and hydrogen, but producing bright spots of phosphorescence. This expectation is satisfied by an experiment made first by E. Goldstein, who also found that the canal-rays passing between the two plates mark their paths by a system of curves drawn on the inner surface of the plates. The positive red rays were found to be very bright and sharp in hydrogen. They are not deflected by a

magnetic field of moderate strength. If the electromagnet is placed near to the point where the red rays cut the glass wall, the cathode rays will be collected into a sharp blue beam turning, by a suitable motion of the electromagnet, round the surface of a cone whose vortex lies in the red beam.

Fig. 22.



In conclusion I wish to express my heartiest thanks to Professor J. J. Thomson for his kind interest and suggestive help throughout the course of this research, which was carried out in the Cavendish Laboratory.

Cambridge, 5th March, 1908.

XII. *On the Emission of Polarized Light by Fluorescent Gases. By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University*[*].

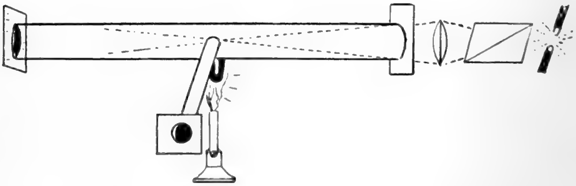
PREVIOUS attempts to detect polarized light in the emission of fluorescent vapours have yielded negative results. Schmidt's observations were made with a nicol only, and he failed to detect any difference in the brilliancy of the fluorescence as the prism was rotated.

I have always felt that the apparent absence of polarization was difficult to reconcile with the theory that the fluorescence is merely a re-emission by electrons vibrating synchronously with the waves of the exciting light. Quite recently I have attacked the problem anew, and by carefully studying the conditions have succeeded in getting as much as 30 per cent. of polarized light in the resonance radiation of sodium and potassium vapour. The polarization of light produced in this way appears to be a wholly new effect, and its study throws considerable additional light upon the mechanism of radiation.

The phenomenon was first detected in the case of potassium vapour by means of a Savart plate which is capable of showing two per cent. of polarization. It was immediately picked up in the fluorescence of sodium and iodine, and it is probable that other vapours will be found to show it as well.

The apparatus used in the work consisted of a steel tube with a lateral branch brazed to its centre for the observation of the fluorescent light at an angle of 90° with the exciting beam. This tube was used in the earlier work upon fluorescence, before the expedient of "end-on" examination had been adopted. The metal was contained in a small retort also brazed to the large tube, immediately below the lateral observation-tube (fig. 1). The light of the arc was focussed by a large lens at the centre of the large tube immediately in front of the lateral branch. Owing to the sensitiveness of the Savart plate it was necessary to eliminate all other possible

Fig. 1.



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[*] Communicated by the Author.

sources of polarization, such as fog or mist in the tube. Exhaustion with a Gaede mercurial pump while the tube was heated was sufficient to completely banish all trace of fog.

The complete absence of fog can be told by illuminating the vapour with an intense beam of light embracing the spectrum region comprised between wave-lengths 5400 and 5700, obtained by prismatic dispersion. Such a beam is incapable of exciting any fluorescence, and if fog is absent the cone of light is absolutely invisible when viewed through the lateral tube. The Savart fringes were very distinct, and the percentage of polarization was determined by compensating it with a pair of glass plates which could be turned about on a vertical axis furnished with a graduated circle. This method gives by far the most accurate results when we are dealing with small percentages of polarization. Cornu's method, which depends upon the unequal brilliancy of two images seen through a Rochon or other double-image prism, cannot be used when there is less than twenty-five or thirty per cent. of polarized light present, for with less than this amount it is difficult or impossible to detect any difference in the brilliancy of the two images. This is true at all events for the green fluorescent light of sodium vapour. The first measurements were made with the exciting light polarized (electric vector) vertically.

It was found that the polarization was strongest when the temperature of the tube was comparatively low, *i.e.* when the fluorescence first appeared. At a higher temperature, with very bright fluorescence, compensation was secured with a single plate at an angle of 59°, or with two plates at an angle of 47°. Taking the refractive index of the glass as 1·52, and making use of the formula which expresses the ratio of the amplitudes of the components of the vibration in and perpendicular to the plane of incidence

$$\frac{D_s}{D_p} = \frac{E_s}{E_p} \cos^2 (\phi - \chi)^*$$

we find the percentage of polarization to be 20.

At the lowest temperature consistent with a fairly bright fluorescence compensation was secured with two plates at an angle of 52°. This gives us 30 per cent. of polarized light. The change in the intensity of the fluorescent spot when viewed through a slowly revolving nicol was easily observed in this case, and a separate determination was made by Cornu's method, which gave 28 per cent. of polarized light.

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* 'Drude's Optics,' page 265, 1st edition.

If the exciting beam was polarized with its electric vector horizontal, no trace of the Savart fringes could be detected, which was to be expected as everything was then symmetrical about the line of sight.

If the exciting light was unpolarized to start with the fluorescent light was found to be polarized, but not to the same extent, the percentage in each case being one half of its former value, which was also to be expected. The question at once arose as to why we have only a partial polarization of the fluorescent light when we start with plane-polarized light.

As I have already shown (Phil. Mag., May 1908) excitation of the vapour with monochromatic light causes it to emit this same wave-length and a large number of other wave-lengths, the spectrum exhibiting in the most typical case a number of very sharp lines spaced at nearly equal intervals along a normal spectrum. It at once occurred to me to see whether the polarization was confined to the line corresponding to the exciting line, for it seemed not impossible that the electron vibrating in synchronism with the exciting light might emit light which was completely plane-polarized, whereas the other disturbed electrons might emit unpolarized light. The vapour was accordingly excited with the light of the cadmium arc, and the spectrum examined with a small spectroscope furnished with a nicol prism. It was found, however, that the polarization was quite as strong in all parts of the spectrum as it was at the lines coinciding in position with the exciting lines. As a check on this observation the following experiment was then tried. The light from the arc was passed through a filter which removed everything above wave-length 5000, *i. e.* which transmitted a deep blue light. In front of the Savart polariscope I placed a dense screen of aurantia which cut off everything below 5000. This removed all the wave-lengths from the fluorescent spectrum which were to be found in the exciting light, transmitting, however, the upper end of the fluorescent spectrum. This light was found to be strongly polarized, the fringes appearing quite as distinct as in the absence of the screens. It will be observed that this experiment completely eliminates all possible sources of error, such as polarization produced by fog or by reflexion from the back wall of the tube.

The D lines appear in the fluorescent spectrum stimulated by white light, and the spectroscope showed that they were polarized to about the same degree as the rest of the spectrum. As I have shown, the D lines can also be caused to appear by stimulation with blue light, but in this case they are too faint to make a study of their polarization possible.

The foregoing experiments prove that we must seek elsewhere for the cause of the partial polarization. The decrease in the amount of polarization with increasing temperature made me think that the increased density of the vapour might have something to do with the phenomenon, in other words, that the depolarizing factor might be the molecular collisions.

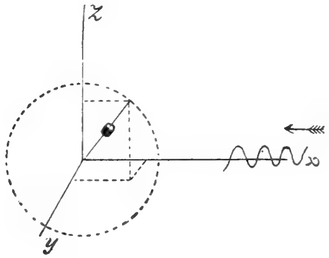
To test this hypothesis a small amount of nitrogen was introduced into the tube, sufficient to raise the pressure to 12 mms. The number of collisions must now be vastly in excess of what obtains with sodium vapour *in vacuo*, for in this case the actual pressure of the metallic vapour is probably never in excess of a millimetre or two, if it is as great as that. In fact I now feel sure that the partial pressure of the sodium vapour can never be greater than the pressure of the residual gas in the tube. In my earlier work I overestimated the density of the vapour, and imagined that it must possess a viscosity, but I am now convinced that this is not so.

The polarization did not appear to be decreased by the presence of the nitrogen, which made it seem probable that molecular collision was not the depolarizing agency. Temperature appears to be the only remaining factor, and I am inclined to attribute the depolarization to the rotation of the molecule while it is traversing its mean free path. The speed of rotation will increase with the temperature, for the energy of a gas is partly energy of translation and partly energy of rotation, the ratio being constant. (Sodium is, however, regarded as monatomic, and the relation may not hold.)

That there is a depolarizing agent is probable from the most elementary theory. If we assume the electrons to be free to move in any direction, under the influence of the electric forces in the light-waves, it seems probable that with a polarized beam of exciting light, we should have plane-polarized light emitted by the vapour in directions making an angle of 90° with the exciting beam. If the stimulating light were plane-polarized to start with, there would be no fluorescent emission at 90° in directions parallel to the electric vector in the exciting light. In other words, the vapour would behave in much the same way as a fog composed of very fine particles, though the physical processes involved would be quite different in the two cases.

Let us now assume that the electron is able to move along a straight line, the position of which is fixed within the molecule. While it is quite improbable that this condition actually holds, the conception of it will enable us to see how the introduction of constrained motion will decrease the amount of polarized light emitted by the vapour. We can imagine as a rough model of our molecule a hollow sphere with a wire passing through its centre, along which a bead can slide. Consider the polarized exciting waves as travelling along the x axis towards the origin (fig. 2), with their direction of vibration parallel to the z axis. It is clear that the bead will vibrate with the greatest amplitude when the direction of the wire is also parallel to the z axis. If the wire lies in the x y plane no vibration will occur. In other positions there will be vibrations of greater or less amplitude, according to the component of the force in the light which is directed along the wire. We may represent the fluorescent gas by an enormous number of these vibrators with their wires pointing in all possible directions. The vibrations of the beads along the wires can each be resolved into two components, one parallel to the x axis, the other parallel to the z axis, and the integrated effects of these components, or rather of their squares, will give us the measure of the intensity of the emitted radiation vibrating parallel to the x and z axes. These integrals stand in the ratio of 6 to 2, which means, since the total intensity is 8, and their difference is 4, that we are to expect a polarization of 50 per cent. with a vibration direction parallel to the z axis. By experiment we find only 30 per cent.

Fig. 2.



As the percentage of polarization appears to decrease as the temperature of the tube is raised, it is possible that at lower temperatures than any which can be employed satisfactorily, the percentage may be higher. As to possible depolarizing agencies, rotation of the molecule would doubtless act in this way if the electrons continued to emit light after the cessation of the incident light, or—expressing it in terms of our imaginary model—if the bead on the wire continued to vibrate after the wire turned into the z y plane. It must be remembered, however, that sodium is regarded as monatomic, and the question arises as to whether we can ascribe much of the energy of the gas to rotation of the molecule. Another possible depolarizing factor is what may be termed secondary fluorescence, or fluorescence excited, not by the primary ray but by the resonance radiation of the gas. Lord Rayleigh has considered the possibility of an analogous action in his treatment of the theory of the colour of the sky and its polarization. The fluorescent light is of course rather feeble in comparison with the exciting light, but it must be remembered that its frequencies are just right, and the radiation from one molecule would without doubt be able to excite vibrations in a neighbouring one.

The discovery of the polarization of light by fluorescing gases will perhaps give us a satisfactory theory of the solar corona.

The radial polarization of the corona amounts to about 11 per cent., its spectrum is continuous, though some observers have found faint indications of the Fraunhofer lines, and it appears to be cold, that is no deflexions are obtained with the bolometer. Polarization is usually ascribed to scattering by small particles, the continuous spectrum to an emission by larger particles (white hot), while the apparent absence of radiant heat cannot very well be reconciled with the presence of white-hot particles. If we regard the corona as a cloud of mixed metallic vapours fluorescing under the terrific radiation from the sun, there seem to be fewer contradictions. The polarization is just about what we should expect, a continuous spectrum, at least with all resolving powers which can be brought to bear, would be almost certain, and there is no inherent difficulty in explaining the absence of radiant heat. The presence of faint traces of the Fraunhofer lines could be ascribed to light from the sky, which is largely due to light from the exposed edge of the sun. The so-called coronium line, and other bright lines peculiar to the corona, may be merely fluorescent lines of well-known elements. As I have shown already, the fluorescent lines of sodium bear no relation to any of the lines excited by other means. It appears to me to be even possible that the Fraunhofer lines are produced by the absorption of this outlying cloud of vapour rather than by a comparatively shallow layer as is usually supposed. These are of course questions that can be more intelligently discussed by those engaged in work upon solar physics, and I am merely drawing attention to a new factor that may possibly be introduced to advantage.

XIII. *On the Radium-Content of Deep-Sea Sediments.* By J. JOLY, *Sc.D., F.R.S., Professor of Geology and Mineralogy in the University of Dublin**.

IN a paper appearing in the Philosophical Magazine of March this present year I have recorded some experiments which appear to show that sea-water possesses a richness in radium not hitherto suspected.

Although the actual amount of radium per cubic centimetre is minute (approximating to $0{\cdot}02 \times 10^{-12}$ grams), the quantity distributed in the ocean is, of course, enormous. We do not as yet know in what state the radioactive matter exists in the water—whether in true solution, or as (possibly) a precipitate or dust in suspension. I have found in some recent experiments that a part of the radium may be filtered from sea-water which contains much organic matter and has been left standing some weeks. Possibly it is precipitated as a sulphate by bacterial actions in the decomposing organic particles. This observation may have a bearing on the results obtained on deep-sea sediments which I have now to record. But whether this be so or not, it is certainly in harmony with the high radioactivity of sea-water to find that the deep-lying sediments of the ocean are exceptionally rich in radium—far richer than average terrestrial rocks.

The materials dealt with in the following experiments are partly from the 'Challenger,' partly from the 'Albatross' collections. I owe these to the kindness of Sir John Murray, F.R.S. For a specimen of Globigerina Ooze, brought up in trawling, I have to thank Mr. S. W. Kemp, of the Irish Fishery Department, and for a specimen of the mud elevated by the volcanic disturbance of 1906, in the Bay of Bengal, Mr. Stephen Dawson, C.E.

Although these materials have been in my possession for some months, most of the experiments are of recent date, and where two are recorded, the second is, in every case, a recent re-examination of the same material. The reason for this postponement was my desire to arrive at a fuller knowledge of the most reliable conditions of investigation before using up material of such value. In the process of acquiring experience of the experimental difficulties involved, various methods of extracting the emanation were tried. According to the nature of the substance these methods have been applied in the observations on deep-sea deposits. It would be out of place to consider these methods here, and their relative

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* Printed with additions from the Proceedings Royal Dublin Society, vol. xi. p. 288. Communicated by the Author.

merits. A short list has to be given, however, of such as have been used in obtaining the data which follow. A reference letter attached to the experiment will then suffice to show the mode of extraction adopted.

(A.) The substance is fused in a platinum crucible with the mixed carbonates of sodium and potassium, and the melt leached in hot water. This is filtered, and the filtrate is closed as the alkaline solution. The residue is treated with hydrochloric acid, and closed as the acid solution. If the acid solution contains or develops a precipitate, this is filtered out and re-fused with the carbonates, the melt being treated as before, *i. e.* divided between the alkaline and the acid solutions. Both solutions are subsequently examined for radium. In a variation of this method the melt after leaching is acidified, and but one acid solution closed.

(B.) The substance is boiled in HCl, and the filtered solution enclosed the requisite time. This is applicable only when there is good reason to believe that the insoluble part contains but little radium.

(C.) The substance is fused with the carbonates, and the leaching effected as in (A). The thoroughly softened and diffused melt and solution are enclosed in the one flask without further treatment. After the lapse of the requisite period it is attacked with HCl, and the emanation withdrawn along with the CO_2 evolved in the process of decomposition. Vigorous boiling finishes the process of extraction. The arrangement of apparatus is such as to secure the absorption of the CO_2, the air and emanation only being transferred to the electroscope. This is a very effective method where the attack with acid secures complete solution.

(D.) The substance in the form of a fine powder is placed in a small flask, and acid run in upon it, the remainder of the treatment being as in method (C). It is, of course, only applicable to carbonates, or soluble substances like manganese dioxide, calcium sulphate, &c.

(E.) The substance is enclosed in a very thin blown glass bulb, which is sealed by the blowpipe. This is preserved for about twenty days. The bulb is then placed in a flask, and after this is attached to the train of receiving apparatus, the bulb is broken by shaking the flask. Acid is then run in, and the process proceeds as in (D). The object here is to correct the loss which attends the direct treatment of powders owing to the large surface and consequent escape of emanation. This loss is shown in experiment (2) on the Globigerina Ooze, from the 'Albatross' collection, when compared with experiment (1) on the same material.

The weights of material used in the several experiments are not corrected for contained hygroscopic moisture. The substances are weighed "air-dry," except in the cases of the calcareous mud and the green sand, which were dried over the water-bath. The radium is in each case recorded in billionths of a gram per gram of material examined.

Blue Mud. Chall. Station, 45. Lat. 38° 34′ N., long. 72° 10′ W. 1240 fathoms. (Off the east coast of N. America.)

This deposit contains a considerable proportion of small rounded pebbles and sand, composed mainly of quartz.

On 8·86 grams treated according to method C.

Radium 3·1.

Terriginous Mud elevated by mud volcano 9 miles N.W. of Cheduba Island, coast of Arakan, Bay of Bengal; Dec. 1906.

For an account of this temporary island see 'Nature' of Feb. 28 and March 14, 1907.

On 10 grams by method A.

Radium 2·9.

Green Sand. S.s. 'Albatross.' Locality not given.

On 9 grains by method A.

Radium 4·5.

Globergina Ooze (from Mr. Kemp). Lat. 51° 37′ N., long. 12° 5′ to 12° 14′ W. 557 to 579 fathoms. (Brought up in trawling off west coast of Ireland.)

This Ooze is not quite free from mineral detritus derived from the land.

(1) On 20 grams by method B (soluble parts 11 grams).

Radium per gram of whole quantity 6·0.

(2) On 10 grams by method A (all in solution).

Radium 6·6.

Globigerina Ooze. Chall. Station, 338. Lat. 21° 13′ S., long. 14° 2′ W. 1990 fathoms. (Middle of South Atlantic.)

(1) On 25 grams by method B (soluble part 22·25 grams).

Radium 6·4.

(2) Same; on fusing insoluble part and adding to acid extract.

Radium 6·7.

Globigerina Ooze. Chall. Station, 296. Lat. 38° 6′ S., long. 88° 2′ W. 1825 fathoms. (Pacific Ocean, west of S. America.)

On 10 grams by method A (soluble part 9·44 grams).
Radium 7·4.

Globigerina Ooze. Albatross Station, 4739. Lat. 22° 11′·1 S., long. 133° 21′ W. 2042 fathoms. (Central Pacific.)

(1) On 5·3 grams by method E.
Radium per gram of whole sample 8·0.
(2) On 7·1 grams by method D (soluble part 6·815 grams).
Radium per gram of whole sample 7·1.

Calcareous Mud. S.s. Albatross, 4531. Lat. 21° 4′ 6″ S.; long. 133° 1′ 2″ W. 2225 fathoms. (East of Society Islands.) A pale buff-coloured mud.

On 6·36 grams by method A: one solution.
Radium 22·2.

Red Clay. S.s. Albatross, 4544. Lat. 10° 38′ N.; long. 105° 47′ 6″ W. 1955 fathoms. (N. Pacific; east of Central America.)

A chocolate-coloured clay containing much manganese.
On 2·4 grams by method A; one solution; not free from precipitate.
Radium 13·0.

Red Clay. Chall. Station, 5. Lat. 24° 20′ N., long. 24° 28′ W. 2740 fathoms. (N. Atlantic, off coast of Africa.)

(1) On 20 grams, method A (14·5 grams soluble).
Radium 15·4.
(2) On 10 grams of the first to settle from about 30 grams suspended in distilled water; by method A.
Radium 13·0.
(3) On 10 grams of the last to settle from the 30 grams; by method A.
Radium 28·0.
(4) On 7 grams by method A, but all in one acid solution; some precipitate left.
Radium 13·9.

Red Clay. Chall. Station, 276. Lat. 13° 28′ S., long. 149° 30′ W. 2350 fathoms. (Central Pacific, near region of Radiolarian Ooze, see under.)

(1) On 8·42 grams by method C. (Some precipitate and undecomposed particles remained.)
Radium 36·9.

(2) Same, but with re-fusion of undissolved particles; all in solution.
Radium 54·5.
(3) On 10 grams.
Part soluble in HCl (7·21 grams). By method B.
Radium per gram of soluble part 64·3.
Insoluble part (2·79 grams). By method A.
Radium per gram of insoluble part 15·7.

Mean radium content per gram of whole amount 50·7.

Radiolarian Ooze. Chall. Station, 272. Lat. 3° 48′ S., long. 152° 56′ W. 2600 fathoms. (Central Pacific.) Magnetic particles had been removed by Sir John Murray.
On 5·61 grams by method A; one solution.
Radium 22·8.

Radiolarian Ooze. Chall. Station, 274. Lat. 7° 25′ S., long. 152° 15′ W. 2750 fathoms. (Central Pacific.) Magnetic particles had previously been removed from this Ooze by Sir John Murray.
(1) On 20 grams by method A.
Radium 50·3.
(2) On 8 grams by method A.
Radium 50·7.
(3) On 6·33 grams, method A, but all in one acid solution.
Radium 49·8.

Manganese Nodule. Chall. Station, 274 (as above).
On 25 grams by method B (nearly all dissolved).
Radium 24·0.

Manganese Nodule. Albatross Station, 4658. Lat. 8° 29′·5 S., long. 85° 36·6′ W. 2370 fathoms. (Pacific Ocean, off coast of Africa.)
On 12 grams by method B, the hard manganese shell only used. Nearly all dissolved.
Radium 21·0.

Magnetic particles. Chall. Station, 241. (N. Pacific.) 2300 fathoms.
On 1·1 grams (supplied by Sir John Murray) by method A; one solution.
Radium 0·6.

It will be seen that the deposits richest in radium are those which occur in the most central parts of the Pacific Ocean. From this region not only the Red Clay, but the Radiolarian

Ooze, is remarkably radioactive. The Globigerina Ooze from the Pacific is also somewhat richer than Atlantic Ooze. The manganese nodules from the central Pacific are, again, rich in radium. The radioactivity of the Blue Mud of the Continental border region is on the other hand comparable with that of some ordinary sedimentary rocks. There is nothing specially remarkable about the mud from the Volcanic Island. With the result for the Green Sand may be compared one which I recently obtained from a Green Sandstone of Werl, Westphalia :—$4{\cdot}9 \times 10^{-12}$. The Globigerina Oozes may be contrasted with a result on Marsupites Chalk which afforded $4{\cdot}2 \times 10^{-12}$.

It may be inferred from the following statement of the comparative amounts of radium and calcium carbonate in some of the deposits, that the amount of radium increases with the antiquity of the sediment. This appears from the inverse relation of the quantities.

	Calcium Carbonate per cent.	Radium $\times 10^{-12}$.
Globigerina Ooze, Chall. 338	92·54	6·7
,, ,, ,, 296	64·34	7·4
Red Clay ,, 5	12·00	15·4
,, ,, 276	28·28	52·6
Radiolarian Ooze ,, 272	10·19	22·8
,, ,, ,, 274	3·89	50·3

The table shows that the deposits richest in calcium carbonate are poorest in radium. This would follow at once if I am correct in assuming that the radium may reach the bottom precipitated in decomposing organic matter, for in the greater depths there would be a diminished quantity of calcareous matter accompanying the precipitated radium. Thus the concentration of the radium would depend upon the supply of organic materials from above, and at the same time would be the greater when the conditions were such as to reduce the amount of associated calcium carbonate. The intensity of the latter conditions determines to a great extent the rate of growth. The more slowly accumulating sediments would thus necessarily become the richest in radioactive matter.

The Red Clay of Chall. Station 276 might appear to be exceptional. It is, however, recorded of this clay that the dredge came up with many manganese nodules and sharks' teeth. This is evidence of high antiquity. The richness in calcium carbonate of this clay may be due to conditions no longer prevailing.

It might be inferred from *à priori* considerations that the uranium which is parent to the radium must be present either in the waters of the ocean or in its deposits: for it is evident that a substance so perishable as radium—disappearing in a very few thousand years—cannot be supplied from the land at a rate adequate to make good its disappearance from so vast a reservoir. Again, we have the evidence of the Chalk, &c., that uranium must enter precipitated deposits. In the legitimacy of any deductions which may be founded on the high radioactivity of the deep-sea oceanic sediments, however, it was necessary to ascertain whether uranium actually existed in these radioactive deposits. So far as I am aware this substance has not hitherto been found either with manganese nodules or in the Oozes and Clays. In the nodules it has been sought in vain ('Challenger' Report, p. 419). Mr. Pollock, of the Royal College of Science, Dublin, who has done so much to extend the availability of Professor Hartley's spectroscopic methods of quantitative analysis, after going fully into the matter found that the spectroscope was not sufficiently sensitive for the research owing to the lack of distinctive and accentuated uranium lines. On the other hand, following the method of P. H. Walker (Journ. Amer. Chem. Soc. 1898, p. 20). Professor Werner, of Trinity College, successfully established the presence of uranium, and even obtained an approximate colorimetric estimate of its amount in the 8·42 grams of the Red Clay of Chall. Station 276, as used in the experiment given above. In a letter dated 28th April, Werner writes: "One can say without doubt that the uranium is present—not less than 0·0006 and not more than 0·0007. It is difficult, however, to be sure that one has got all the uranium, so that the result probably underestimates the real thing." The theoretical quantity of uranium present in the 8·42 grams would be 0 0012.

The result on the magnetic particles seems to show that the cosmic particles which Sir John Murray detected in the slow-forming Oozes cannot be regarded as concerned in the supply of radium or uranium to the ocean. It would therefore be inferred that the oceanic radioactive elements are derived from the land. The total quantity given up to the ocean during geological time must be enormous. It can be determined within limits by methods which I have described when dealing with the derivation of sodium from the land in connexion with the age of the earth. Doubtless much of it has at one time existed in the earlier sediments and been abstracted by secondary denudation.

It is possible to show that a very slow rate of collection of Calcareous Oozes on those areas in the Pacific from which arise the Coral Islands, might, in the course of such periods as geological time permits, give rise to depths of deposit with radio-thermal effects in their more deeply buried parts, adequate to elevate considerably the temperature in the underlying crust of the Earth. This effect will be of greater intensity if the buried sub-oceanic earth-crust is itself radioactive, as it very probably is. The mean radioactivity of igneous and sedimentary rocks of the upper crust is not less than 4×10^{-12} upon my experiments, and if certain specially radioactive rocks are taken into account the mean result would be higher still. The igneous rocks stand somewhat higher than the sedimentary, and the sub-oceanic crust probably partakes of the qualities of the latter. The thickness of this radioactive layer over the earth we do not know. But on the assumption that it extends to a depth of five miles, and assuming a rate of accumulation of Calcareous Oozes of five centimetres in a century over the disturbed and relatively shallow areas of the Pacific, and that this rate has persisted over 10 millions of years; I find the resulting radiothermal effects would be adequate to reduce the thickness of the rigid crust by as much as 25 or even 30 per cent. That is, if the isogeotherm of 800° is a temperature at which crustal materials lose their rigidity, this isogeotherm will be shifted upwards from its probable existing depth sufficiently to reduce the rigid crust as stated.

Thus it seems not improbable that the problem of the unstable areas of the Pacific is in its nature continuous with that of mountain-building along the continental margins, and that both alike are dependent on the thermal effects accompanying radioactive transformations progressing in sedimentary accumulations.

XIV. *Notices respecting New Books.*

The Theory of Light; a Treatise on Physical Optics. By RICHARD C. MACLAURIN, M.A., LL.D. In three parts, Part I. Pp. vii + 326. Cambridge University Press, 1908.

THERE have been so many advanced treatises on Physical Optics in the last few years that it might be thought superfluous to produce another. The present volume is, however, of so singular and at the same time of so important a character that no excuse is necessary for its birth. "If Theætetus, you have a wish to have any more embryo thoughts, you will be all the better for the present investigation, and if not, you will be soberer and humbler and gentler to other men, not fancying that you know what you do not know" (Plato). Such is the superscript to Chapter I. on the scope and method of the enquiry, in which, after a somewhat metaphysical discussion on the chief end of science (which seems somewhat remote from the particular subject of the treatise), he decides on a selection of the Principle of Least or Stationary Action as one which is wide enough to comprehend the whole of mechanical science, including all physics in that sense, and the aim of the author is "to show by means of it that all the varied and complex phenomena of physical optics may be woven together harmoniously by regarding them as due to periodic disturbances in a medium that we call the ether."

The work consists of much that is common to other treatises on Optics. The distinctive feature is that a large part of the volume embodies in a modified form the substance of a series of papers by the author published within recent years by the Royal Society. These deal with reflexion and refraction by transparent crystals, propagation of light in absorbing isotropic media, Newton's rings formed by metallic reflexion, and on some optical properties of thin metallic plates, together with other kindred topics.

We may observe that in the treatment of the question of Newton's rings, the author perpetuates the time-honoured method of developing the formula from the case of *parallel* plates. Fringes so formed are strictly speaking attributable to Haidinger and not to Newton; and it is not rigorously correct to develop the formula for the latter from the case of parallel plates. It would give an erroneous notion of the book if we were to lay stress on a small consideration like this. In its thoroughness of treatment of the more recondite cases of interference there is no treatise in the field to compete with it. Not the least merit is that although the book is mathematical in nature (actual experiments are seldom referred to), every important result is illustrated by curves which serve to reveal the nature of the conclusions which would be hidden from many readers if they remained merely in the form of an equation. We recommend this book to every serious student in physical optics who has previously gained familiarity with the more ordinary experimental phenomena and theoretical methods from other text-books, such as Mascart's *Traité d'Optique* or Preston's *Light.* But we recommend him at the same time to complete the purpose of the book by himself conducting an experimental enquiry, and thus extend our knowledge of this recondite subject.

Text-books of Physical Chemistry. Edited by Sir WM. RAMSAY, K.C.B.: *Thermochemistry* by JULIUS THOMSEN, translated from the Danish by KATHARINE A. BURKE, D.Sc. Pp. xv+495. Longmans, Green & Co.: London, 1908. Price 9*s.*

EVERY student and other worker in physical chemistry will welcome this translation of Thomsen's classical treatise. Although, of course, great advances have been made, both experimentally and theoretically, since the fourth volume of the 'Thermochemische Untersuchungen' appeared (1886), yet in it we have the foundation of all subsequent work in connexion with heats of combustion in their chemical bearing. This treatise was unique inasmuch as every conclusion was based exclusively upon measurements made by the author himself. The measurements were all carried out in a uniform manner, with the same apparatus and under the same external conditions; and the results were all calculated for the same temperature and physical condition in order that they might be directly comparable. This is one of the characteristics of the work which render it of permanent value. With regard to the present translation, we congratulate Miss Burke on the character of her work. The translation does not, as is so often the case, bear unmistakable evidence of passage from one language into another. It has also been most carefully edited; we have detected no serious slip, typographical or otherwise. We have only one criticism. As stated in the preface, certain statements have been modernised in order to represent more correctly the current conceptions. We think that this plan has been a mistake, especially as it has not been carried out uniformly. In a volume which has great historic interest it is most important to preserve the original thought. The student who is anxious to trace out the historical development of physical chemistry must not take the existing translation as a guide. We think this is so important a point, that we venture to express the hope that in a future edition (may it be soon called for!) every modernised phrase will be recast into the equivalent of the original form; and that where any explanations are necessary, in order that the modern student may interpret the statement in terms of modern conceptions, these should be reserved for footnotes or appendices.

One other slight criticism. The character of the volume is so exceedingly different from the other volumes in the series that we hardly know why it is grouped with them. These are emphatically critical collections and expositions of the work of many observers, especially of those whose work is most recent. Thomsen's treatise, as we have indicated, is individual and classical. It would have been better, and it is able, to stand by itself.

XV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xv. p. 580.]

March 4th, 1908.—Prof. W. J. Sollas, Sc.D., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

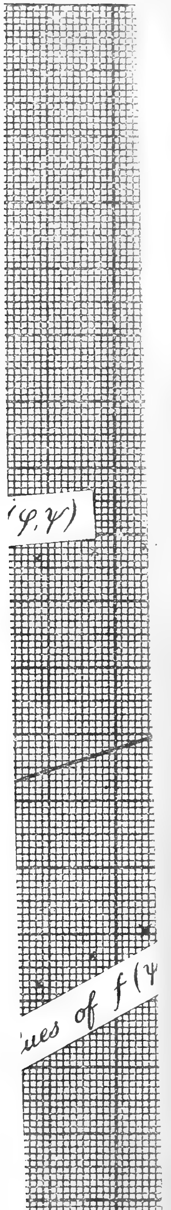
1. 'On *Metriorhynchus brachyrhynchus*, Deslong., from the Oxford Clay near Peterborough.' By E. Thurlow Leeds, B.A.

2. 'The High-Level Platforms of Bodmin Moor, and their Relation to the Deposits of Stream-Tin and Wolfram.' By George Barrow, F.G.S.

In this area there are three platforms:—one, which is marine and of Pliocene age, terminating in a steep slope at 430 feet above the sea; a second, at a height of 750 feet, seen about Camelford and at the foot of Delabole Hill; and a third, a little under 1000 feet, first recognized on Davidstow Moor. The valleys cutting the lowest platform are found to have been much deepened since the uplift of the platform to its present level; but the features thus caused gradually die out in the higher part of the valleys, disappearing in the River Camel about 22 miles from the sea. At the higher parts of all these platforms, marshes are frequently found.

The superficial deposits which bear tin above the 750-foot platform differ markedly at times from those below it, as here ancient wash is preserved—possibly protected, by a snowfield or by being frozen, from the denudation which has destroyed them below this level. These deposits are not so concentrated as the stream-sorted material below, but they have been frequently worked in past times until the industry languished, in consequence of the difficulty or impossibility of separating the wolfram contained in the enriched portion of these deposits from the tin-ore. This difficulty having been overcome, and the wolfram being even more valuable than the tin-ore, the industry is now reviving. The veins from which the wolfram is derived have been found close to the points where the 'wash' is enriched by their denudation. The method of working is described, and it is shown that the success of it depends to some extent on the slope of the granite-floor on which the detritus rests; otherwise the deposit becomes water-logged, and the method of separation adopted is expensive to carry out.

On Bodmin Moor, the larger marshes have a floor of kaolinized granite; but there is a difficulty in working it at many points, in consequence of the water-logging by peaty water. This difficulty does not exist at Stannon Marsh, which has sloping sides instead of a flat base, the cycle of denudation in this case being incomplete.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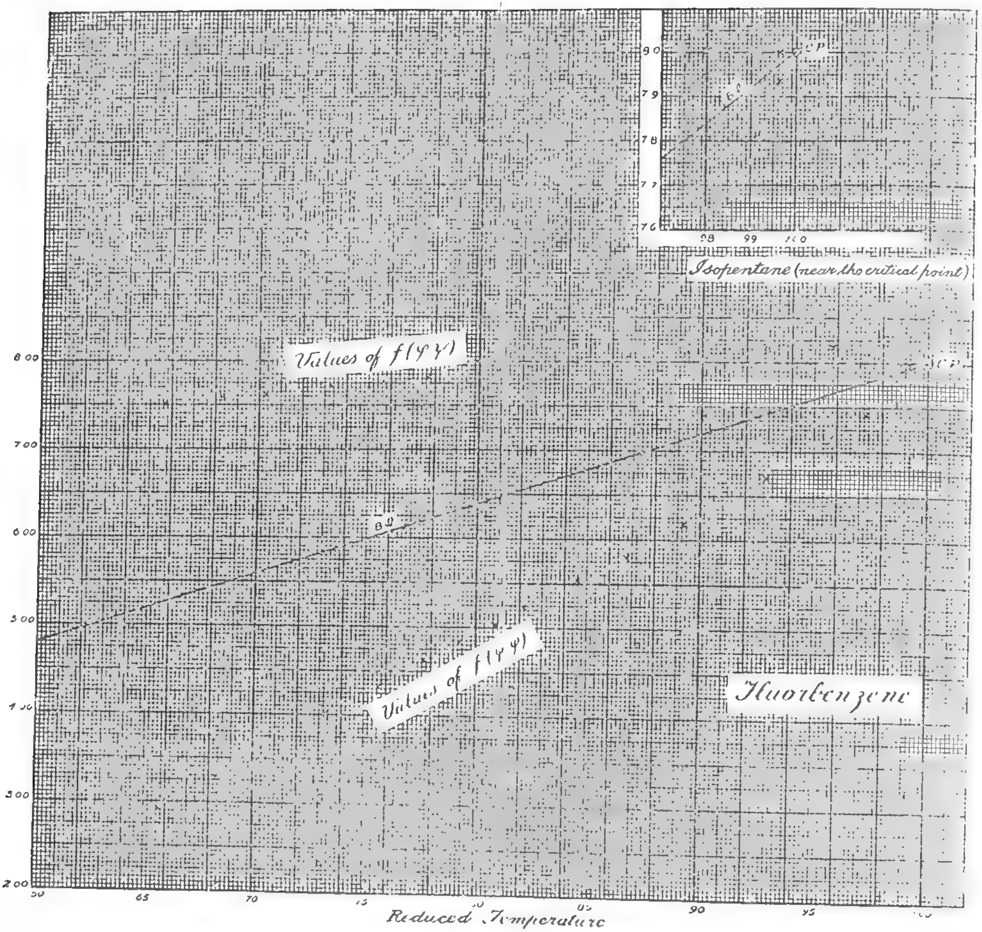
90
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C.P.
B.P.
Isopentane (near the critical point)
Values of f(φψ)
C.P.
B.P.
800
700
600
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85
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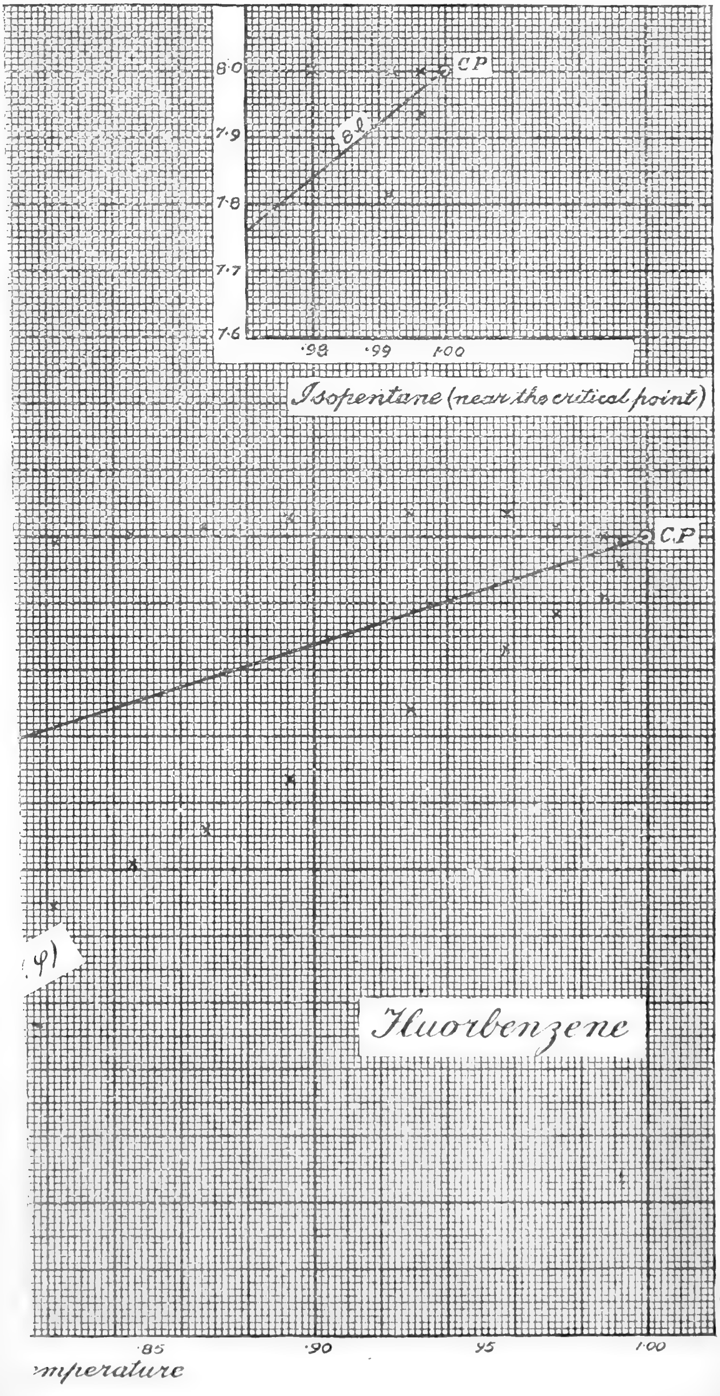
Values of f(φψ)
Fluorbenzene
Reduced Temperature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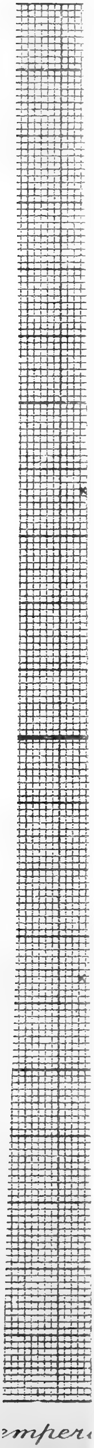
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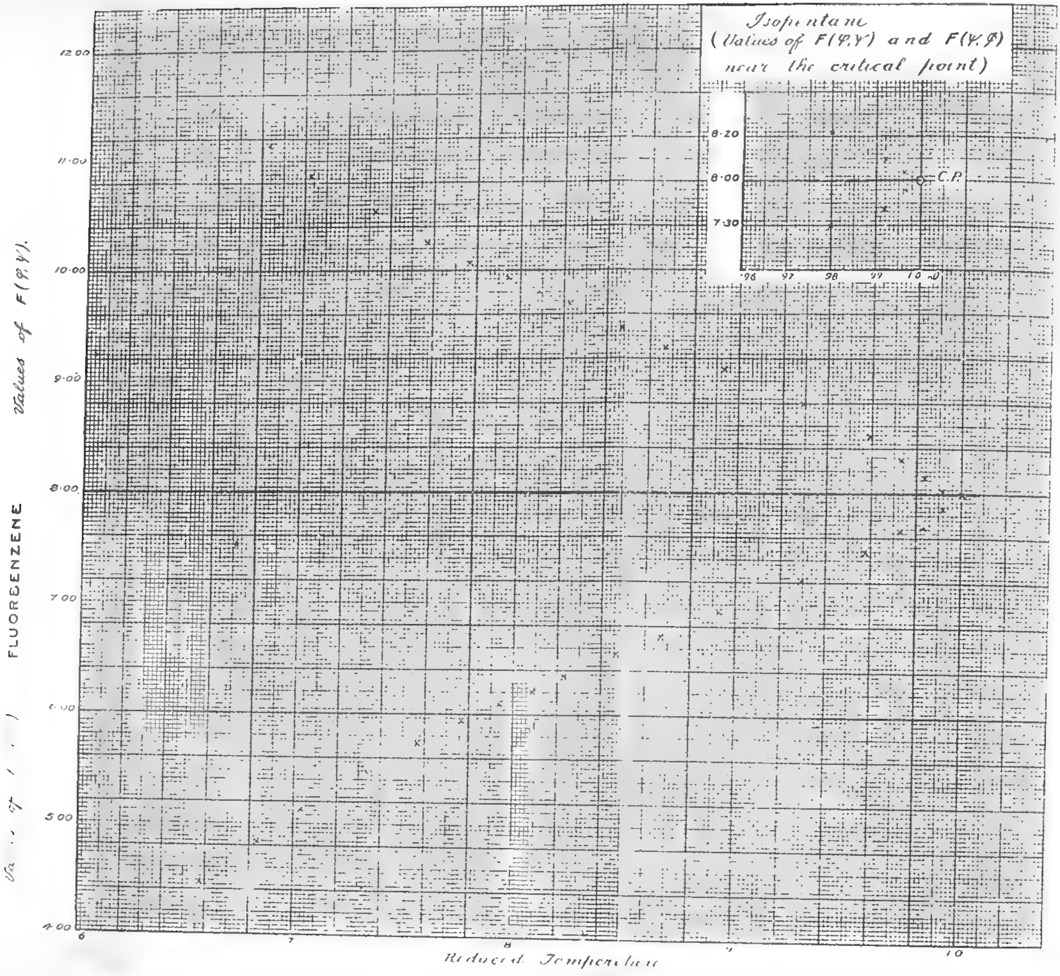
Isopentane
(Values of F(φ,ψ) and F(ψ,φ)
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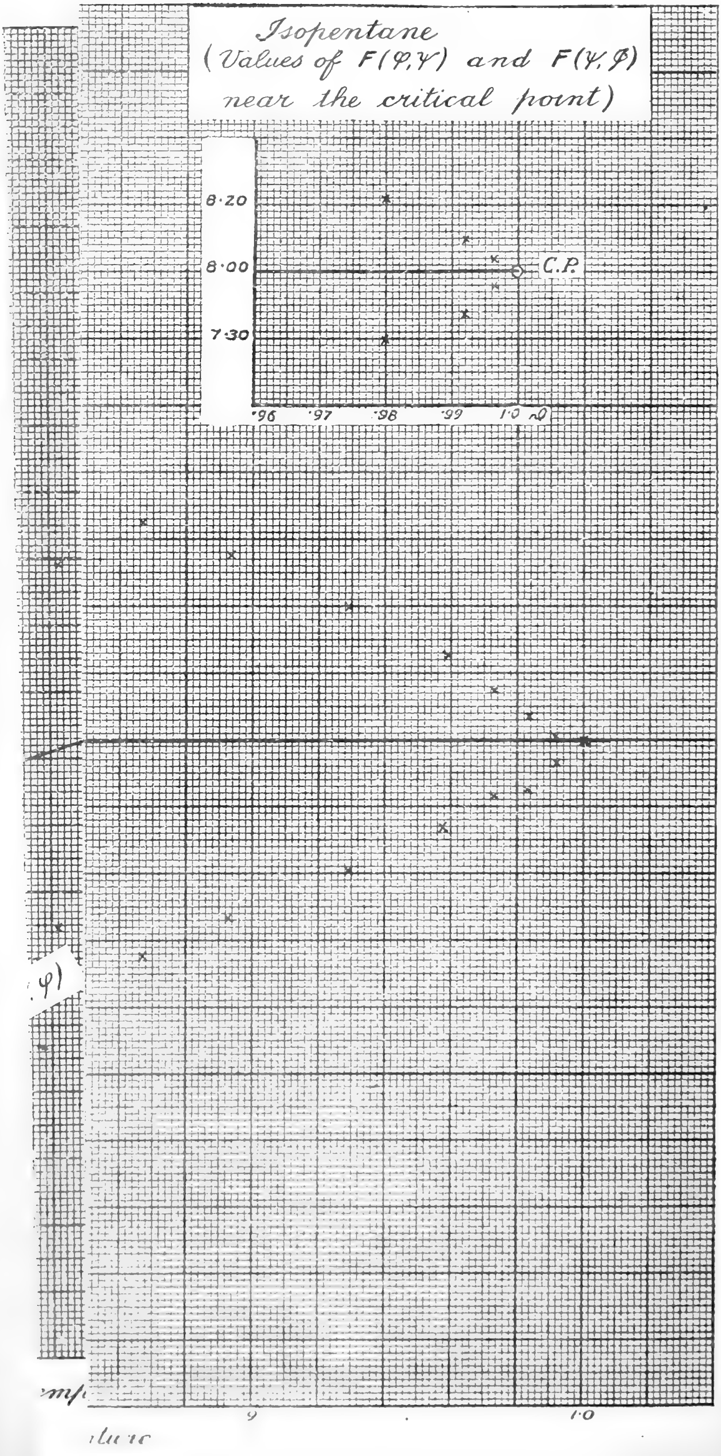
Values of F(φ,ψ).
FLUORBENZENE
Reduced Temperature


Isopentane
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AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

AUGUST 1908.

XVI. *On Orthobaric Volumes in relation to Pressure and Temperature.*

By EDWARD HAIGH, *M.A., B.Sc., Senior Master at Monkton Combe School, near Bath* *.

[Plates VI. & VII.]

Introduction.

MANY years ago, in connexion with an attempt to obtain a corrected form of van der Waals's equation, the writer commenced a detailed study of the particular case in which a liquid is in equilibrium with its saturated vapour. It is evident from the numerous theorems which have been formulated relating to "corresponding states," that those properties of a substance which depend upon the relations of pressure, temperature, and volume are intimately connected with the values of the three critical constants. Reduced data have accordingly been employed almost exclusively in this paper, the primary aim of the investigation being to ascertain whether any equation could be found connecting pressure, temperature, and volume without the employment of any other constants than simple functions of the critical values of these variables. The problem has long baffled solution, but recently it has been found possible to formulate an equation of the desired type which is in substantial agreement with the results of experiment. On a pressure-volume diagram, the equation connects the coordinates of two isobaric points on each isothermal below the critical point. Since no attempt has been made to take account of the anomalies due directly to polymerization, the equations given below have

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* Communicated by Professor Young, F.R.S.

only reference to that class of substances in which no marked degree of polymerization is apparent.

§ 1. *On a Reduced Equation connecting Orthobaric Volumes with Pressure and Temperature.*

The fundamental proposition which it is the object of this article to establish may be stated as follows :—

The orthobaric volumes of all "normal" substances are connected with vapour-pressures and temperatures of ebullition by the reduced equation

$$\left\{\pi + \left(1-\theta\right)\left(\frac{1}{\phi\psi} - \pi\right) + \frac{3}{\phi^2}\right\}\left(3\phi - 1\right)$$
$$+ \left\{\pi + \left(1-\theta\right)\left(\frac{1}{\phi\psi} - \pi\right) + \frac{3}{\psi^2}\right\}\left(3\psi - 1\right)$$
$$= 16\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the above equation π, θ represent reduced vapour-pressure and temperature, ϕ, ψ are respectively the reduced volumes of the saturated vapour and of the liquid.

Essentially, the equation is a dual form of van der Waals's reduced equation, for if the function $\left(1-\theta\right)\left(\frac{1}{\phi\psi} - \pi\right)$ is removed, it becomes

$$\left(\pi + \frac{3}{\phi^2}\right)\left(3\phi - 1\right) + \left(\pi + \frac{3}{\psi^2}\right)\left(3\psi - 1\right) = 16\theta \quad . \quad . \quad (2)$$

This latter equation, though approximately true, does not exhibit the close agreement with experimental results which will be shown to be a characteristic feature of equation (1).

At the critical point $\left(1-\theta\right)\left(\frac{1}{\phi\psi} - \pi\right)$ vanishes, and since $\phi = \psi$ the equation reduces to van der Waals's well known form.

Since equation (1), or any of the forms in which it can be expressed, connects the properties of two phases of the same substance, it will be referred to as the "dual" equation.

The introduction of the function $\left(1-\theta\right)\left(\frac{1}{\phi\psi} - \pi\right)$* is due to an attempt to take account of the interacting forces between a liquid and its saturated vapour at the surface of separation. It may be well to state at once that the equation obtained must be regarded as an empirical result, since the method of investigation has been necessarily tentative, though with some guidance from theoretical considerations in the selection of the functions employed.

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* See paper "On the Variation of Molecular Surface Energy with Temperature," by W. Ramsay, F.R.S., and Dr. J. Shields, Phil. Trans. vol. 184 A. p. 647. (The factor $1 - \theta$ corresponds to τ, the temperature from the critical point measured downwards.)

Dividing both sides of equation (1) by θ, and rearranging the terms, we obtain the more concise but less suggestive form

$$\left\{\pi + \left(\frac{1}{\theta} - 1\right)\frac{1}{\phi\psi} + \frac{3}{\theta\phi^2}\right\}\left(3\phi - 1\right)$$
$$+ \left\{\pi + \left(\frac{1}{\theta} - 1\right)\frac{1}{\phi\psi} + \frac{3}{\theta\psi^2}\right\}\left(3\psi - 1\right)$$
$$= 16 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It will be observed that the left-hand side of the equation is now an invariant function of the variables, and is also symmetrical with respect to ϕ, ψ. Putting

$$F\left(\phi, \psi\right) = \left\{\pi + \left(\frac{1}{\theta} - 1\right)\frac{1}{\phi\psi} + \frac{3}{\theta\phi^2}\right\}\left(3\phi - 1\right),$$

we have

$$F\left(\psi, \phi\right) = \left\{\pi + \left(\frac{1}{\theta} - 1\right)\frac{1}{\phi\psi} + \frac{3}{\theta\psi^2}\right\}\left(3\psi - 1\right),$$

and hence

$$F\left(\phi, \psi\right) + F\left(\psi, \phi\right) = 16 \quad . \quad . \quad . \quad . \quad (4)$$

or briefly $\qquad \Sigma = 16.$

Both forms of the fundamental equation can of course be expressed in terms of any other system of units by substituting

$$\pi = \frac{p}{p_0}, \quad \theta = \frac{t}{t_0}, \quad \phi = \frac{v}{v_0}, \quad \psi = \frac{u}{v_0},$$

where v, u represent the volumes of unit mass in the vapour and liquid phases respectively, t the absolute temperature, p the vapour-pressure, and p_0, t_0, v_0 the critical values of the pressure, temperature, and volume.

Equation (1) thus transformed becomes

$$\left\{\frac{p}{p_0} + \left(1 - \frac{t}{t_0}\right)\left(\frac{v_0^2}{vu} - \frac{p}{p_0}\right) + \frac{3v_0^2}{v^2}\right\}\left(\frac{3v}{v_0} - 1\right)$$
$$+ \left\{\frac{p}{p_0} + \left(1 - \frac{t}{t_0}\right)\left(\frac{v_0^2}{vu} - \frac{p}{p_0}\right) + \frac{3v_0^2}{u^2}\right\}\left(\frac{3u}{v_0} - 1\right)$$
$$= 16\frac{t}{t_0}.$$

It is obvious from its form that this equation is one of great generality, and the degree of concordance with experimental results is shown in the tables given below.

In compiling these tables the values of the invariant function, which forms the left-hand side of equation (3), have been calculated for various substances from the experimental data supplied by the researches of Young, Ramsay, and their collaborators.

For the sake of comparison, tables for methyl alcohol and propyl alcohol have been added. Ramsay has proved that these alcohols are polymerized in the liquid state to a high degree, and it will be seen that the agreement of the dual equation with the experimental values is in these cases less precise. In some of the tables the reduced data have been given in full, but where this is not the case, the reduced pressure has been tabulated for convenience of reference, and Young's published papers will supply the remaining data.

A short table has also been annexed giving the critical constants employed in obtaining reduced data, where such results have been directly calculated by the writer from values given in another form.

Table I.—*Fluorbenzene.*

	π.	θ.	ϕ.	ψ.	$\Sigma=16$.	Deviation.
1 ……	·0295	·6565	81·36	·3805	15·92	−·08
2 ……	·0442	·6827	55·47	·3887	15·99	−·01
3 ……	·0590	·7028	42·16	·3957	15·98	−·02
4 ……	·0885	·7335	28·40	·4069	16·02	+·02
5 ……	·1179	·7574	21·39	·4166	16·01	+·01
6 ……	·1474	·7771	17·14	·4252	16·01	+·01
7 ……	·1769	·7940	14·26	·4329	15·98	−·02
8 ……	·2064	·8092	12·20	·4406	16·00	……
9 ……	·2359	·8228	10·62	·4482	16·04	+·04
10 ……	·2949	·8464	8·376	·4624	16·02	+·02
11 ……	·3539	·8667	6·886	·4763	16·02	+·02
12 ……	·4423	·8930	5·352	·4979	16·04	+·04
13 ……	·5898	·9288	3·731	·5365	16·02	+·02
14 ……	·7372	·9579	2·711	·5858	15·98	−·02
15 ……	·8256	·9731	2·223	·6263	15·95	−·05
16 ……	·8846	·9830	1·908	·6635	15·82	−·18
17 ……	·9436	·9919	1·627	·7138	15·87	−·13
			Mean	value …	15·98	

Table II.—*Isopentane.*

	π.	$\Sigma=16$.	Deviation.
1 ……	·0224	15·95	−·05
2 ……	·04423	15·95	−·05
3 ……	·08847	15·99	−·01
4 ……	·14744	16·04	+·04
5 ……	·2064	15·99	−·01
6 ……	·2949	16·02	+·02
7 ……	·44232	16·00	……
8 ……	·5898	16·00	……
9 ……	·7372	15·95	−·05
10 ……	·8257	15·95	−·05
11 ……	·8846	16·01	+·01
12 ……	·9436	15·98	−·02
13 ……	·9731	16·00	……
	Mean	…… 15·986	

TABLE III.—*Benzene and other Hydrocarbons.*

		Benzene.		*n*-Pentane.		Di-isopropyl.		*n*-Hexane.		Di-isobutyl.		*n*-Octane.		Hexamethylene.	
	π.	Σ.	Deviation.	Σ.	Deviation.	Σ.	Deviation.	Σ.	Deviation.	Σ.	Deviation.	Σ.	Deviation.	Σ.	Deviation.
1...	·044232	15·85	−·15	15·81	−·19	16·11	+·11	15·77	−·23	15·45	−·55	15·17	−·82	16·14	+·14
2...	·088465	16·00	...	15·98	−·02	16·12	+·12	15·84	−·16	15·51	−·49	15·52	−·48	16·03	+·03
3...	·14744	16·10	+·10	15·94	−·06	16·08	+·08	16·00	...	15·73	−·27	15·75	−·25	16·13	+·13
4...	·20642	16·14	+·14	15·95	−·05	16·10	+·10	16·00	...	15·84	−·16	15·83	−·17	16·11	+·11
5...	·29488	16·12	+·12	15·98	−·02	16·06	+·06	16·00	...	15·87	−·13	15·87	−·13	16·02	+·02
6...	·44232	16·04	+·04	15·99	−·01	16·02	+·02	15·98	−·02	15·90	−·10	15·89	−·11	16·03	+·03
7...	·58978	15·96	−·04	15·97	−·03	15·98	−·02	15 95	−·05	15·94	−·06	15·92	−·08	15·98	−·02
8...	·73721	16·07	+·07	15·93	−·07	15·99	−·01	15·94	−·06	15·95	−·05	15·91	−·09	15·98	−·02
9...	·82568	15·95	−·05	15·95	−·05	15·97	−·03	15·96	−·04	15·92	−·08	15·94	−·06	15·99	−·01
10...	·88465	15·97	−·03	15·96	−·04	15·97	−·03	15·96	−·04	15·95	−·05	...	...	15·97	−·03
11...	·94363	...	...	15·97	−·03	15·98	−·02	15·97	−·03	15·96	−·04	...	...	15·97	−·03
12...	·97313	...	...	15·99	−·01	16·00	...	16·00	...	...	...	...	...	15·99	−·01
	Means ...	16·02	..	15·95	...	16·03	...	15·95	...	15·82	...	15·76	...	16·03	

Table IV.

Carbon Tetrachloride.

	π.	θ.	φ.	ψ.	Σ.	Deviation.
1	·04263	·6707	54·20	·3876	15·77	−·23
2	·06995	·7067	34·02	·3998	15·85	−·15
3	·1090	·7426	22·40	·4133	15·97	−·03
4	·1621	·7786	15·23	·4282	15·97	−·03
5	·2311	·8145	10·59	·4457	15·95	−·05
6	·3200	·8505	7·493	·4676	15·94	−·06
7	·4329	·8865	5·347	·4951	15·95	−·05
8	·5774	·9224	3·797	·5322	16·00	......
9	·7469	·9584	2·590	·5908	15·93	−·07
10	·9604	·9943	1·545	·7282	15·99	−·01
				Mean...	15·93	

Stannic Chloride.

	π.	θ.	φ.	ψ.	Σ.	Deviation.
1	·01766	·6304	128·8	·3678	15·33	−·67
2	·03189	·6642	74·69	·3780	15·53	−·47
3	·05331	·6980	45·95	·3892	15·66	−·34
4	·08433	·7318	29·62	·4017	15·76	−·24
5	·12660	·7656	19·75	·4154	15·77	−·23
6	·18323	·7994	13·62	·4310	15·80	−·20
7	·25776	·8332	9·607	·4503	15·88	−·12
8	·35310	·8670	6·852	·4738	15·93	−·07
9	·47339	·9008	4·885	·5034	15·95	−·05
10	·62158	·9346	3·437	·5448	15·94	−·06
				Mean...	15·75	

Table V.—*Ether.*

	π.	θ.	φ.	ψ.	Σ.	Deviation.
1	·0340	·6702	70·51	·3816	15·66	−·34
2	·0472	·6917	51·80	·3890	15·67	−·33
3	·0641	·7131	38·86	·3952	15·76	−·24
4	·0851	·7345	29·49	·4028	15·79	−·21
5	·1099	·7559	22·78	·4109	15·74	−·26
6	·1415	·7773	17·81	·4209	15·80	−·20
7	·1794	·7987	14·09	·4309	15·95	−·05
8	·2251	·8201	11·20	·4430	15·95	−·05
9	·2776	·8415	8·969	·4565	15·97	−·03
10	·3383	·8630	7·232	·4714	15·97	−·03
11	·4084	·8844	5·861	·4886	16·04	+·04
12	·4901	·9058	4·738	·5080	16·00	......
13	·5831	·9272	3·807	·5317	16·00	......
14	·6900	·9486	3·012	·5650	15·99	−·01
15	·8046	·9700	2·319	·6164	16·04	+·04
16	·9428	·9914	1·624	·7128	16·00	......
				Mean...	15·89	

TABLE VI.—*Alcohols.*

Methyl Alcohol.

	π.	θ.	φ.	ψ.	Σ.	Deviation.
1	·0016	·5711	1601·5	·3435	15·60	−·40
2	·00436	·6101	618	·3505	15·61	−·39
3	·01046	·6491	270	·3595	15·83	−·17
4	·02246	6881	130·33	·3692	15·97	−·03
5	·0439	·7271	68·15	·3804	16·11	+·11
6	·0796	·7661	38·02	·3934	16·19	+·19
7	·1352	·8051	22·33	·4086	16·27	+·27
8	·2182	·8441	13·62	·4282	16·31	+·31
9	·3365	·883	8·525	·4540	16·37	+·37
10	·499	·922	5·349	·4991	16·14	+·14
11	·713	·961	3·141	·5540	16·09	+·09
12	·844	·981	2·287	·6160	16·01	+·01
13	·964	·996	1·618	·7330	16·04	+·04
				Mean...	16·04	

Propyl Alcohol.

	π.	θ.	φ.	ψ.	Σ.	Deviation.
1	·0221	·6946	121·6	·3756	15·53	−·47
2	·0316	·7132	85·86	·3811	15·58	−·42
3	·0441	·7319	61·64	·3869	15·54	−·46
4	·0602	·7505	45·40	·3935	15·58	−·42
5	·0806	·7691	34·12	·4004	15·65	−·35
6	·1063	·7878	25·81	·4084	15·67	−·33
7	·1381	·8064	19·90	·4169	15·80	−·20
8	·1756	·8250	15·52	·4270	15·72	−·28
9	·2199	·8436	12·25	·4378	15·83	−·17
10	·2746	·8622	9·74	·4504	15·93	−·07
11	·3358	·8808	7·79	·4648	15·86	−·14
12	·4086	·8994	6·233	·4815	15·97	−·03
13	·4900	·9181	4·953	·5016	15·96	−·04
14	·5816	·9367	3·910	·5261	15·87	−·13
15	·6870	·9553	3·043	·5592	15·86	−·14
16	·8076	·9740	2·339	·6082	15·82	−·18
17	·9470	·9926	1·706	·7047	16·05	+·05
				Mean...	15·78	

TABLE VII.—*Critical Constants and References.*

	p_0 in mm.	t_0 Cent.	v_0 in c.c.	Authority.
Fluorbenzene (1)	33,912	286·55	2·822†	Young.
Ether (2)	27,060	194	3·801†	Ramsay & Young.
Methyl alcohol (3)	59,700	240	3·683*	do.
Propyl alcohol (4)	38,120	264	3·634†	do.
Carbon tetrachloride (5).	34,180	283·15	1·799†	Young.
Stannic chloride (5)	28,080	318·7	1·347†	do.
Isopentane............... Benzene..................	"Thermal properties of Isopentane" (Young, Proc. Physical Soc. vol. xiii. p. 657). (Reduced data.)			
n-Pentane .... di-isopropyl .... di-isobutyl............... *n*-Hexane .... *n*-Octane	"Vapour pressures, etc. of di-isopropyl and di-isobutyl" (Young & Fortey, Jour. Chem. Soc. Sept. 1900, pp. 1141–42). (Comparative table of reduced data.)			
Hexamethylene.........	Jour. Chem. Soc. Sept. 1899, p. 882 (Young & Fortey).			

(1) Jour. Chem. Soc. 1889, vol. lv. pp. 486–521.

(2) Phil. Trans. 1897 A, p. 57 *et seq.* "A study of the thermal properties of Ethyl oxide." (Ramsay & Young.)

(3) Phil. Trans. 1887 A, pp. 313–334. "Thermal properties of Methyl alcohol." (Ramsay & Young.)

(4) Phil. Trans. 1889 A, pp. 137–158. "Thermal properties of Propyl alcohol." (Ramsay & Young.)

(5) Jour. Chem. Soc. 1891, vol. lix. pp. 911–936.

† See Dr. S. Young's paper, "On the determination of the Critical Volume," Phil. Mag. Dec. 1892, p. 503.

* See paper (3) named above, Phil. Trans. 1887 A, p. 330.

NOTES ON THE TABLES.

TABLE I.—Fluorbenzene has been frequently employed by Young as a standard substance with which to compare the properties of other compounds which he has experimentally investigated, and this substance was selected by the writer (in 1895) as a typical example for detailed study. From the data of the table here given the properties of a very large number of functions have been examined, and from these results equation (1) was ultimately obtained. For this compound the deviations from the normal value, $\Sigma=16$, are generally small and irregular in sign. It is only in the near neighbourhood of the critical point, where the experimental difficulties are greatest, that the deviation exceeds one per cent., and the mean deviation, $-·02$, is only a small fraction of this amount.

Table II.—The maximum deviation for isopentane in no case exceeds one-third per cent., and the mean deviation, —·014 in 16, is less than one part in one thousand. These magnitudes are not far removed from the limits of experimental error. In view of the fact that this substance has been investigated in great detail, and with especial care to make due allowance for all known sources of error, it is highly satisfactory to find so close an agreement of the equation with experimental results.

Table III.—Benzene, di-isopropyl, and hexamethylene closely resemble each other in the magnitude and character of their deviations, which are small and mainly positive. In four other cases, viz., *n*-pentane*, *n*-hexane, di-isobutyl, and *n*-octane, the deviations are negative in sign and numerically much greater, being highest at the lowest temperature and decreasing numerically as the temperature increases.

Table IV.—Carbon tetrachloride closely resembles *n*-hexane in the negative sign and numerical magnitude of its deviations, and consequently in the value of the mean.

Stannic chloride † similarly resembles *n*-octane, the deviations being numerically much greater.

Table V.—This table has been calculated at intervals of 10° C. from 40° C. to 190° C. ($\theta = \cdot 6702$ to $\theta = \cdot 9914$). As a distinctly normal substance the deviations for ether are greater than one would expect to find, being not much less than for propyl alcohol.

Leduc ('Nouvelles recherches sur les Gaz,' Paris, 1899) has similarly found that his calculated results for the isothermals of ether are in defect. He attributes the deficiency to a possible experimental error. [" Il faut remarquer que le volume occupé par la vapeur dans le piézomètre n'est que d'un centimètre cube environ. L'écart . . . . doit être attribuée sans hésitation à une erreur de $0{,}0^{\text{mgr}}$ sur la pesée, ce que correspond à 5^{mmc} ou 6^{mmc} sur la volume observée."]

Table VI.—Results for two alcohols have been added as examples of substances for which there is evidence of marked polymerization. It will be seen that even in the case of a highly polymerized substance like methyl alcohol the equation is still approximately true.

Table VII.—Many of the numerical calculations required for this investigation were made at a relatively early date, and this table gives only the critical constants actually employed in obtaining "reduced" values of the variables. Some of the critical volumes have since been slightly altered by later determinations of the critical densities. [See Young, "Note on the law of Cailletet and Mathias," Phil. Mag. vol. l. p. 291 (1900). The differences between "old" and "corrected" critical densities usually are so

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* See note by Dr. S. Young.

† See note by Dr. S. Young.

small that the general results contained in Tables I.–VI. would hardly be affected. With the necessary alteration the first value of Σ for benzene, Table III., becomes 15·857, and in other cases the correction would be still smaller.]

It is evident from these tables that the initial proposition of this article is substantially true, but there are, in some cases, outstanding deviations of considerable magnitude which remain unaccounted for. It is difficult to say in what proportions such deviations must be ascribed to the inadequacy of the equation, to experimental error, or to circumstances of the problem which have not been taken into account. For example, no allowance has been made for any degree of polymerization whether occurring in the vapour or in the liquid phase of the substance.

Stress may rightly be laid upon the closeness of the agreement in the case of isopentane, for if the dual equation were radically defective, its inadequacy would at once be made evident by employing it to represent the properties of a compound for which the experimental investigation has been of the most exact character. The contrary is, however, the case and in some instances, where the agreement is not so satisfactory, there is reason to believe that the determination of some of the magnitudes involved has been less precise *. Stannic chloride gives values of Σ deviating from the norm to a much greater extent than those of carbon tetrachloride ; but reference to Young's paper on the former compound will show that there is some doubt as to the exact value of the critical temperature, and consequently of the critical volume, in this case.

Where the law of Cailletet and Mathias does not strictly hold good a slight uncertainty attaches to the value of the critical volume, if determined by this method, and small errors in the value of this constant have a marked influence on that of the invariant function when calculated for low temperatures. The factor $3\psi-1$, or $\psi-\frac{1}{3}$ (which in the reduced equation is the analogue of van der Waals's factor, $v-b$), is very sensitive to small variations in the values of its terms when these approach equality. Such variations may be due to small errors in the measurement of the volume of the liquid, in the determination of the critical volume, or may be caused by variations in the value of "b." In van der Waals's original investigation it is pointed out that the introduction of the factor $v-b$ is subject to the condition that "b" is relatively small compared with "v" and that below the limit $v=2b$ the formula for gases cannot be expected to hold good owing to the intersection of the spheres of action of the

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* See note by Dr. S. Young.

molecules in configurations of greater density *. This condition is violated when the equation is applied to volumes of a liquid at temperatures much below the critical point where the limit $v=b$ (or $\psi=\cdot 3333\ldots$.) is more nearly approached.

Taking a few examples :

Carbon tetrachloride, Deviation $= -\cdot 23$ when $\psi=\cdot 3876$
Stannic chloride, ,, $= -\cdot 67$,, $\psi=\cdot 3678$
n-Pentane, ,, $= -\cdot 19$,, $\psi=\cdot 3885$
n-Octane, ,, $= -\cdot 83$,, $\psi=\cdot 3826$
Di-isobutyl, ,, $= -\cdot 55$,, $\psi=\cdot 3864$
Benzene, ,, $= -\cdot 15$,, $\psi=\cdot 3870$

It must, however, be observed that relatively large deviations are not invariably connected with small values of ψ, for we have also

Isopentane, Deviation $= -\cdot 05$ when $\psi=\cdot 3908$
Fluorbenzene, ,, $= -\cdot 08$,, $\psi=\cdot 3805$

Whilst, therefore, a diminution in the value of "*b*" would increase the value of $3\psi-1$, and tend to annul deviations of negative sign, it is evident that such variations can only be of very small magnitude, for otherwise deviations of positive sign would be produced.

As showing the sensitiveness of the invariant function to slight changes in volume, one or two numerical examples may be given. In Table IV. the values for carbon tetrachloride have been calculated, at temperature intervals of 20° C., from 100° C. to 280° C. inclusive. The calculated value at a lower temperature, $T=90°$ C., gives $\Sigma=15\cdot 72$, the volume of unit mass of the liquid being ·6971 c.c. A difference of ·01 c.c. in excess of this value would make $\Sigma=16\cdot 01$. The critical volume of unit mass is 1·799 c.c., and a similar result would be produced on reducing this value by one and a half per cent. Again, in the case of stannic chloride the values of ϕ and ψ have been calculated from the critical volume $v_0=1\cdot 347$ c.c. If we take the smaller value $v_0=1\cdot 325$ c.c., the following results for the first and last lines of the table will be obtained:—

Line (1), $\Sigma=15\cdot 86$ in place of $15\cdot 33$.
(10), $\Sigma=16\cdot 10$ in place of $15\cdot 94$.

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* "There can be no doubt that molecules are not spheres in shape ..... they are more probably, without exception, flattish discs of very small thickness." (O. E. Meyer, 'Kinetic Theory of Gases.' English Translation from 2nd Revised Edition by R. E. Baynes, p. 323.)

Hence it is open to question how far conclusions based upon the hypothesis of the spherical character of molecular action can be pressed to the limit when, as in the liquid state, molecules are densely packed, however convenient the conception may be from a mathematical point of view.

The extreme difference between the values of Σ is reduced by this change from ·61 to ·24.

Whatever emendation equation (1) may still require, it is obvious, from these examples, that it can only be successfully attempted when data of very great exactitude are available. It certainly does not seem advisable to modify the dual equation by the introduction of small arbitrary constants (which would destroy its generality) until the necessity for their presence has been more fully demonstrated.

It should also be noted that the usual integral value, $-273°$ C., has been taken as the absolute zero of temperature. The changes in the value of θ which would be produced by using any other admissible value* can only be of minor importance, but yet are not quite negligible, at temperatures much below the critical point, if it is desired to arrive at the closest approximation warranted by experimental evidence.

Analogy with the Law of Cailletet and Mathias.

This well-known law expresses the fact that the means of the densities of a liquid and its saturated vapour are a linear function of the temperature. It is obvious from its form that the dual equation may be similarly stated.

Putting
$$f(\phi, \psi)=\theta \,.\, \mathrm{F}(\phi, \psi) \quad \text{and}$$
$$f(\psi, \phi)=\theta \,.\, \mathrm{F}(\psi, \phi),$$
equation (1) may be written
$$\tfrac{1}{2}\{f(\phi, \psi)+f(\psi, \phi)\}=8\theta,$$
i. e., for normal substances, *the means of the values of the functions* $f(\phi, \psi)$ *and* $f(\psi, \phi)$ *are proportional to the absolute temperature.*

Or again, taking the invariant form, equation (3) may be written
$$\tfrac{1}{2}\{\mathrm{F}(\phi, \psi)+\mathrm{F}(\psi, \phi)\}=8,$$
i. e., *the means of the values of the functions* $\mathrm{F}(\phi, \psi)$ *and* $\mathrm{F}(\psi, \phi)$ *are constant.*

The following tables and accompanying diagrams (Plates VI. & VII.) illustrate this relation in the case of Fluorbenzene. As, for this compound, the values of the two functions are rather irregular in the neighbourhood of the critical point, a few corresponding values for isopentane have also been calculated and plotted on an enlarged scale.

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* Leduc (*Nouvelles recherches sur les Gaz*) employs the value $-273°{\cdot}2$. (The following note has been kindly communicated by Dr. S. Young.)

D. Berthelot, "Sur les thermomètres à Gaz,"[1] finds $-273°{\cdot}09$ and E. Buckingham, "On the establishment of the thermodynamic scale of temperature by the constant volume thermometer,"[2] $-273°{\cdot}13$.

[1] *Travaux et Mémoires du Bureau International des Poids et Mesures*, 1903.

[2] Bulletin of the Bureau of Standards, vol. iii. p. 237 (Washington, 1907).

Fluorbenzene.

Values of $f(\phi, \psi)$ and $f(\psi, \phi)$ in relation to 8θ.

θ.	8θ.	$f(\phi, \psi)$.	$f(\phi, \psi)-8\theta$.	$f(\psi, \phi)$.	$8\theta-f(\psi, \phi)$.
·6565	5·252	7·514	2·262	2·936	2·316
·6827	5·462	7·609	2·147	3·306	2·156
·7028	5·622	7·637	2·015	3·596	2·026
·7335	5·868	7·730	1·862	4·018	1·850
·7574	6·059	7·787	1·728	4·351	1·708
·7771	6·217	7·828	1·611	4·613	1·604
·7940	6·352	7·877	1·525	4·835	1·517
·8092	6·474	7·926	1·452	5·023	1·451
·8228	6·582	7·969	1·387	5·227	1·355
·8464	6·771	8·024	1·253	5·547	1·224
·8667	6·934	8·069	1·135	5·813	1·121
·8930	7·144	8·137	0·993	6·195	0·949
·9288	7·430	8·181	0·751	6·701	0·729
·9579	7·663	8·149	0·486	7·169	0·494
·9731	7·785	8·074	0·289	7·436	0·349
·9830	7·864	7·990	0·136	7·547	0·317
·9919	7·935	7·943	0·008	7·792	0·143
Isopentane (in the neighbourhood of the critical point).					
·9800	7·840	8·046	0·206	7·644	0·196
·9918	7·934	7·034	0·100	7·813	0·121
·9963	7·970	8·006	0·036	7·933	0·037

Fluorbenzene.

Values of F (ϕ, ψ) and F (ψ, ϕ) in relation to the constant 8.

	θ.	F (ϕ, ψ).	F $(\phi, \psi)-8$.	F (ψ, ϕ).	$8-$F(ψ, ϕ).
1	·6565	11·45	3·45	4·47	3·53
2	·6827	11·15	3·15	4·85	3·15
3	·7028	10·86	2·86	5·12	2·88
4	·7335	10·54	2·54	5·48	2·52
5	·7574	10·27	2·27	5·74	2·26
6	·7771	10·07	2·07	5·94	2·06
7	·7940	9·92	1·92	6·09	1·91
8	·8092	9·80	1·80	6·20	1·80
9	·8228	9·69	1·69	6·35	1·65
10	·8464	9·48	1·48	6·54	1·46
11	·8667	9·31	1·31	6·71	1·29
12	·8930	9·11	1·11	6·93	1·07
13	·9288	8·81	0·81	7·21	0·79
14	·9579	8·50	0·50	7·48	0·52
15	·9731	8·30	0·30	7·65	0·35
16	·9830	8·13	0·13	7·69	0·31
17	·9919	8·01	0·01	7·86	0·14
Isopentane (near the critical point).					
	·9800	8·21	0·21	7·80	0·20
	·9918	8·10	0·10	7·88	0·12
	·9963	8·04	0·04	7·96	0·04

§ 2. *On the Determination of Critical Constants from Observations at Temperatures considerably below the Critical Point.*

The invariant form of the dual equation may be directly employed as a test to ascertain whether given values assigned to the critical constants of a normal substance form a consistent system. If these values are substituted in the function

$$\left\{\frac{p}{p_0}+\left(\frac{t_0}{t}-1\right)\frac{v_0^2}{uv}+\frac{3v_0^2t_0}{v^2t}\right\}\left(\frac{3v}{v_0}-1\right)$$
$$+\left\{\frac{p}{p_0}+\left(\frac{t_0}{t}-1\right)\frac{v_0^2}{uv}+\frac{3v_0^2t_0}{u^2t}\right\}\left(\frac{3u}{v_0}-1\right),$$

the result must approximate to the constant value 16. From the fact that every experimental determination of orthobaric volumes at a known vapour-pressure and temperature gives a relation between the values of the three critical constants, a still more important deduction may be drawn. The law of Cailletet and Mathias makes it possible to express the critical temperature in terms of the critical volume. The critical temperature being thus eliminated, an equation is obtained connecting the two remaining critical constants in which the critical pressure occurs only to the first power. From two such equations the critical pressure is easily eliminated, giving finally a cubic equation in v_0 of the form

$$\mathrm{P}v_0^3-\mathrm{Q}v_0^2+\mathrm{R}v_0-\mathrm{S}=0\,,$$

where P, Q, R, S are functions of the orthobaric volumes, vapour-pressures, and temperatures obtained from any two determinations.

Let u_1, u_2 be the volumes of unit mass of liquid, and v_1, v_2 the volumes of unit mass of saturated vapour, determined respectively at vapour-pressures p_1, p_2, and temperatures t_1, t_2. Let A, B be constants in the linear function of the temperature which expresses the sum of the densities, *i. e.*

$$\frac{1}{u}+\frac{1}{v}=\mathrm{A}-\mathrm{B}t$$
$$=f(t),$$

or briefly
$$=f.$$

Hence also
$$\frac{2}{v_0}=\mathrm{A}-\mathrm{B}t_0,$$

or
$$t_0=\frac{1}{\mathrm{B}}\left(\mathrm{A}-\frac{2}{v_0}\right).$$

Employing the substitutions,

$$f_1=\frac{1}{u_1}+\frac{1}{v_1}, \qquad f_2=\frac{1}{u_2}+\frac{1}{v_2},$$

$$g_1=\frac{1}{u_1v_1}, \qquad g_2=\frac{1}{u_2v_2},$$

$$\mathrm{H}_1=2p_1t_1, \qquad \mathrm{H}_2=2p_2t_2,$$

$$\mathrm{K}_1=3p_1t_1(u_1+v_1), \qquad \mathrm{K}_2=3p_2t_2(u_2+v_2),$$

$$\mathrm{L}_1=3f_1^2\mathrm{A}-6g_1\mathrm{A}+2f_1g_1, \qquad \mathrm{L}_2=3f_2^2\mathrm{A}-6g_2\mathrm{A}+2f_2g_2,$$

$$\mathrm{M}_1=9f_1^2+9f_1\mathrm{A}-8g_1, \qquad \mathrm{M}_2=9f_2^2+9f_2\mathrm{A}-8g_2,$$

$$\mathrm{N}_1=16\mathrm{A}+8f_1, \qquad \mathrm{N}_2=16\mathrm{A}+8f_2,$$

the critical volume is a root of the cubic

$$(\mathrm{H}_1\mathrm{L}_2-\mathrm{H}_2\mathrm{L}_1)v_0^3-(\mathrm{H}_1\mathrm{M}_2-\mathrm{H}_2\mathrm{M}_1+\mathrm{K}_1\mathrm{L}_2-\mathrm{K}_2\mathrm{L}_1)v_0^2$$
$$+(\mathrm{H}_1\mathrm{N}_2-\mathrm{H}_2\mathrm{N}_1+\mathrm{K}_1\mathrm{M}_2-\mathrm{K}_2\mathrm{M}_1)v_0-(\mathrm{K}_1\mathrm{N}_2-\mathrm{K}_2\mathrm{N}_1)=0.$$

Deduction of the cubic equation in v_0.

From equation (1)

$$\left\{\pi+(1-\theta)\left(\frac{1}{\psi\phi}-\pi\right)+\frac{3}{\phi^2}\right\}(3\phi-1)$$
$$+\left\{\pi+(1-\theta)\left(\frac{1}{\psi\phi}-\pi\right)+\frac{3}{\psi^2}\right\}(3\psi-1)=16\theta,$$

$$\therefore \quad \theta\pi(3\phi+3\psi-2)+(1-\theta)\left(\frac{3}{\phi}+\frac{3}{\psi}-\frac{2}{\psi\phi}\right)$$
$$+9\left(\frac{1}{\phi}+\frac{1}{\psi}\right)-3\left(\frac{1}{\phi^2}+\frac{1}{\psi^2}\right)=16\theta,$$

$$\therefore \quad \theta\pi(3\phi+3\psi-2)+12\left(\frac{1}{\phi}+\frac{1}{\psi}\right)-3\left(\frac{1}{\phi}+\frac{1}{\psi}\right)^2$$
$$+\frac{4}{\psi\phi}-\theta\left(\frac{3}{\phi}+\frac{3}{\psi}-\frac{2}{\psi\phi}\right)=16\theta,$$

$$\therefore \quad \theta\pi(3\phi+3\psi-2)=16\theta+\theta\left(\frac{3}{\phi}+\frac{3}{\psi}-\frac{2}{\psi\phi}\right)$$
$$+3\left(\frac{1}{\phi}+\frac{1}{\psi}\right)^2-12\left(\frac{1}{\phi}+\frac{1}{\psi}\right)-\frac{4}{\psi\phi}.$$

Dividing both sides of the equation by θ,

$$\frac{1}{\pi}=\frac{3\phi+3\psi-2}{\left\{16+\left(\frac{3}{\phi}+\frac{3}{\psi}-\frac{2}{\psi\phi}\right)\right\}+\frac{1}{\theta}\left\{3\left(\frac{1}{\phi}+\frac{1}{\psi}\right)^2-12\left(\frac{1}{\phi}+\frac{1}{\psi}\right)-\frac{4}{\psi\phi}\right\}}.$$

Substituting $\frac{p}{p_0}=\pi$, $\frac{t}{t_0}=\theta$, $\frac{u}{v_0}=\psi$, $\frac{v}{v_0}=\phi$,

$$p_0=\frac{pt\left(\frac{3v}{v_0}+\frac{3u}{v_0}-2\right)}{t\left\{16+3v_0\left(\frac{1}{v}+\frac{1}{u}\right)-\frac{2v_0^2}{uv}\right\}+t_0\left\{3v_0^2\left(\frac{1}{v}+\frac{1}{u}\right)^2-12v_0\left(\frac{1}{v}+\frac{1}{u}\right)-\frac{4v_0^2}{uv}\right\}}\cdot \quad (6)$$

an equation from which p_0 can be found when v_0 and t_0 are known.

Substituting in this equation the values of p, t, u, and v determined by a first observation,

$$p_0=\frac{p_1t_1\left(\frac{3v_1+3u_1}{v_0}-2\right).}{t_1\left\{16+3v_0\left(\frac{1}{v_1}+\frac{1}{u_1}\right)-\frac{2v_0^2}{u_1v_1}\right\}+v_0t_0\left\{3v_0\left(\frac{1}{v_1}+\frac{1}{u_1}\right)^2-12\left(\frac{1}{v_1}+\frac{1}{u_1}\right)-\frac{4v_0}{u_1v_1}\right\}}$$

$$=\frac{\frac{K_1}{v_0}-H_1}{t_1\{16+3f_1v_0-2g_1v_0^2\}+\left(\frac{Av_0-2}{B}\right)\{(3f_1^2-4g_1)v_0-12f_1\}}$$

$$=\frac{\frac{B}{v_0}(K_1-H_1v_0)}{Bt_1\{16+3f_1v_0-2g_1v_0^2\}+(Av_0-2)\{(3f_1^2-4g_1)v_0-12f_1\}}\cdot$$

From the denominator of this fraction, Bt_1 can be eliminated by means of the relation

$$f_1=A-Bt_1\,; \qquad \therefore \quad Bt_1=A-f_1\,;$$

and, rearranging the terms,

$$\frac{p_0v_0}{B}=\frac{K_1-H_1v_0}{(3f_1^2A-6g_1A+2f_1g_1)v_0^2-(9f_1^2+9f_1A-8g_1)v_0+(16A+8f_1)}$$

$$=\frac{K_1-H_1v_0}{L_1v_0^2-M_1v_0+N_1}\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the law of Cailletet and Mathias holds good, B, and therefore $\frac{p_0v_0}{B}$, may be regarded as constant; and hence the value of the ratio on the right-hand side of the equation is the same from whatever set of observations the values of the coefficients are obtained. Hence

$$\frac{H_1v_0-K_1}{L_1v_0^2-M_1v_0+N_1}=\frac{H_2v_0-K_2}{L_2v_0^2-M_2v_0+N_2},$$

from which we obtain the cubic equation

$$(H_1L_2-H_2L_1)v_0^3-(H_1M_2-H_2M_1+K_1L_2-K_2L_1)v_0^2$$
$$+(H_1N_2-H_2N_1+K_1M_2-K_2M_1)v_0-(K_1N_2-K_2N_1)=0. \quad (8)$$

In the cases which have been examined this cubic has three real and positive roots, but only the mean root is common to all the cubics relating to the same substance. As this method of obtaining the critical volume is new, it will be well to examine its application in detail, taking for the purpose a normal substance whose properties are well known.

Isopentane.

From Young's paper ("Thermal Properties of Isopentane") the following data of five experimental determinations are taken :—

T (Centigrade).	t (Abs. temp.).	p, in mm.	u, in c.c. (from curve).	v, in c.c. (from curve).
10°	283°	390·4 *	1·5885	607·5
30°	303°	815·5 *	1·6413	303·0
60°	333°	2036·5 †	1·7329	127·9
100°	373°	5345·5 †	1·8940	49·45
120°	393°	8018 †	2·0037	32·20

* Dynamical method. † Mean of experimental values.

The relation between the liquid and vapour densities is expressed by the equation

$$\frac{1}{u}+\frac{1}{v}=A-Bt,$$

where $A=\cdot 8872$ or 8872×10^{-4},

$B=\cdot 000908$ or 908×10^{-6}.

From the above data we obtain

$$\begin{aligned}
T = 10^\circ\,\text{C.}\quad H_1 &= 220{,}966,\\
K_1 &= 201{,}882 \times 10^{3},\\
L_1 &= 1{,}052{,}960 \times 10^{-6},\\
M_1 &= 859{,}877 \times 10^{-5},\\
N_1 &= 19{,}237{,}088 \times 10^{-6}.
\end{aligned}$$

$$\begin{aligned}
T = 30^\circ\,\text{C.}\quad H_2 &= 494{,}193,\\
K_2 &= 225{,}827 \times 10^{3},\\
L_2 &= 988{,}894 \times 10^{-6},\\
M_2 &= 824{,}295 \times 10^{-5},\\
N_2 &= 19{,}091{,}808 \times 10^{-6}.
\end{aligned}$$

$$\begin{aligned}
T = 60^\circ\,\text{C.}\quad H_3 &= 1{,}356{,}310,\\
K_3 &= 263{,}734 \times 10^{3},\\
L_3 &= 891{,}615 \times 10^{-6},\\
M_3 &= 771{,}200 \times 10^{-5},\\
N_3 &= 18{,}873{,}888 \times 10^{-6}.
\end{aligned}$$

$$\begin{aligned}
T = 100^\circ\,\text{C.}\quad H_4 &= 3{,}987{,}743,\\
K_4 &= 307{,}120 \times 10^{3},\\
L_4 &= 756{,}698 \times 10^{-6},\\
M_4 &= 700{,}224 \times 10^{-5},\\
N_4 &= 18{,}583{,}328 \times 10^{-6}.
\end{aligned}$$

$$\begin{aligned}
T = 120^\circ\,\text{C.}\quad H_5 &= 6{,}302{,}148,\\
K_5 &= 323{,}335 \times 10^{3},\\
L_5 &= 682{,}585 \times 10^{-6},\\
M_5 &= 664{,}230 \times 10^{-5},\\
N_5 &= 18{,}438{,}048 \times 10^{-6}.
\end{aligned}$$

The numerical values of the functions H, K, L, and M vary greatly. H increases rapidly, and K slowly, with rise of temperature; L, M, and N decrease slowly as the temperature rises.

Since n observations can be combined to form $\frac{n(n-1)}{2}$ pairs, these five determinations yield data for the formation of ten cubic equations, of which the values of the coefficients for five have been calculated. As it is important to avoid the introduction of errors due to premature attempts at approximation, significant figures have been retained in excess of the number probably sufficient for accuracy.

First Cubic.—The first cubic equation calculated by this method was obtained from data at temperatures 60° C. and 120° C., giving the equation

$$469{,}319\, v_0^3 - 14{,}784{,}759\, v_0^2 + 83{,}569{,}800\, v_0 - 123{,}986{,}496 = 0.$$

This cubic has three positive roots, of which the values are approximately

2·397, 4·260, 24·846.

Second Cubic, from data at 10° C. and 100° C.

$$403{,}175 v_0^3 - 20{,}326{,}881 v_0^2 + 129{,}983{,}430 v_0 - 215{,}643{,}367 = 0.$$

The roots of this equation are approximately

2·892, 4·277, 43·24.

Comparing these results, we infer that the extreme roots of the cubic equation are irrelevant and that the mean root gives the true critical volume. In the equations which follow only the mean root has been calculated.

Third Cubic, from data at 10° C. and 60° C.

$$123{,}112 v_0^3 - 10{,}765{,}884\, v_0^2 + 73{,}280{,}079\, v_0 - 126{,}317{,}603 = 0.$$

Mean root, 4·260.

Fourth Cubic, from data at 60° C. and 100° C.

$$254{,}067\, v_0^3 - 9{,}637{,}135\, v_0^2 + 57{,}457{,}144\, v_0 - 89{,}824{,}667 = 0.$$

Mean root, 4·231.

Fifth Cubic, from data at 10° C. and 30° C. (Low temperatures and a smaller temperature interval.)

$$30{,}185\, v_0^3 - 4{,}057{,}493\, v_0^2 + 28{,}301{,}939\, v_0 - 48{,}996{,}154 = 0.$$

Mean root, 4·315.

Summarizing these results, we get for v_0 :—

First cubic . . .	4·260	60° and 120° C.
Second cubic . .	4·277	10° and 100° C.
Third cubic . .	4·260	10° and 60° C.
Fourth cubic . .	4·231	60° and 100° C.
Fifth cubic . . .	4·315	10° and 30° C.

5)21·343

4·2686

as against Young's value, 4·266 c.c.

Taking Young's value for the critical volume as a standard, the greatest deviation is in the case of the fifth cubic, where the temperatures are both low, and the law of Cailletet and Mathias holds less exactly. The deviations from the norm are not always in the same direction and we may infer that the critical volume will probably lie between the greatest and least of the mean roots of the several cubic equations, and that the mean of their sum will be a close approximation to its actual value[*]. A value for the critical volume having been obtained, the critical temperature can be deduced from the law of Cailletet and Mathias, and hence also the critical pressure from the dual equation.

The number of substances for which the critical constants can be directly determined by experiment is very small, and the method here described may therefore be useful in obtaining approximate values for these important constants in cases where experimental observations can only be made at temperatures falling considerably below the critical point.

Regarded as a test of the applicability of the cubic equation to determine the critical volume, the foregoing investigation is open to the objection that the value of A which has been employed has been obtained from the complete series of liquid and vapour densities observed between 10° C. and a temperature verging closely upon the critical temperature. If observations are confined within a more limited range, it is conceivable that somewhat different values of A, B may be obtained, and the values of the roots of the cubic correspondingly affected. To this objection it may be replied that Young's investigations have shown that in the case of normal substances such deviations are only of small magnitude, and hence no great alteration in the values of the coefficients of the terms in the cubic equation will be thereby produced. In the hypothetical case in which it is assumed that we have at our disposal only a small number of experimental observations, falling within a restricted range of temperature, mean values of A and B may be determined from the whole series of available observations or, taking each pair of observations independently, values of

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[*] Perhaps a preferable method would be to "weight" the results by multiplying each mean root by the corresponding interval of temperature and divide the total thus obtained by the sum of these temperature intervals. Applied to the five roots given above this method leads to the "weighted" mean value $r_0 = 4{\cdot}265$.

A and B may be obtained from the equations

$$A=\frac{f_1t_2-f_2t_1}{t_2-t_1},$$

$$B=\frac{f_1-f_2}{t_2-t_1}.$$

From the form of these expressions it will be seen that it is inadvisable to select pairs of observations in which the temperature interval is small. Further to test this point the coefficients of the five cubic equations already investigated have been recalculated, substituting for A the values obtained by treating each pair of observations independently.

For the first cubic $A = \cdot 8888$, yielding the equation

$$470{,}375\,v_0^3-14{,}833{,}255\,v_0^2+83{,}786{,}976\,v_0-125{,}483{,}646=0.$$

The coefficients in this equation only differ slightly in value from those previously obtained. The mean roots of the five cubics recalculated in this manner are respectively

First cubic	4·176
Second ,, ...	4·230
Third ,, ...	4·329
Fourth ,, ...	4·226
Fifth ,, ...	4·280
Mean of five roots	4·248

(The "weighted" mean is here only 4·240.)

Compared with 4·266 as a normal value this shows a deviation of about three-sevenths per cent. in defect.

As a test example isopentane is a very favourable case, and generally greater differences in the values of the mean roots of the cubic may be expected to occur. The validity of this method of finding the critical volume depends upon the exactitude with which the law of Cailletet and Mathias is fulfilled by the substance under investigation. Regarded geometrically, if, on a density-temperature diagram, the position of a series of points on the line of mean density has been determined by experiment, the assumption is made that the series of lines obtained by joining pairs of these points will, on being produced, pass through the point representing the critical density. Any slight curvature of the diameter at the extremity, such as Young has observed in many cases, will, to the extent that it occurs, invalidate the result. Provided, however, that the substance is fairly normal and that an adequate length of the mean-density line has been experimentally constructed, it is very unlikely that the point representing the critical density will lie on the same side of all the lines so obtained. Hence a useful indication will be afforded of the limits within which the true critical volume will most probably lie even when experimental investigation in the neighbourhood of the critical point is not feasible.

To Dr. S. Young (to whom the first manuscript copy of this article was sent), I desire here to tender very cordial thanks for the helpful notes and criticism with which he has favoured me whilst preparing this paper for publication. I am also indebted to Mr. A. G. Wilkinson for careful clerical assistance.

Note by SYDNEY YOUNG, *D.Sc., F.R.S.,*
Trinity College, Dublin.

The proofs of the correctness of his "dual" equation which Mr. Haigh has brought forward appear to be very complete and satisfactory, and it is probable that some, though not all, of the deviations of the calculated values of Σ from the theoretical value, 16, may be due to experimental errors.

It may be pointed out that such errors are in general most likely to occur in the determinations of the volumes of saturated vapour at the lower temperatures, and it is probable that the single rather large deviation in the case of normal pentane at the lowest temperature may be explained in this way. The results with *n*-pentane should be specially accurate, and the greatest of the remaining deviations, 0·07, is small. Omitting the first result, the mean value of Σ would be 15·965 instead of 15·95.

Serious experimental difficulties were encountered with stannic chloride and carbon tetrachloride, owing to the action of these substances on mercury, stannic chloride under all conditions and carbon tetrachloride at the higher temperatures. In both cases it was necessary to devise special methods for the determination of the vapour pressures and specific volumes, and it is not to be expected that the data for these substances can be so accurate as for the others.

I have pointed out (Phil. Mag. vol. l. p. 291 (1900)) that although the law of Cailletet and Mathias is applicable to all the normal substances examined with a close approach to accuracy, yet the deviations are too regular to be ascribed to experimental error. The relation between the mean densities of liquid and saturated vapour and the temperature is represented with great accuracy by the formula

$$D_t = D_0 + \alpha t + \beta t^2,$$

where α is always negative and β may be either positive or negative. The direction and extent of the curvature of the diameter is indicated by the sign and magnitude of the constant β.

The close connexion between Mr. Haigh's dual equation and the law of Cailletet and Mathias is shown by the following table in which the normal substances, excluding carbon tetrachloride and stannic chloride, are arranged in order of magnitude of the mean values of Σ. It will be seen that with one exception the values of $\beta \times 10^{10}$ follow the same order, Σ falling from 16·03 to 15·76 while $\beta \times 10^{10}$ changes from + 791 to − 1046. The one deviation, that shown by di-isopropyl, is small; and it is probable that the mean value of Σ for *n*-pentane should be slightly higher and of *n*-hexane slightly lower than 15·95, and that $\beta \times 10^{10}$ for the latter substance should have a small negative value.

	Mean value of Σ.	$\beta \times 10^{10}$.
Hexamethylene	16·03	+ 791
Di-isopropyl	16·03	+ 413
Benzene	16·02	+ 693
Isopentane	15·986	+ 463
Fluorbenzene	15·98	+ 293
n-Pentane	15·95	0
n-Hexane	15·95	0
Ether	15·89	− 475
Di-isobutyl	15·82	− 592
n-Octane	15·76	−1046
Carbon tetrachloride	15·93	+1480
Stannic chloride	15·75	+ 977

The connexion seems to break down altogether when the two chlorides are compared with the other substances, but it is possible that a considerable part of the discrepancy may be explained by the relatively large experimental errors to which reference has been made.

XVII. *The Secondary γ Rays due to the γ Rays of Radium C.*

By A. S. Eve, *D.Sc., Associate Professor of Mathematics, Lecturer in Radioactivity, McGill University, Montreal* [*].

THE Röntgen rays and the γ rays from radioactive substances have so many properties in common that they are generally believed to be fundamentally of the same nature. But the secondary radiations caused by X rays and by γ rays, respectively, appear at first to be widely different. Whilst the γ rays give rise to secondary radiations following the order of the densities of the radiators, the X rays cause secondary radiations strongly diverging from that order. Thus Townsend [†] found actually more secondary radiation from solid paraffin than from lead. The values he obtained were :—

TABLE I.

X Rays, Secondary Radiation.

Radiator.	Rays through Air.	Rays through ·25 mm. of Aluminium.
Air	2	1
Aluminium	6·0	3·5
Glass	7·5	3·0
Lead	24	6·0
Solid Paraffin	30	15·5
Brass	66	2·5
Zinc	68	3·0
Copper	70	2·5

Let us compare the secondary radiations from the γ rays of radium inclosed in lead.

TABLE II.

γ Rays, Secondary Radiation [‡].

Radiator.	
Lead	100
Copper	61
Brass	59
Aluminium	30
Glass	35
Solid Paraffin	20

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[*] Communicated by the Author.

[†] Proc. Camb. Phil. Soc. vol. x. p. 217 (1899).

[‡] Phil. Mag. Dec. 1904.

In this case the order of secondary radiation is that of density.

The remarkable dissimilarity in the two cases is at first sight perplexing, and the object of the present paper is to explain to some extent the cause of the apparent differences.

In the first place it must be pointed out that a comparison of the two tables above given is an unfair one, because the first table really shows secondary radiation of the X-ray type, for the cathode rays were absorbed by air before they reached the testing apparatus. But the second table gives mainly the *cathode* secondary radiation due to γ rays, for in this case the cathode rays produce a much greater effect in the electroscope than the secondary rays of the γ type.

A few experiments recently made may be worth recording. The X rays from a very hard tube were employed, such as were used in some previous experiments to compare the ionizations of various gases by γ and X rays. These hard penetrating[‡] rays were found to ionize gases almost in the same manner as γ rays. In the present case the X rays struck plates of the substances named in Table III., and the incident secondary rays were measured by the electroscope, described later, used throughout these experiments. The cathode secondary rays were absorbed by the air between the secondary radiator and the electroscope. The incident

TABLE III.

Secondary Rays from X and γ Rays.
Cathode rays removed by absorption.

Secondary Radiator.	Thickness in cms.	X.	γ.
Books (edges)	11	280	2·5
Paraffin..............	4	230	2·0
,, ...	6·5	...	2·7
Brick..................	6	170	3·0
,, ...	14	...	3·6
Slate	6	160	3·0
Wood	11	125	1·7
Cement................	21	103	3·8
Lead	5	61	1·0
Iron	5	58	3·3

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[*] Phil. Mag. Nov. 1904.

secondary radiations from the same plates were also measured, due to 14 mgs. of pure radium bromide placed inside a hollow steel* cylinder, 2·2 cms. thick, having stopped ends. The cathode secondary rays were in this case screened from the electroscope by aluminium 1·63 mms. thick, placed just in front of the very thin face of the electroscope. The results given show that when the cathode rays are in each case removed, the orders are *not* those of atomic weights. Very thick radiators are needed to get the full value of the γ rays from the lighter substances.

Lead is a poor secondary radiator in both cases, but iron radiates well with the γ rays and badly with the X rays. It is unnecessary to examine these results more closely, because the secondary X rays have been carefully investigated by Barkla and others, while the secondary γ rays will be discussed in this paper.

As regards the secondary cathode rays from X rays, β rays, and γ rays, it has been shown by J. J. Thomson, McClelland, and Kleeman, respectively, that the radiation intensities follow the order of the atomic weights.

It will be seen later that the secondary γ rays from a thick block of iron may amount to 25 or 30 per cent. of the total secondary cathode and γ rays from the same block. Moreover, the velocity of the secondary cathode rays due to γ rays is nearly equal to that of the secondary cathode rays due to β rays. The values of the so-called coefficients of absorption by a screen of aluminium 0·4 mm. thick, placed before the electroscope, I find to be as follows :—

Primary β	21·5
Cathode secondary from lead, due to β and γ rays,	24·5
Cathode ,, ,, ,, γ rays only,	31·0

Hence, the velocities of the cathode secondary rays are a little less for γ than for β rays, and both these groups have less velocity than that of the β primary rays.

On the other hand, the coefficient of absorption by lead of the secondary γ rays due to γ primary, reflected from lead or iron, is about 4, nearly equal to the coefficient of absorption found by Godlewski for the primary γ rays of actinium, greater than the coefficient of absorption of the γ rays from uranium, and yet greater than that of radium (Phil. Mag. April 1906). It may, therefore, be concluded that γ rays give rise to secondary rays of the γ type, and not merely to very penetrating cathode rays. This will be seen more clearly from the diagrams given later.

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* After completing the work I learn that this was made of nickel-steel, 5 per cent. nickel.

The fact that the cathode secondary rays due to β or to γ rays have velocities comparable with that of the primary β rays is a very important one. The secondary cathode rays due to X rays have much less velocity. Bragg has pointed out that it is probably more than a coincidence that the secondary cathode rays due to X rays have velocities of the same order as those of the cathode rays in the X-ray tube, whilst the secondary cathode rays due to γ rays approximate in velocity to that of the primary β rays. These relations, if more than accidental, do not necessarily furnish an argument in favour of the view recently advocated with so much skill by Professor Bragg as to the material character of X and γ rays. For it may be that æther pulses striking a solid body cause the ejection of some of those corpuscles only which have velocities in their orbit or free path approximating to those of the corpuscles which first gave rise to the æther pulses.

One fundamental difficulty arises in writing on secondary radiation. The investigations of H. W. Schmidt*, and of Crowther †, indicate that secondary cathode radiation consists mainly, or entirely, of scattered primary rays; for he has proved that β particles, in passing through matter, lose little or no velocity and are diffusely scattered. On the other hand Kleeman, in treating of secondary rays due to primary γ rays, writes of "electrons ejected by γ rays." Now the electrons which constitute the secondary cathode radiation, due to β and to γ rays respectively, have nearly equal velocities; and it seems unreasonable to suppose that in the one case we have scattered primary rays, and in the other case electrons ejected from the atoms of the secondary radiator. It must be admitted that Bragg's theory of the close similarity of β and γ rays—the difference being merely the important one of charge—removes all these difficulties as far as secondary radiation is concerned. Nor does his theory seem more complicated than the conception of an æther pulse with discrete centres of energy on the surface of the spherical shell of the æther pulse. But apparently other difficulties arise. Again, H. Starke in *Le Radium* for February 1908, finds that β rays striking a solid do not give rise to secondary γ rays; and my observations tend in that direction also, for the secondary γ rays appear to be caused solely by the primary γ rays. Nevertheless, it is remarkable that the impact of cathode rays should give rise to X rays, and that the impact of β rays should not give rise to γ rays. However, we have no knowledge of the effect of concentration of the

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* *Phys. Zeit.* June 1907.

† *Le Radium*, March 1908.

impact of β rays. As matters stand at present, the most notable difference between X and γ rays is that the former arise where the cathode rays are stopped or absorbed, and the latter where the β rays originate.

The following experiments show clearly that primary γ rays give rise to secondary γ rays, that the intensity depends upon the material surrounding the radium employed, upon the nature of the secondary radiator and upon the thickness and material of the screens placed in front of the electroscope, and that the intensity of the secondary γ radiation does not follow the order of the atomic weight, or of the density, of the secondary radiator. In all these particulars there is a similarity between secondary X and secondary γ rays, and this accounts to some extent for the apparent differences noted at the beginning of this paper.

In a previous paper (Phil. Mag. June 1908) I have noted that books, carbon, cement, or bricks give rise to more penetrating rays than lead, when these substances are exposed to the β and γ rays of radium, provided the electroscope is screened from the secondary radiator by a sufficient thickness of aluminium, or by a thick book. It was shown, too, that some of these secondary rays came from a depth of at least 4 cms. in the case of carbon, 6 cms. for wood, 3·5 cms. for slate. Moreover, the primary γ rays had first to penetrate those thicknesses. It is these very penetrating rays that are under consideration. The secondary radiators and screens were all tested, when the radium was not present, and they were found free from any radioactive effects under the conditions of the experiments.

Fourteen milligrams of pure radium bromide were placed in a test-tube within cylinders of (1) lead, 1 cm. thick, or (2) nickel-steel, 2·2 cms. thick. The radiators were 5 cms. or more thick, and measured $22{\cdot}5 \times 22{\cdot}5$ centimetres. The necessarily large size and thickness of the radiators made it difficult to procure suitable substances for the experiments, and I have worked mainly with lead, iron, brick, and slate. The screens placed in front of the electroscope were either of (1) aluminium or (2) lead. The electroscope, $10 \times 10 \times 16$ cms., was made of zinc and mounted on a platform. One face of the electroscope was removed and replaced by two very thin aluminium sheets, each ·00031 cm. thick. The electroscope and screens were guarded from the radium and the cylinder containing it by blocks of lead 10 cms. thick. The effect with no radiator present, except air, was deduced from the effect with the stated radiator present; this was done for all the screens used. The secondary rays from air are easily absorbed, so that the results given are quite reliable for secondary rays of the γ type.

The electroscope here, as in most cases, is affected not merely by the secondary γ rays which traverse it, but also by all the secondary rays caused by them from the sides of the electroscope and from the inner side of the screens. There seems no way of evading this complexity; and if all the conditions are identical, except the radiating plates employed, the results obtained do indicate the nature and magnitude of the secondary rays of the γ type passing from the radiator and entering the electroscope.

The measurements obtained are given in the following four tables and the corresponding four diagrams. The radium bromide was in the same position, as nearly as possible, for all four series. The rays under investigation are all "incident," not "emergent."

TABLE IV. (See fig. 1.)

Radium in *lead* 1 cm. thick.
Aluminium screens. Secondary radiators stated.

Thickness of screens in mms.	Lead, 5 cms.	Iron, 5 cms.	Brick, 6 cms.
0	12·2	8·4	5·9
0·41	4·26	3·81	2·25
0·82	1·74	2·56	1·77
1·75	·57	1·92	1·45
3·40	·22	1·78	1·43
7·10	·16	1·64	1·22

Fig. 1.

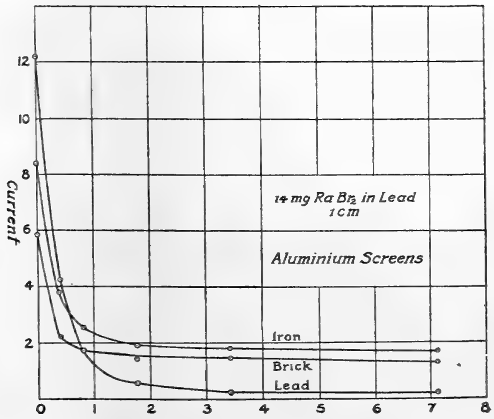


TABLE V. (See fig. 2.)

Radium in *steel* 2·2 cms. thick.
Aluminium screens.

Thickness of screens in mms.	Lead, 5 cms.	Iron, 5 cms.	Brick, 6 cms.
0	17·8	10·4	8·00
0·41	4·4	4·70	4·09
0·82	2·21	3·56	3·91
1·75	1·02	3·41	3·80
3·40	·59	3·28	3·35
7·10	·56	3·04	3·08

Fig. 2.

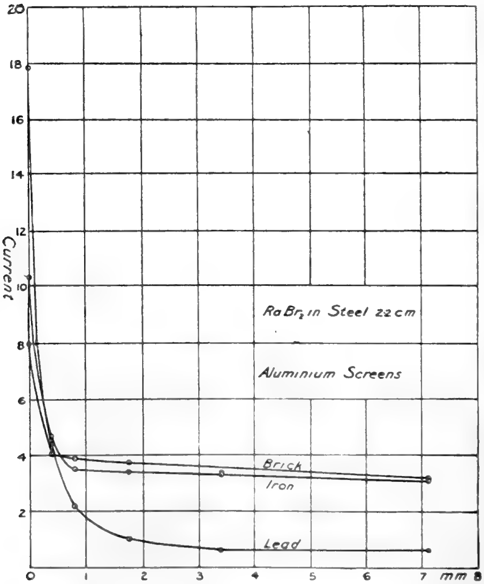


TABLE VI. (See fig. 3.)

Radium in *lead*.
Lead screens.

Thickness of screens in mms.	Lead, 5 cms.	Iron, 5 cms.	Brick, 6 cms.
0	12·7	8·4	5·6
0·15	1·76	3·63	2·61
0·75	·69	2·25	1·45
2·00	·31	1·08	·78
4·00	·19	·53	·38

Fig. 3.

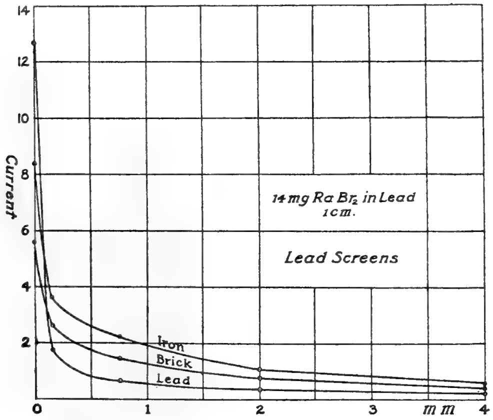
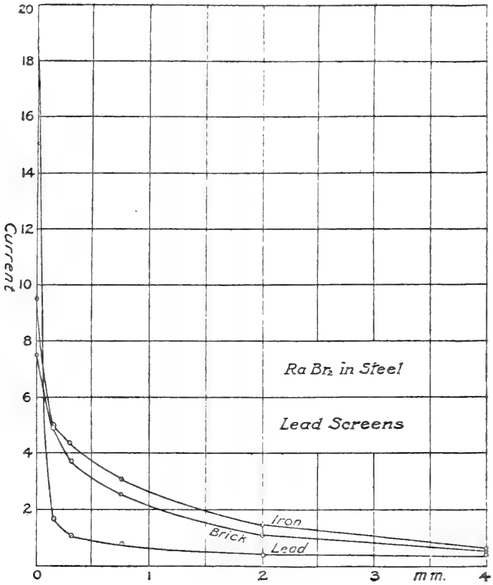


TABLE VII. (See fig. 4.)

Radium in *steel* 2·2 cms. thickness.
Lead screens.

Thickness of screens in mms.	Lead, 5 cms.	Iron, 5 cms.	Brick, 6 cms.
0	19·2	9·5	7·5
0·15	1·7	5·0	4·9
0·30	1·1	4·4	3·7
0·75	·80	3·1	2·52
2·00	·34	1·42	1·06
4·00	·30	·57	·43

Fig. 4.



From these results and diagrams the following deductions may be made :—

1. It is noteworthy that the radium in 2·2 cms. of nickel-steel gives an effect about 1·5 times as great as when the radium is in 1 cm. of lead. From the relative densities we should expect 2·2 cms. of steel to be equivalent to 1·5 cms. of lead and, therefore, the radium in the steel cylinder should give, by the density law, two-thirds the effect of the radium in the lead. It actually gives one-and-a-half times as much. This remarkable result was confirmed by direct reading of the primary γ rays using different electroscopes. Thus the primary γ rays traverse steel much more readily than lead, but the rays passing through iron are subsequently absorbed more readily by lead than if the radium were in lead. The values for λ, the coefficient of absorption by lead, between 2 and 4 cms. were as follows :—

$$\left.\begin{array}{ll}\text{Radium in lead (1 cm.)} & \lambda = \cdot 47 \\ \text{,, \quad steel (2·2 cms.)} & \lambda = 1\cdot 1 \\ \text{,, \quad ,, \quad (4 cms.)} & \lambda = \cdot 75\end{array}\right\}\begin{array}{c}\text{primary} \\ \gamma\text{ rays.}\end{array}$$

2. The secondary rays of the γ type from lead are feeble compared with those from iron or brick. This is true whether

the radium is in iron or lead, and whether the absorbing screens are of aluminium or lead.

3. It will be seen that 1 or 2 mm. of lead or aluminium absorb the cathode rays from the lead, iron, or brick radiators acted upon by γ rays.

4. With radium in steel, and with aluminium screens, brick gave more secondary rays than iron. In the other three cases brick gave less than iron. However, 5 cms. of iron give almost maximum secondary rays, whilst 6 cms. of brick do not give full value. Slate gives secondary cathode and γ rays, both somewhat less intense than brick.

5. When the radium was in a glass test-tube, without steel or lead around it, the β and γ rays gave from a secondary radiator of lead a current measuring 250 scale-divisions a minute in the electroscope, the γ rays gave 7·5 per cent. of that amount. The latter could be divided into two parts, cathode and γ in type. The γ type was the following percentages of the total (cathode and γ): for lead radiators 6·2, for iron 25, for brick 28.

6. The values of the coefficients of absorption by a sheet of aluminium, 0·41 mm. thick, are as follows:—

Primary γ rays	21
Secondary cathode due to β and γ rays striking—	
(*a*) Lead	24
(*b*) Iron	35
Secondary cathode due to γ rays striking—	
(*a*) Lead	31
(*b*) Iron	34

Thus the β rays cause secondary cathode rays slower than the primary rays which cause them, and the γ rays cause secondary cathode rays yet slower. But all these rays have velocities of the same general order, and greater than the secondary cathode rays due to the X rays. This has already been proved by Dorn, Allen, Kleeman, and others.

7. The values of the coefficients of absorption of the secondary γ rays due to primary γ rays were also determined for lead screens, changing the thickness from 2 to 4 mms.

		λ.
(*a*) Radium in lead (1 cm.)...	Lead radiator	2·46
	Iron ,,	3·70
	Brick ,,	3·68
(*b*) Radium in steel (2·2 cms.)	Lead ,,	4·35
	Iron ,,	4·65
	Brick ,,	4·60

These may be compared with the coefficients of absorption of the primary γ rays passing through lead*: —

	λ.
Radium	·57–·45
Uranium	1·4
Actinium	4·7–2·7

Hence the secondary γ rays, due to the primary γ rays, using lead, iron, or brick as secondary radiators, are absorbed to a degree approximating to that of the primary γ rays of actinium. It would be interesting to examine the secondary γ rays due to the primary γ rays of actinium. These would probably be absorbed even more readily, and would approximate more closely to the X rays. The effect would be difficult to obtain except with a considerable quantity of actinium.

The reasons for considering the penetrating secondary rays to be of the γ type, and not of the cathode, are as follows:—

1. There is a well-marked bend in the absorption curves shown in the diagrams. This change of character is also well marked when the logarithms of the ordinates are plotted.

2. The primary rays penetrate several centimetres into substances such as brick or slate; some of the secondary rays emerge from that depth, and will then penetrate several millimetres of lead.

3. The values of the coefficients of absorption by lead of these penetrating rays equal about 4, or nearly the value of the coefficient of absorption by lead of the primary γ rays of actinium.

4. If the secondary radiator, such as brick, be placed in a strong magnetic field, the ionization current in the electroscope, due to the penetrating secondary radiation from the brick, caused by γ rays, is unaffected by the absence or presence or direction of the magnetic field.

The laws which govern the magnitude of the secondary γ radiation are not yet clear.

If possible, further experiments will be made using different screens, radiators, and cylinders inclosing the radium.

McGill University, Montreal.
April 1908.

Phil. Mag. Feb. 1907. *For* "Omaha Sea-Salt," *read* "Inagua Sea-Salt, imported by Evans and Saunders, Toronto."

Phil. Mag. Sept. 1906. p. 109. *For* "9×10^9 per c.c. per second," *read* "9×10^{14} per second."

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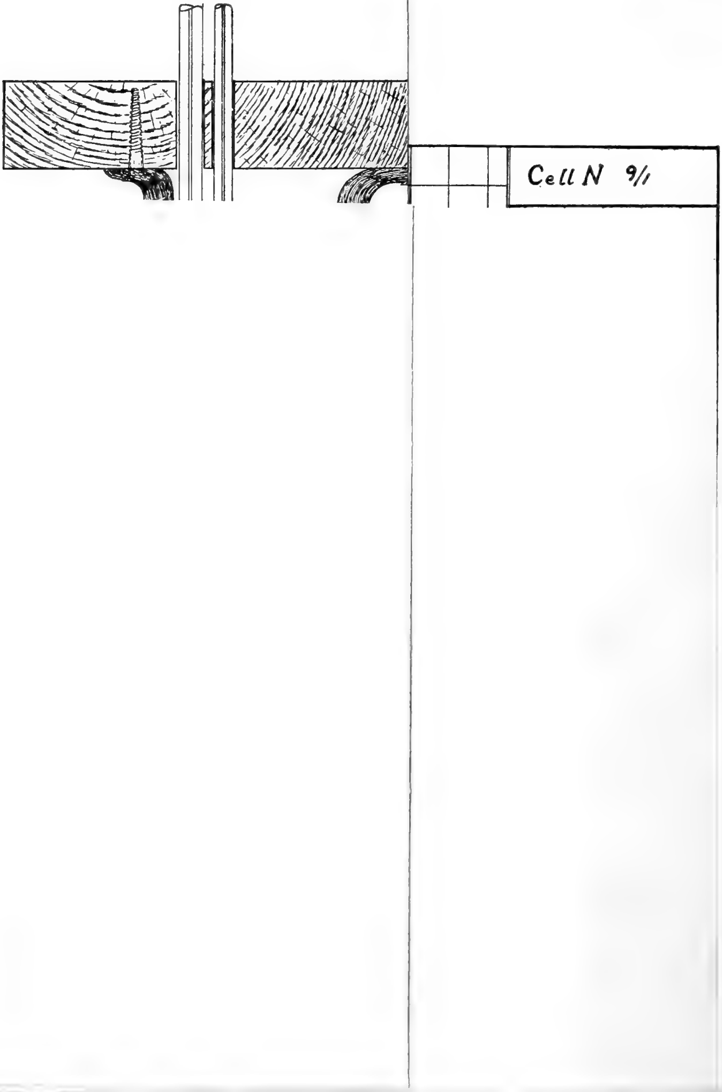
* Phil. Mag. April 1906.

FIG. 1.



XVIII. *Acoustical Notes.*—VIII.

Partial Tones of Stretched Strings of Variable Density—Maintenance of Vibrations by Impact of Water Drops—Discrimination between Sounds from directly in front and directly behind the Observer—The Acousticon—Pitch of Sibilants—Telephones.

By Lord Rayleigh, *O.M., Pres.R.S.*[*]

Partial Tones of Stretched Strings of Variable Density.

If ρ_0 be the longitudinal density of a string of length l stretched with tension T_1, the periodic time (τ_r) of the rth component vibration is given by

$$\tau_r^2 = \frac{4l^2\rho_0}{r^2 T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (0)$$

In 'Theory of Sound,' 2nd ed. § 140, an approximate theory is given applicable when the density, in place of being strictly uniform, has the value $\rho_0 + \delta\rho$ where $\delta\rho$ is relatively small. We have

$$\tau_r^2 = \frac{4l^2\rho_0}{r^2 T_1}\left\{1 + \frac{2}{l}\int_0^l \frac{\delta\rho}{\rho_0}\sin^2\frac{r\pi x}{l}\,dx\right\} \quad . \quad . \quad . \quad (1)\dagger$$

"If the irregularity take the form of a small load of mass m at the point $x=b$, the formula may be written

$$\tau_r^2 = \frac{4l^2\rho_0}{r^2 T_1}\left\{1 + \frac{2m}{l\rho_0}\sin^2\frac{r\pi b}{l}\right\}. \quad . \quad . \quad . \quad (2)$$

These values of τ_r are correct so far as the first power of the small quantities $\delta\rho$ and m, and give the means of calculating a correction for such slight departures from uniformity as must always occur in practice.

As might be expected, the effect of a small load vanishes at nodes, and rises to a maximum at the points midway between consecutive nodes. When it is desired merely to make a rough estimate of the effective density of a nearly uniform string, the formula indicates that attention is to be

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[*] Communicated by the Author.

[†] The r^2 in the denominator was inadvertently omitted. It may be worthy of note that the method is not limited to the case of density originally uniform. In general, if Y be the normal function corresponding to a variable density ρ, τ_r^2 is altered in the ratio

$$1 + \frac{\int \delta\rho\, Y^2\, dx}{\int \rho\, Y^2\, dx}.$$

FIG. 1.

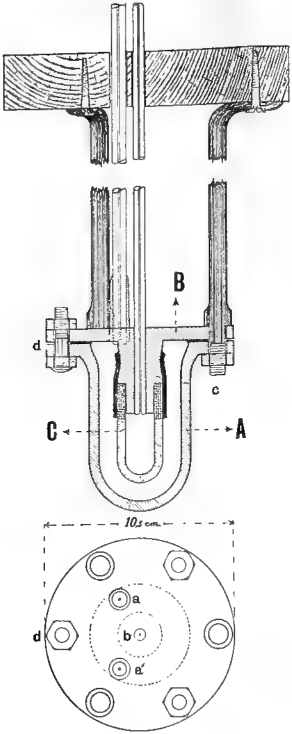


FIG. 2.

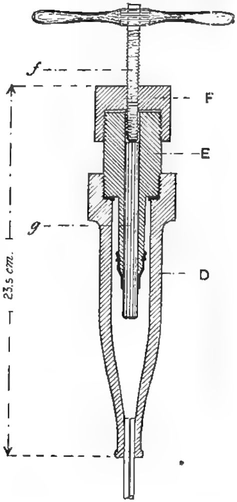


FIG. 6.

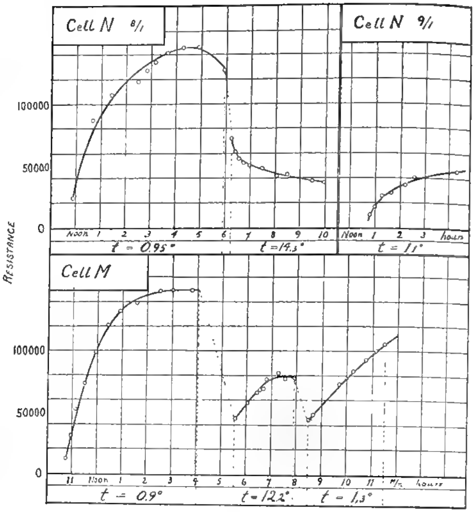


FIG. 3.

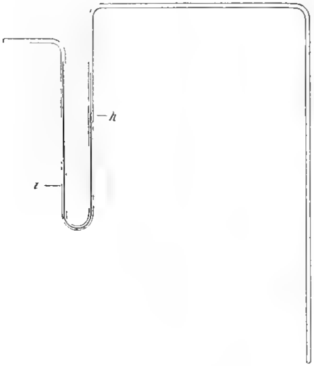


FIG. 4.

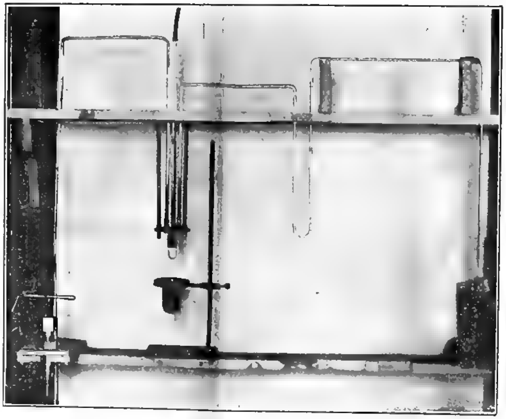
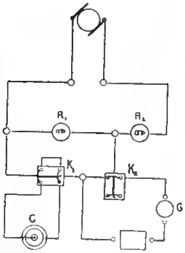


FIG. 5.



given to the neighbourhood of loops rather than to that of nodes.

The effect of a small variation of density upon the period is the same whether it occur at a distance x from one end of the string, or at an equal distance from the other end. The *mean* variation at points equidistant from the centre is all that we need regard, and thus no generality will be lost if we suppose that the density remains symmetrically distributed with respect to the centre. Thus we may write

$$\tau_r^2 = \frac{4l^2\rho_0}{r^2 T_1}(1+\alpha_r), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\alpha_r = \frac{2}{l}\int_0^{\frac{1}{2}l} \frac{\delta\rho}{\rho_0}\left(1-\cos\frac{2\pi r x}{l}\right)dx. \quad . \quad . \quad . \quad (4)$$

In this equation $\delta\rho$ may be expanded from 0 to $\frac{1}{2}l$ in the series

$$\frac{\delta\rho}{\rho_0} = A_0 + A_1\cos\frac{2\pi x}{l} + \ldots + A_r\cos\frac{2\pi r x}{l} + \ldots, \quad (5)$$

where

$$A_0 = \frac{2}{l}\int_0^{\frac{1}{2}l}\frac{\delta\rho}{\rho_0}dx, \qquad A_r = \frac{4}{l}\int_0^{\frac{1}{2}l}\frac{\delta\rho}{\rho_0}\cos\frac{2\pi r x}{l}dx. \quad . \quad (6, 7)$$

Accordingly,

$$\alpha_r = A_0 - \tfrac{1}{2}A_r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This equation, as it stands, gives the changes in period in terms of the changes of density supposed to be known. And it shows conversely that a variation of density may always be found which will give prescribed arbitrary displacements to all the periods. This is a point of some interest.

In order to secure a reasonable continuity in the density, it is necessary to suppose that $\alpha_1, \alpha_2, \ldots$ are so prescribed that α_r assumes ultimately a constant value when r is increased indefinitely. If this condition be satisfied, we may take $A_0 = \alpha_\infty$, and then A_r tends to zero as r increases.

As a simple example, suppose that it be required so to vary the density of a string that, while the pitch of the fundamental tone is displaced, all other tones shall remain unaltered. The conditions give

$$\alpha_2 = \alpha_3 = \alpha_4 = \ldots \alpha_\infty = 0.$$

Accordingly,

$$A_0 = A_2 = A_3 = \ldots = 0, \qquad A_1 = -2\alpha.$$

Thus by (5)

$$\delta\rho/\rho_0 = -2\alpha_1\cos(2\pi x/l). \quad . \quad . \quad . \quad . \quad . \quad (9)”$$

I have recently made a few observations on the vibrations of loaded wires in illustration of these formulæ. A simple case is afforded by (2). A lump of wax is attached at the centre of a stretched wire, so that $\sin^2(r\pi b/l)=0$ when r is even, and when r is odd takes the value unity, independently of the particular value of r. It is easily verified on trial that the partial tones of even order are undisturbed, and that those of odd order, though displaced, still constitute a *harmonic series*. The observation is best made with the aid of resonators by comparison with the partial tones of a note on the harmonium. The load may conveniently be chosen so as to depress the pitch by one or more complete semitones. If also the tension (due to a weight) be suitably adjusted, both series of partial tones may be brought into tune with the harmonium, either exactly, or (what is better in practice) approximately.

A more elaborate experiment was next attempted in illustration of the result expressed in (9). But some modification is necessary, inasmuch as in practice we are limited to *positive* loads. But a uniform loading has little significance from our present point of view, lowering all the partial tones by the same musical interval and being capable of compensation by varying the tension (T_1). It suffices therefore to take $\delta\rho/\rho_0$ proportional to $1-\cos(2\pi x/l)$; and the experiment consists in verifying that the first partial is depressed relatively to all the other tones, and that these latter retain their harmonic relations.

The length of the wire was adjusted to 720 mm., and loads proportional to $1-\cos(2\pi x/l)$ were attached at intervals of 30 mm., beginning at $x=0$ and corresponding to angles 0°, 15°, 30°, &c. The unit load (about $\frac{1}{4}$ gm. of wax) was at the points distant from the ends by one quarter of the length (90°, 270°), and the maximum load (2) was at the centre (180°). At the ends (0°, 360°) the loads were zero. By varying the tension the whole was tuned conveniently to suit the harmonium.

The results agreed fairly well with theoretical anticipations. The second and third partials retained very accurately their harmonic relation (fifth). The fourth and fifth partials were too sharp relatively to the second and third by nearly half a semitone. The depression of the first partial relatively to the second and third was 3 semitones or a minor third.

These estimations of pitch were made separately by Mr. Enock and myself, and in the case of the higher partials demanded some care. Useful indications are afforded by but partially depressing the key of the harmonium note, whereby the pitch is lowered relatively to the normal. On the other hand it appeared, rather to my surprise, that a lowering of the bellows pressure (sometimes convenient in order to diminish the intensity of sound) slightly *raises* the pitch.

When the loads of wax were all removed, the first partial tone rose nearly an octave, indicating that the loading had been very severe.

In a second experiment the loads were reduced to less than half, the unit being taken equal to 0·1 gm., the distribution of the loads and the length of the wire being as before. Comparisons, either directly with the harmonium or with forks as intermediaries, gave the following results. The second partial of the wire was 5 beats per second flat on (the octave overtone of) harmonium B. The third partial was 4 beats per second flat on the corresponding partial of B. The fourth partial was 2 beats flat on B, and the fifth partial was 2 beats sharp on B. If we regard the two last partials as in tune with B, the second partial is out by 5 vibrations in about 256, or one in 55, viz. between a third and a quarter of a semitone. The first partial of the loaded wire was almost exactly two semitones below harmonium B.

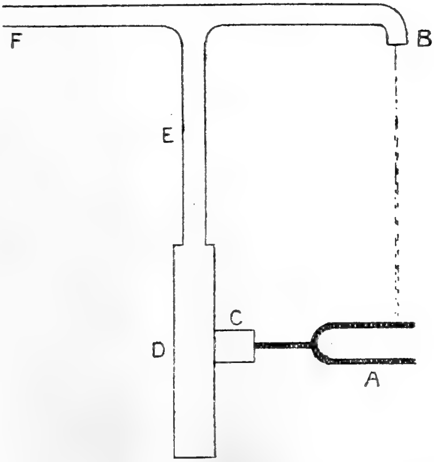
I had supposed that the small deviations from harmonic relations exhibited by the second and higher partials might be due to the discontinuity of the loading or to the fact that the loads were not sufficiently concentrated upon the line of the wire. But subsequent observations upon an unloaded wire showed very similar deviations. The length was the same but the tension was diminished so as to bring the pitch back to B. The first partial of the wire was now one per second flat, the second $1\frac{1}{2}$ per second flat, the third 2 per second flat, the fourth 1 per second *sharp*, the fifth $3\frac{1}{2}$ per second sharp, and the sixth about 8 per second sharp, all referred to the corresponding partials of harmonium B. Since the partials of the harmonium note are necessarily in tune, harmonic relations among the partials of the wire would require beats always upon the same side and numerically as the natural numbers 1, 2, 3, 4, 5, 6. It may be noted that the wooden bridges, by which the vibrating portion of the wire was limited, were provided above and below with sharp edges, and were free to turn. In this way the vibrating portion was well defined, and the tension (due to weights hung over a pulley) was freely transmitted.

Maintenance of Vibrations by Impact of Water Drops.

It is known that jets of liquid tend to resolve themselves under capillary force into more or less uniform processions of drops, the distance between the drops, or the number of drops passing a given point in unit time, depending upon the diameter and velocity of the jet. When a jet, otherwise undisturbed, is under the influence of a regular vibrator of suitable pitch, the resolution becomes absolutely uniform and takes its frequency from the vibrator[*]. If the procession of drops thus regularized is caused to strike a second vibrator of like pitch, the latter will usually be excited. The arrangement is simplified and any question of insufficient agreement of pitch is eliminated, if both parts be assigned to the *same* vibrator which at once regularises the resolution of the jet and is itself maintained in vibration by the impact of the drops.

The experiment has been tried with tuning-forks of pitch 256 and 320. The reaction between the fork A and the jet issuing at B (fig. 1) is effected through a branch tube E terminating in a metal box D. The box is provided with a wooden socket cemented on a flexible face, to which the fork is screwed. The vibrations of the fork, transmitted through its stalk, cause the flow at B to be slightly variable, and if the adjustments are suitable determine a stream of drops of the same frequency. The orifice at B, perforated in a thin metal plate, is of about 2 mm. diameter. The tubes are of lead, allowing slight adjustments by bending; the supply

Fig. 1.



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[*] The theory of these effects, on lines roughly sketched by Savart and Plateau, is given in Proc. Roy. Soc. xxix. p. 71, 1879; Scientific Papers, i. p. 377; or 'Theory of Sound,' 2nd edition, ii. p. 362.

of water may be either directly from a tap or preferably from an aspirator bottle. The head of water, about 30 cm., must be adjusted; and it is to be remarked that the question is not merely one of accommodating the natural pitch of the jet to that of the fork. There is also the phase to be considered, for the impact of the drops may check, as easily as encourage, an existing vibration. A slight alteration in the distance between A and B may here be useful. In practice attention should be given to the place of resolution of the jet, easily discerned in a suitable light. When this is brought up as near to the orifice as possible, it will be known that the vibration is vigorous and that the phase relation is suitable.

The experiment was quite successful. Both the forks referred to spoke well and steadily when suitable resonators were held near their prongs. But the arrangement is hardly to be recommended for general purposes. The use of water is messy, and unless care be taken is likely to end in rusting the forks. Moreover, the vibrations are not especially vigorous—in comparison, for example, with those which may be obtained electromagnetically. Another objection is to be found in the circumstance that drops of water remaining attached to the fork must render the precise pitch uncertain.

Discrimination between Sounds from directly in front and directly behind the Observer.

As already[*] mentioned, I am now unable to make the discrimination myself, even in the case of the voice used naturally; so that all that I can report relates to the observations of others. It would seem, however, that even youthful listeners are not always able to pronounce with certainty. In experiments made with some young people in a long corridor, they were able to discriminate among themselves whether a voice came from in front or behind, but when I spoke they made mistakes. The speaker facing towards the listener gave, for example, the numerals one—two—three &c.; and there were enough assistants moving backwards and forwards to eliminate information which might otherwise be given by footsteps. Why my voice afforded less foundation for a judgment was not clear—possibly in consequence of its graver pitch, or because its quality was less familiar. The corridor was so long that the observations were not appreciably disturbed by echos.

As mentioned before, Mr. Enock is able in many cases to

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[*] Phil. Mag. vol. xiii. p. 231 (1907).

discriminate front and back when the voice is used naturally. But I find that both indoors and outside he could be deceived. Thus when standing on the lawn only a short distance in front of him, but facing *from* him, I gave the numerals, he judged that I was behind him, and this erroneous judgment was not disturbed even when I conversed freely with him. It would appear that there is not much to go upon, and that when an erroneous impression has once been made it is not easily disturbed by the slight indications available. Probably the turning away of the speaker softens the sibilants and other high elements in the sound, somewhat in the same way as is done by the external ears of the listener when he faces away from the sound. It must be understood that in these experiments the ears were used in a natural manner, without the aid or hindrance of special reflectors.

The repetition and extension of these observations would be of interest ; it would be best carried out under the supervision of a physicist young enough to be able himself to form judgments as to the front or back situation of the easier sounds, *e.g.* of the voice. The precautions necessary are indicated in former papers.

The Acousticon.

This instrument, intended to aid the hearing of the partially deaf, is composed of a simple battery, microphone, and telephone circuit. There is nothing special about the battery (one or two dry cells) or the telephone. But the microphone is unusually efficient. The disk which receives the sound is of carbon, about $\frac{1}{2}$ mm. thick, and is clamped at the circumference. Bearing against it are six groups of small ($\frac{1}{2}$ mm.)

Fig. 2.

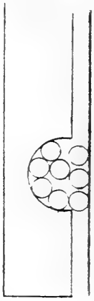
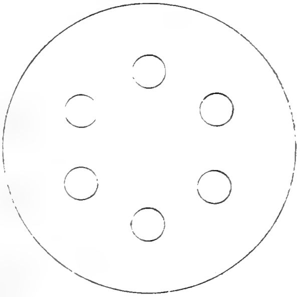


Fig. 3.



carbon spheres, having the appearance of shot, held in hemispherical cups cut out in a thick plate of carbon (figs. 2, 3). In use the microphone may be worn like a medal upon the breast, or it may stand upon the table, *e. g.* at dinner. In a large model there are two microphones, as described, connected in parallel. The instruments upon which I experimented were kindly lent me by a friend who had found them efficient, though fatiguing to the ear.

For my purpose the microphone and telephone were placed in separate rooms, so that nothing could be heard except through the instrument. The reproduction of speech, given at about one foot away from the microphone, was better than anything I had ever heard before. The first impression was that all the consonantal sounds were completely rendered, but this turned out to be an illusion. In listening to the numerals, given in order, the observer would feel confident that he heard the *f* in *five* and the *s* in *six*. But if the initial sound was prolonged—*f f five*, *s s six*, the observer could not tell until he heard the sequel which it was going to be. Further, if the sounds were given as *s s ive*, *f f ix*, they were heard normally as five and six. It was plain that there was no difference in the rendering of *f* and *s*. I am informed that this is a well-known difficulty in ordinary telephoning, and that in spelling a name containing *f* or *s* it is usual to say "*f* for Friday" or "*s* for Saturday." But the articulation of the acousticon is so superior that it was surprising to find the failure complete. The characterisation of *sh* was not much better, though after a little practice I could distinguish it from *s* or *f*, but probably only by a greater loudness.

These failures might have been ascribed to my rather defective hearing, but other observers with normal hearing did no better. When, however, the iron plate of the telephone was replaced by one three times as thick, a difference between *f* and *s* could be detected, though both were rather weak. The above observations were made with the small model and usually with but one battery cell. In the case of the large model microphone and with two cells in action, it was just possible to hear some difference between *f* and *s*, the usual iron plate of the telephone being employed.

The question arises as to *how* the acousticon aids defective hearing. A failure to distinguish *f* and *s* seems a bad beginning. I could not find that the general loudness of speech was increased by the instrument. When the speaker stood some 20 feet away from the microphone, I could hear better directly from the situation of the microphone than when in the further room I listened through the instrument. Possibly a clue may be found in the behaviour of the acousticon in presence of low notes. These are very feebly transmitted. Pure tones from forks making 128, 256, 384 vibrations per second, held in front of Helmholtz resonators and close to the microphone, were poorly heard, and of the sound received the greater part seemed to be overtones. Of course low notes are not necessary for speech, otherwise women would be at a disadvantage, contrary to all tradition. But can we suppose that low notes are actually deleterious?

At this point one recalls the observations of A. M. Mayer [*] upon the obliteration of higher sounds by graver ones. These observations have not attracted the attention they deserve. The author himself sufficiently emphasises their importance but he does not appear to have followed them up, as he announced the intention of doing. It was proved that while higher and feebler sounds could be entirely obliterated by louder and graver ones, on the other hand a feeble graver sound remained audible in the presence of a more powerful acuter one. "Indeed in this case as in all others where one sound remains unaffected by intense higher notes, the observer feels as though he had a special sense for the perception of a graver sound—an organ entirely distinct from that which receives the impress of the higher tones.

"That one sonorous sensation cannot interfere with another which is lower in pitch is a remarkable physiological discovery . . . ."

If we suppose, as I think we may, that one type at any rate of deafness involves obtuseness to the higher elements of sound upon which the intelligibility of speech largely depends, while the hearing of graver sounds is unimpaired, Mayer's principle suggests that advantage may ensue from an instrumental suppression of the graver components. A scientific friend has informed me that a relative of his was insensitive to grave sounds and that when addressed in a railway carriage expostulated against being shouted to, as if his hearing was less interfered with by the noises of the train than that of normal persons. There is said indeed to be one type of deafness which finds advantage in such noises, but perhaps only because people speak louder. It would be interesting to experiment upon such a case in detail. For my own part I can hear scarcely anything of what is said to me in the train.

Another indication of the importance of the higher elements in speech is afforded by the advantage experienced by many deaf people from placing the hands behind the ears, palms forward and curved. The tick of a clock, for example, is much enhanced. Perhaps the most striking effect is upon the sound of the wind whistling through trees. Artificial reflectors may of course replace the hands, but for the best results they need to be rather nicely shaped.

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[*] Phil. Mag. ii. p. 500 (1876).

Pitch of Sibilants.

In connexion with the audibility of sibilants it is desirable to have some idea of their character in respect of pitch. Doubtless this may vary over a considerable range. In my experiments the method was that of nodes and loops [*], executed with a sensitive flame and sliding reflector. A hiss given by Mr. Enock, which to me seemed very high and not over audible, gave a wave-length (λ) equal to 25 mm. with good agreement on repetition. A hiss which I gave was graver and less definite, corresponding to $\lambda = 32$ mm. The frequency of vibration would be of the order 10,000 per second, more than 5 octaves above middle *c* [†].

Telephones.

Some miscellaneous observations upon telephones may here be recorded. From the fact that an improved articulation of the sibilants and some other consonants accompanies a thickening of the telephone plate, although at considerable cost in other respects, it was thought that a similar advantage might be attained by the introduction of a condenser into the electrical circuit. This entails no further complication if the transmitter, as well as the receiver, be a Bell instrument; but if a microphone be employed as transmitter, a small transformer must also be introduced, whose ratio of transformation may, if desired, be 1 : 1. The line, receiver, and condenser then constitute electrically a secondary circuit, and by choice of a suitable capacity the proper tone of this circuit may be tuned to any desired pitch. The earliest consideration of resonance in an electrical circuit in response to a periodic force was probably by Maxwell [‡] in connexion with Grove's "Experiment in Magneto-Electric Induction." If L, R be respectively the self-induction and resistance of a circuit, C the capacity of the interposed condenser, the current (dx/dt), elicited by the imposed electromotive force $\mathrm{E}e^{int}$, is given by

$$\left(-\mathrm{L}n^2 + i\,\mathrm{R}n + \frac{1}{\mathrm{C}}\right)x = \mathrm{E}\ ;$$

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[*] Phil. Mag. vii. p. 149 (1879); Scientific Papers, i. p. 406.

[†] Compare Wiersch, *Drude Ann.* xvii. p. 1001 (1905). "Sieht man von ihren tiefsten Partialtönen ab, welche lediglich infolge Resonanz der Mundhöhle beigemischt sind, so entstehen die eigentlichen Reibelaute durch eine Schwingungszahl, welche minimal derjenigen des Grundtones der Luftsäule einer einseitig gedeckten Pfeife von ca. 14 mm. Länge entspricht, maximal aber im Bereiche der Unhörbarkeit liegt." This paper contains some interesting observations upon the influence of the *proper tone* of a telephone plate upon the articulation.

[‡] Phil. Mag. May 1868; Maxwell's Scientific Papers, ii. p. 121.

so that the maximum effect occurs when

$$CLn^2 = 1,$$

i. e., when the natural frequency of the circuit coincides with that of the imposed force. *For this pitch* the self-induction is compensated. The effect of short-circuiting the condenser may be represented by taking $C = \infty$. If, apart from phase, the current is unaltered by short-circuiting the condenser, the capacity in action must be equal to one-half of the most favourable capacity, or else must be so great as not to be distinguishable in experiment from infinity. It is to be noted that the accurate compensation of self-induction can be effected for only one pitch, and that in practice the advantage will be limited to a range of pitch not exceeding an octave.

Such experiments as I have been able to make did not exhibit any improvement in articulation as the result of including a condenser in the circuit. It is possible that the simple theory above stated is too much interfered with by complications such as eddy-currents in the iron or hysteresis in the action of the condenser. A distinct resonance could be attained in the region of the higher notes of my harmonium (about 2000 vibrations per second) when an *additional* self-induction was included in the circuit. Such resonance would be practically limited to a region including 3 or 4 semitones, and when at the best pitch the condenser was put out of action by a short-circuiting key there was a very marked falling off of intensity. It is probable that this subject has already received attention from those engaged in the endeavour to improve the telephone as a practical instrument; if not, I think it would be worthy of investigation. There should be no great difficulty in securing several electrical resonances at pitches suitably distributed, in addition to the mechanical resonance of the plate.

If my memory serves me, it was observed in the early days of telephony that the sounds remained audible even though the usual ferrotype plate were replaced by one of other material. The experiment is easily tried. When a telephone provided with a copper or aluminium plate was included in a circuit with a battery (of one or two cells) and a simple carbon microphone (after Hughes), the ticking of a watch placed near the microphone was easily audible, and (it happened) with different quality in the two cases. On the other hand a plate of mica was silent under similar conditions, although when the excitation is very violent, as with a make-and-break arrangement, sounds may be heard without a plate at all. The telephone employed was bipolar and of modern manufacture.

In another experiment the permanent steel magnets were removed from the telephone and replaced by a soft-iron U which could be magnetized at will by an independent electric current, the coils and pole-pieces of the telephone remaining undisturbed. Without a magnetizing current but little of the ticks of the watch could be heard from the copper plate, but when the soft iron was magnetized the sounds became distinct as before.

I had supposed at first that this experiment might discriminate between the two possible explanations of the sound, the one depending upon traces of iron as an impurity in the copper or aluminium, the other invoking the action of induced currents circulating in the metallic plates. But it appears that in either case the efficiency would be promoted by a high constant magnetization of the pole-pieces.

The copper disk, weighing about one gram, was of a kind unlikely to contain appreciable iron and its action was not affected by washing with hydrochloric acid. When a mica disk, which of itself gave no sound, was dusted over with 1 mg. of fine iron filings attached with varnish, only a very faint sound could be made out. A similar mica disk coated with $\frac{3}{4}$ gm. of copper filings from the same material as that of the disk, yielded no sound. A similar telephone with copper disk was included in the circuit for the sake of rapid comparison throughout the experiments.

From these results it appeared unlikely that the effects were to be attributed to traces of iron in the other metals, and this conclusion was confirmed in a varied form of the experiment tried later. Mr. Enock prepared two flat coils of fine covered copper wire weighing together about 2 gms. These were mounted separately on pieces of mica afterwards cemented with wax to the main disk so as to encircle the magnetic poles. When the ends of the flat coils were disconnected, nothing was heard; but on completing the circuit of one or both coils the effects were very distinct, both with the carbon microphone and watch as before used or with another arrangement giving a more powerful action. We may conclude, I think, that the sounds of a copper disk are due to alternating currents induced in it and reacting upon the nearly constant magnetism of the pole-pieces.

Terling Place, Witham,
Jan. 1908.

XIX. *Researches upon Osmosis and Osmotic Pressure.* *By* L. VEGARD, *Cand. real.* (*Research Student at the Cavendish Laboratory, Cambridge*) *.

[Plate VIII.]

Introduction.

1. THE following paper gives some results obtained from a series of investigations upon osmotic properties. Most of the work has been done at the Physical Institute, Christiania; but some experiments carried out at the Cavendish Laboratory are also included.

These researches have been going on for about two years, as the construction of the cells and first pieces of apparatus was done as early as in March 1906. The reason why such a considerable time has been required to obtain the results is due to several circumstances. In the first place the difficulties to be dealt with were greater than anticipated, and secondly, for most of the time I had only a few hours of the day to devote to the work. The greater part of this time has been spent in preparing the cells and working out the method, and most of the experiments have been made during the past autumn and winter.

During the experiments I have had the advantage of gathering experience from the works of Morse and Frazer †, and later from the work by Berkeley and Hartley ‡.

Besides a description of the method used, the paper will deal with the following subjects :—

1. A study of the properties of the membrane by its behaviour for electric currents.
2. General theoretical considerations as to the direct measurements of osmotic pressure.
3. Measurements of the equilibrium pressure for the cane-sugar solutions.
4. Experimental determination of the velocities of osmotic flow corresponding to different pressures. (Velocity-Curves.)
5. The effect of temperature upon the reversion pressure (π_0').

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* Communicated by Prof. J. J. Thomson, F.R.S.

† H. N. Morse and J. C. W. Frazer: "The Preparation of Cells for Measurements of High Osm. Press.," Am. Ch. Journ. July 1902; "The Osm. Press. and Freezing-points of Solutions of Cane Sugar," Am. Ch. Journ. July 1905.

‡ Earl of Berkeley and E. G. J. Hartley: "On the Osm. Press. of some Concentrated Aqueous Solutions," Phil. Trans. of R. S. London, series A, vol. ccvi. pp. 481–507.

§ 1.

2. The constructions of the various pieces of apparatus that have been tried have (all of them) been made upon the principle that the solution, and consequently the pressure, was to be placed outside the cell. This arrangement allows a better tightening of the cell, and at the same time the latter will be more capable of resisting great pressures, as by a proper construction we can always arrange matters so that the cell substance is only subject to compression. The same principle with other arrangements has been used by Berkeley and Hartley.

The construction of the apparatus finally used is shown in Pl. VIII. figs. 1, 2, 3. It consists essentially of three parts:

The osmometer itself (fig. 1), the compressor (fig. 2), and the manometer (fig. 3).

The osmometer again chiefly consists of three parts : the cell C and the two pieces A and B made of cast-steel.

The cup A, which has an inner volume of 118 cm.^{3}, can be fixed to the disk B by means of six set-screws with nuts passing through perforations equally distributed round the circular edge of the cup and the disk. The tap (*c*) that serves for fastening the cell forms a part of the disk B, and is cast in the same piece.

The cell has at the top a cylindrical form, but the bottom is made spherical as to ensure that the cell is only acted upon by stresses tending to compress it. The upper part of the cell is glazed. The fastening of the cell to the osmometer is easily seen from fig. 1. I have used the principle to let the osmotic pressure itself take care of the fastening and tightening. To this end the steel tap as well as the glazed part of the cell are covered with a piece of rubber tubing of a suitable diameter. By this arrangement it is ensured that the pressure will have no tendency to produce any leak between the steel tap and the cell. An increase of pressure, on the contrary, will only cause the cell to be pressed with a great force up to the steel tap, and at the same time the extensible rubber is pressed with the whole pressure up to the walls of the cell and the steel tap.

In order to prevent every possibility of leak at this point the ends of the rubber tubing during the experiments have been tied round with a cotton thread.

By the arrangement here shown one of the corrections required by the method of Berkeley and Hartley has been eliminated, namely, the so-called " guard-ring leak."

The disk B besides the six screws already mentioned has three other cylindric perforations (*a*, *a′*, *b*) for three glass capillaries. One (*b*) (inner diameter 0·49 mm.) is open at both ends and connects the interior of the cell with the air, the other two capillaries go to the compressor and to the manometer. In order to give these two capillaries a better support the two perforations end in two steel tubes.

The glass capillaries are fixed to the tube in the following manner. The tubes used were somewhat conical, and had such dimensions that only a certain length could pass the tube. The place where it stopped was noticed, and in the neighbourhood of it the capillary was heated and covered with sealing-wax. Simultaneously the steel tube was heated and the capillary pulled through from beneath.

In the course of the experiments the disk B, as well as the glass tubes, the compressor, and the manometer could be fixed. Only the steel cup A and the cell had to be taken down for each trial.

For the fastening of the osmometer three steel rods (length 31 cm., diam. 1·0 cm.) were fixed to the disk, the upper ends of which formed horizontal flanges with screw holes, and the other ends serving as set-screws for fixing the cup A.

The glass tubes went for some distance straight upwards, and were thus protected from damage by the three steel rods. Further, by this arrangement the osmometer could be put into a thermostat so as to secure a constant temperature.

The Compressor.

3. By means of the compressor the pressure could be raised to the height desired. The construction of it is shown in fig. 2. The apparatus is chiefly made of brass, only the screw (*f*) and the cylindrical piston (*g*) are made of steel. The piston (diam. 0·95 cm.) passes through a cylindrical perforation of exactly the same diameter as the piston. The piece (E) ends in a conical tap, that goes down into the cup (D). The tightening is brought about in the same manner as in the case of the cell; a piece of rubber tubing put on to the end of the brass tube covers the connexion with the piston. The pieces (E) and (F) are screwed to the cup and tightened by a leather ring. The cup had a perforation at the bottom for the glass capillary that led to the osmometer, and this tube was fixed with sealing-wax in the manner already described.

The Manometer.

4. For measuring the pressure I used the usual way of compressing air in a glass capillary. The length of the manometer was about 135 cm., exterior diam. 7·5 mm., and the average inner diameter 0·472 mm. It was given the form shown in fig. 3 (Pl. VIII.). In this form the manometer could be made long without being inconvenient, and the temperature accurately determined as the column of air in the vertical part of it could be put into a thermostat. With this form the vertical part must have a small diameter; it ought not to surpass 0·6 mm.

The manometer joined on to a U-shaped capillary with an inner diameter 1·01 mm., that was filled with mercury, and thus the mercury level in the U tube had only to move a relatively short distance to fill the whole manometer with mercury.

As the exactitude of the results greatly depends upon the manometer, I shall give a more minute description of its construction.

The capillary itself was graduated, the distance between each mark being 0·5 cm. The marks were cut in wax by means of a cutting-machine marking with an accuracy of about 1/50 of a mm., and the marks etched to the glass. The manometer was then given its final form, cleaned and calibrated.

The calibration was carried out in the following manner. The manometer-tube was placed horizontally on a table. By means of a rubber tubing put on one end, the column of mercury could be given the position desired. The ends of the mercury column were measured relatively to the nearest marks on the manometer by means of a microscope with a vertical filament movable along a horizontal steel rod and furnished with a micrometer-screw. By these means I was able to measure with an accuracy of about 1/50 mm.

For each position the mercury column was pushed forward as nearly as possible its own length. In the calculation, the length from the end of one position to the beginning of the next was considered to have the average diameter of the neighbouring position. The end where the volume of air was to be measured was calibrated with a smaller mercury column.

The calibration finished, the U-tube was put on at the point *h*. The capillary was well cleaned and a current of air drawn through it, the air being dried by passing through a solution of NaOH and over dry $CaCl_2$. Without disturbing the connexion to the drying apparatus the U-tube was filled with well-cleaned mercury, taking care in doing this that no air from without followed the mercury. Then the manometer was left to itself till the following day, and the temperature in the room, which was found to keep fairly constant, examined.

Just before closing the manometer the following observations were made:—

1. The pressure of the air observed by means of a mercury barometer by which the pressure could be read with an accuracy of 1/25 mm.; the barometer was compared with the standard barometer at the Meteorological Institute, Christiania.
2. Reading of the temperature of the room.
3. Reading of the mercury level in the manometer.
4. Reading of the position of the open end.

The end was closed very quickly by putting a drop of melted glass into the opening and at the same time using the flame. It took no more than 10 seconds from the time the gas-flame was lighted till the end was quite closed. Furthermore, the manometer was protected from change in temperature by means of an asbestos plate put on the end of the manometer.

The manometer then was sealed to the capillary from the osmometer, and the latter filled with water. This was done by drawing back the mercury with a water-pump and letting the water flow back into the tube. This was done to reduce the volume to be filled by the osmotic flow.

The constants of the manometer are the following:—

The air-pressure on closing... $B_0 = 754{\cdot}6$ mm. Hg at 0°;
,, abs. temperature ,, ... $T_0 = 287{\cdot}5$;
,, volume of air ,, ... $v_0 = 22{\cdot}762$ vol. units.

For the pressure q in the manometer at a temperature T and a volume v we have

$$q = \frac{B_0}{760}\frac{v_0}{T_0}\frac{T}{v}(1+\kappa) = 0{\cdot}07861\frac{T}{v}(1+\kappa).$$

κ is a correction introduced because the air does not exactly follow Boyle's law. I have put

$$1+\kappa = \frac{pv}{p_0 v_0},$$

where p_0 is one atmosphere and all pressures are made at 0°, and this value I have taken from the measurements made by Regnault and Amagat.

The volume v was determined by observing the position of the mercury column by means of a cathetometer furnished with a filament movable by a micrometer-screw reading with an accuracy of about 1/50 mm. It was somewhat more difficult, however, to get an exact determination of the other end of the air column as the tube, on account of the melting, ended in a tip. It is especially at high pressures that an exact determination is of importance. The position of the lowest point, as well as the point where the diameter began to diminish, could be determined with great precision. This lowest part had very nearly the form of a cone, and thus the position of the end could be found if the tube had been throughout cylindrical. Furthermore, I afterwards succeeded in calibrating the manometer quite up to the tip. The two methods gave results for the end reading differing only by 1/10 mm. In the calculation I have used the mean value.

As this error that may arise from the determination of the end point when measuring somewhat high pressures is predominant, we can conclude that even for pressures up to 50 atmospheres the error in q would not exceed 0·2 atm., and lower pressures could be measured much more accurately.

In the following table is given the volume of air corresponding to a series of readings at the temperature of 15° centigrade. All the numbers are derived directly from observations. The values of v for intermediate readings have been found by interpolation. The volume is expressed in an arbitrary unit, which is the volume of the largest mercury column used in the calibration.

Reading.	Volume.	Reading.	Volume.
1·592 cm.	0·2380	60·282 cm.	9·9580
3·060 ,,	0·4761	66·077 ,,	10·9512
4·520 ,,	0·7141	72·140 ,,	11·9898
5·988 ,,	0·9522	78·073 ,,	12·9968
7·439 ,,	1·1902	83·914 ,,	13·9952
8·887 ,,	1·4283	89·712 ,,	14·9877
10·329 ,,	1·6663	95·488 ,,	15·9797
11·768 ,,	1·9044	101·305 ,,	16·9778
12·160 ,,	1·9692	107·205 ,,	17·9783
18·306 ,,	2·9666	112·674 ,,	18·9030
24·399 ,,	3·9654	118·114 ,,	19·8285
30·489 ,,	4·9642	123·553 ,,	20·7484
36·572 ,,	5·9639	128·952 ,,	21·6743
42·601 ,,	6·9603	134·313 ,,	22·6025
48·535 ,,	7·9569	139·587 ,,	23·5290
54·434 ,,	8·9580		

The temperature of the air when the manometer was closed was 14°·5 C.; at other temperatures the volume per length-unit will be altered on account of the dilatation of the glass. For the temperatures actually used this change need not be considered.

The whole apparatus as it was put up at the Physical Institute at Christiania is shown in the photograph fig. 4 (Pl. VIII.).

§ 2.

The Semipermeable Membrane.

5. The membrane used in these measurements is the usual one consisting of copper-ferrocyanide. In preparing the cells I used electrolysis, practically the same method as used by Morse and Frazer, and later by Berkeley and Hartley.

It proved, however, to be very difficult to get a cell which gave a good membrane, and I tried several sorts, till I found one which gave satisfactory results.

At first I tried cells made of porcelain, but these proved either too weak or else so hard as not to permit of the fluid passing through.

Some cells of fayence made at the Fayence Factory, Egersund, showed better qualities, but were not fully satisfactory.

At last I got cells, made of "Pukalische Masse," from C. Desaga, Heidelberg, that proved very good.

For the electrolysis a somewhat variable potential was used, arranging matters so that the voltage increased with increasing resistance in the cell until for resistances of about 50,000 ohms it kept a fairly constant value of 115 volts. This method was originally chosen, as I had to use currents of 230 volts; but I also consider it good for the forming of the membrane, as the voltage is small as long as the membrane is weak.

The arrangement is shown in fig. 5. R_1 and R_2 are two equal resistances, consisting of two 16 candle-power incandescent lamps. By means of two commutators, K_1 and K_2, the cell C can be put as a shunt to one of the lamps. The resistance of the membrane as well as the voltage at a certain moment could be measured by means of a torsion galvanometer G, furnished with a resistance-box with resistances of 900, 9900, and 99,900 ohms, the resistance of the galvanometer being 100 ohms.

I have not treated more than four cells of this type, and all of them have attained an electric resistance of more than 125,000 ohms; one of them especially, which I shall call S, has shown very good qualities as the resistance has gone up to 400,000 ohms. This resistance, however, was first obtained after it had been long in use, and after it had several times been tested for osmosis. This, my first cell, has been used in all my measurements.

It seems as if I have succeeded in finding a type of cell *with constant qualities and very convenient for the production of semipermeable membranes.* The cell substance has a suitable porousness, is very homogeneous, and can at the same time stand great pressures.

In making the membrane the following method of proceeding has been used.

The forming of the first beginning of the membrane for three of the cells was done in the way described by Berkeley and Hartley *.

One of my cells (A), however, has been treated in a somewhat different way. In this case I took the dry cell and let it soak the two solutions simultaneously, the potassium ferrocyanide from the outside and the copper sulphate from the inside, whereupon the cell was placed in distilled water and the whole placed in the vacuum for about twenty-four hours. The result was very satisfactory, the resistance rose more suddenly than in any of the other cells.

The solution of copper sulphate used contained 50 gr. in one litre, and the solution of potassium ferrocyanide 42 gr. in the litre. The positive electrode consisted of a copper rod, and the vessel containing the solution served as the negative electrode. In order to prevent the potassium hydrate produced by the electrolysis from acting upon the membrane, the cell was separated from the vessel by a porous cup also filled with potassium ferrocyanide solution. In the electrolysis the positive electrode was fixed to the cell by a cork with perforations, and the cell hung up by the current wire.

At the beginning of the electrolysis the resistance suddenly rose within two minutes to about 3–4000 ohms, and then increased more slowly until after $1\frac{1}{2}$–2 hours it reached a maximum value. As an instance I shall give the observations for the first electrolysis of the cell A:

Electrolysis begun Nov. 10, 1907, $1^h\ 8^m$ P.M.

Time.	Temp.	Potential.	Resistance.
$1^h\ 9^m$	9° C.	65 volts	3,000 ohms
11	7	96 ,,	4,500 ,,
33	6	107 ,,	11,400 ,,
48	5	110 ,,	13,500 ,,
2 25	4	111 ,,	18,800 ,,
3 30	3·5	111·5 ,,	20,200 ,,

If the electrolysis is continued after maximum resistance

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* Earl of Berkeley and E. G. J. Hartley, *loc. cit.* p. 486.

is reached we shall generally notice a fall in the resistance, especially when the maximum resistance is small. In the best cell I could not detect any fall, although the electrolyis was continued for one hour after the maximum resistance was reached.

When the electrolysis has finished the resistance falls very rapidly, as will be seen from the curve fig. 6 (Pl. VIII.). And for each time the process is repeated, we shall have an increase of resistance from a value which is only a small fraction of the maximum value of the resistance. Even in the case when it got up to 400,000 ohms it was only 51,000 to begin with.

In the following tables is shown the development of the membrane for the two cells S and A, these being chosen because they have been subject to a somewhat different treatment.

CELL S.

Date.	Duration of electrolysis.		Temp.	Potential.	Resistance.
1906, Nov. 21...	0^{h}	30^{m}	...	→ 96 volts	4,500 ohms
,, ,, 22...	1	10	...	→114 ,,	60,000 ,,
,, ,, 23...	1	0	9°	→111 ,,	56,000 ,,
,, Dec. 5...	...		6°	→114 ,,	45,000 ,,
,, ,, 11...	1	5	...	→114 ,,	40,000 ,,
,, ,, 11...	0	20	...	230 ,,	65,000 ,,
,, ,, 28...	1	0	12°·2	115 ,,	100,000 ,,
1907, June 11...	1	2	16°	,,	97,000 ,,
,, ,, 15...	2	5	...	,,	180,000 ,,
,, Sept. 19...	1	0	10°	,,	220,000 ,,
,, Oct. 14...	1	40	4°·5	,,	320,000 ,,
,, ,, 24...	1	18	3°	,,	290,000 ,,
,, Nov. 12...	1	52	1°·6	,,	400,000 ,,
,, ,, 28...	3	0	0°·9	,,	290,000 ,,
,, Dec. 4...	2	50	2°·5	,,	360,000 ,,

CELL A.

Date.	Duration of electrolysis.		Temp.	Potential.	Resistance.	
1907, Nov. 10...	2^{h}	20^{m}	5°	→111·5 volts	20,000 ohms	
,, ,, 15...	1	5	11°	→114	36,000 ,,	
,, ,, 17...	2	30	1°·1	115	75,700 ,,	Solutions interchanged.
,, ,, 18...	1	37	1°·5	116 & 230	118,000 ,,	
,, ,, 21...	2	30	2°·0	115	178,000 ,,	
,, ,, 23...	1	30	2°·5	,,	182,000 ,,	
,, ,, 25...	3	0	3°	,,	230,000 ,,	
,, ,, 29...	2	0	0°·9	,,	276,000 ,,	

For general use I have found that the least voltage is about 115 volts. When the maximum resistance has reached a value of about 50,000 ohms, I have found it to have a good effect for about 20 or 30 minutes, to use the double voltage (230 volts). After this treatment I have generally observed a considerable increase in the maximum resistance when going back to 115 volts.

For the cell A the solutions have been interchanged, the copper-sulphate solution being used on the outside. Before the change the cell ought to be placed for one or two days in distilled water ; further, in the electrolyses I had repeatedly to change the solution of potassium ferrocyanide as to prevent action from potassium hydrate. This was also done for one of my other cells, and effected in both cases a considerable increase in the maximum resistance.

The Effect of Temperature upon the Membrane.

6. The temperature has a great influence upon the maximum resistance obtainable. In order to examine the effect more closely I have made some experiments with my two other cells, which I may call M and N. The experiments were in the following manner :—The cell was electrolysed at first at a temperature near 0° until maximum was reached. Then the temperature was raised as quickly as possible and the electrolysis continued until maximum. By this somewhat hard treatment the cell might change its original quality, and for that reason the electrolysis was repeated by going down to 0°. The results of these measurements are given in the following tables and graphically represented by the curve fig. 6 (Pl. VIII.).

CELL M.

Jan. 7, 1908.—Mean Potential 118 volts.

Temperature 0°·9.		Temperature 12°·2.		Temperature 1°·3.	
Time.	Resistance.	Time.	Resistance.	Time.	Resistance.
h m		h m		h m	
10 48 A.M.	13 × 10³ ohms	5 25 P.M.	48 × 10³ ohms	8 30 P.M.	45 × 10³ ohms
11 8 ,,	53 ,, ,,	5 44 ,,	48 ,, ,,	8 40 ,,	49 ,, ,,
11 30 ,,	74 ,, ,,	6 4 ,,	58 ,, ,,	9 45 ,,	74 ,, ,,
11 55 ,,	100 ,, ,,	6 14 ,,	62 ,, ,,	10 0 ,,	78 ,, ,,
12 25 P.M.	122 ,, ,,	6 24 ,,	67 ,, ,,	10 15 ,,	83 ,, ,,
12 55 ,,	133 ,, ,,	6 34 ,,	68·8 ,, ,,	10 30 ,,	90·7 ,, ,,
1 40 ,,	139 ,, ,,	6 44 ,,	71·8 ,, ,,	10 45 ,,	93 ,, ,,
2 30 ,,	150 ,, ,,	6 49 ,,	78 ,, ,,	11 10 ,,	100 ,, ,,
3 10 ,,	150 ,, ,,	7 14 ,,	83 ,, ,,	11 30 ,,	106 ,, ,,
3 40 ,,	150 ,, ,,	7 30 ,,	78 ,, ,,		

CELL N.

Mean Potential 115 volts.

Jan. 8.				Jan. 9.	
Temperature 0°·9.		Temperature 14°·3.		Temperature 1°·1.	
Time.	Resistance.	Time.	Resistance.	Time.	Resistance.
h m		h m		h m	
11 55 A.M.	24·5×10³ ohms	6 15 P.M.	73 ×10³ ohms	12 48 P.M.	10·8×10³ ohms
12 40 P.M.	88·5 ,, ,,	6 25 ,,	62·2 ,, ,,	1 0 ,,	17·0 ,, ,,
1 25 ,,	109 ,, ,,	6 35 ,,	56·5 ,, ,,	1 15 ,,	27·0 ,, ,,
2 30 ,,	119 ,, ,,	6 45 ,,	53·0 ,, ,,	1 45 ,,	28·2 ,, ,,
3 10 ,,	135 ,, ,,	7 0 ,,	52·0 ,, ,,	2 15 ,,	35·3 ,, ,,
3 40 ,,	143 ,, ,,	7 30 ,,	48·6 ,, ,,	4 25 ,,	46·0 ,, ,,
4 15 ,,	147 ,, ,,	8 5 ,,	42·5 ,, ,,		
4 55 ,,	147 ,, ,,	8 30 ,,	44·0 ,, ,,		
5 45 ,,	128 ,, ,,	9 30 ,,	38·5 ,, ,,		

In both cases the temperature has a great influence upon the maximum resistance. We see from the last experiment that the effect of temperature partly consists in a weakening of the membrane. The resistance is broken down and does not regain its original size when going back to the low temperature.

In the first experiment the membrane seems to have kept more constant during the treatment; but still we notice a very great temperature effect upon the maximum resistance. The membrane is, however, not unaltered, so the maximum resistance will not exactly correspond to equal membranes. Comparing the two curves for the low temperature, we see that the cell during the treatment has undergone a change; for in the last curve the resistance increases more slowly.

Unfortunately the experiment could not be continued till maximum was reached; but when the experiment was broken off (11^{h} 30^{m} p.m.) the resistance was still increasing, and the curve seems to show that the resistance has a tendency to regain a value near to its original maximum value.

It seems then that the temperature, even if the mechanical structure could be kept constant, would exercise a great influence upon the resistance at the membrane.

That this is the fact is brought to full evidence by an experiment carried out at the Cavendish Laboratory.

The cell A was first electrolysed at 11°·3 up to maximum of resistance, then the temperature was brought down to 1° C. During the time-interval the temperature was lowered the electrolysis was stopped. The experiment had the result shown in the table.

Electrolysis begun $10^h\ 30^m$ A.M.

Temperature 11°·3.		Temperature 1°·0.	
Time.	Resistance.	Time.	Resistance.
h m		h m	
11 15 A.M.	171×10^3 ohms.	12 54 P.M.	310×10^3 ohms.
11 50 „	192 „ „	1 15 „	320 „ „
12 15 P.M.	196 „ „	1 30 „	314 „ „
12 34 „	192 „ „	1 45 „	319 „ „
		3 20 „	276 „ „
12 44 P.M.	El. stopped.		

It appears from the table that the resistance on lowering the temperature rose from 192 to 310 thousand ohms. As the electrolysis had been stopped during the interval, this increase cannot be due to any building up of the membrane. On the contrary, the resistance will fall with time, but this will only cause a diminution in the effect, and we see that the resistance at the low temperature first increases for some time. As resistances that most nearly correspond to the same system we should also this time have to take the maximum resistances.

If in the experiment with the cells M and A we assume that the maximum resistances at the two temperatures correspond to nearly equal membranes, the temperature effect calculated from the maximum values should nearly give the temperature coefficient corresponding to a constant system. When the temperature effect is defined in the usual way, the two experiments give the following result :—

Cell.	Temperature Coefficient.
M	−0·072
A	−0·063

Since continuing the electrolysis after maximum we generally get some decrease in the resistance, the value found for cell M will be somewhat too large and the value for A too small ; and we see that the temperature effect found is greater for cell M than for cell A. The temperature effect that the membrane would show if we were able to maintain a constant structure should lie between the two values.

In order to explain this large temperature effect it would be necessary to know the nature of the conductivity at maximum.

As long as the resistance is small and increasing, we can be sure that the conductivity is mainly of electrolytic nature; but it is also possible that electricity can pass through the membrane without being carried by the ions of the fluids, and when the membrane becomes tighter this nonelectrolytic conductivity might even be predominant.

That at maximum resistance a considerable *electrolytic* conductivity must take place is evident from the following fact.

As we have seen (fig. 6) the resistance after electrolysis has been stopped will very rapidly diminish; but we must necessarily assume that this breaking-down process is also going on under the electrolysis, only that we now have a counteracting process in the new building of the membrane. At maximum of resistance there must be an *electrolytic conduction* just sufficient for balancing the breaking-down process. And further, if we would imagine that for a moment the conductivity was mainly due to a conduction through the membrane substance, the current would call forth disturbances in the porous structure of the membrane, and the latter would very soon break down and give rise to electrolytic conduction.

From this it seems probable that the conductivity even at maximum resistance is chiefly of electrolytic nature. The electric conductivity would then measure the degree of permeability of the membrane for the two ions $\overset{+}{\mathrm{C}}\mathrm{a}{:}$ and ${\vdots}\mathrm{Fe}(\overset{-}{\mathrm{CN}})_6$, and the temperature effect would mean that *by increasing temperature the permeability of the membrane is largely increased.*

The Dependence of the Resistance upon the Potential.

7. In an experiment carried out for preparing the membrane with a higher potential, it was noticed that the latter had a great effect upon the resistance of the membrane. In this experiment, the cell N was electrolysed first by 110 volts until a maximum of resistance of 126,000 ohms was reached, then the potential was raised to 220, and the electrolysis continued for about 15 minutes until the membrane had got a resistance of 116,000 ohms. It might seem as if the high potential had diminished the resistance, but by going back to the original potential the resistance suddenly rose to 196,000 ohms.

This experiment shows the good effect of using a higher potential for a short time. This will have a similar effect as the remaking of the membrane under pressure which is used by Berkley and Hartley. But at the same time the experiments show that the resistance of the membrane, when the latter is kept unaltered, largely depends upon the potential.

The effect is examined more closely by some measurements carried out at the Cavendish Laboratory. The mode of proceeding was about the same as in the first experiment. The cell A was electrolysed at constant temperature up to maximum of resistance. Then the potential was changed as suddenly as possible and the resistance measured. The measurements were made by a d'Arsonval galvanometer put as a shunt to the head circuit, and the resistance was directly compared with a standard resistance of 100,000 ohms put into the circuit instead of the cell. With different potentials I had to use a different shunt-resistance so as to get a suitable deflexion, but the deflexion for the standard resistance was found for each potential, the resistance being thus directly compared with the standard.

As the electrolysis had to be stopped for some minutes during the experiments, some change in the membrane resistance was to be feared, and, as a matter of fact, by going back to the original potential the resistance had fallen about 1·4 per cent.; but as the time for each reading was noticed, by assuming a constant rate of fall the measurements could be reduced to the same point of time. The result is given in the table.

Temperature 11°·5.

Potential.	Resistance.	$\alpha = \frac{1}{R}$.
41 volts.	208×10^3 ohms.	$4{\cdot}81 \times 10^{-6}$
85 „	200 „ „	5·00 „
117 „	191 „ „	5·24 „
153 „	176 „ „	5·68 „
199 „	147 „ „	6·80 „

As we see, the current system does not follow Ohm's law, the resistance falls with increasing potential, and the greater the potential the more rapid the fall.

The table also contains the quantity $\alpha = \frac{1}{R}$, which measures the conductivity of the system. The experiments give α as a function of the potential v, this function can be given the form

$$\alpha = \alpha_0 + \alpha_1 v + \alpha_2 v^2 + \ldots$$

α_0 would then be the conductivity corresponding to $v=0$. By putting the values found into a curve we should get for this special case $\alpha_0 = 4{\cdot}75 \,.\, 10^{-6}$ ohm^{-1}.

If an electromotive force were required to make the system a conductor, we should get $\alpha_0 = 0$, then $\alpha - \alpha_0$ will give the conductivity produced by the electromotive force, and we see that the conductivity for higher potentials is made up of two parts, one part $\alpha - \alpha_0$ produced by the electromotive force and one part α_0 belonging to the system.

In our case α_0 is great in comparison to $\alpha - \alpha_0$ even for potentials up to 175 volts. For $v = 115$ volts $\frac{\alpha - \alpha_0}{\alpha_0} = 0{\cdot}1$. From this we can conclude that the large temperature effect which is measured by a potential of 115 volts must be mainly due to the effect upon α_0.

In view of the constitution of the membrane, a natural explanation of the potential effect can be got by assuming that it is due to an inner motion in the membrane produced by the mechanical action of the electric force. This also gives an explanation of the fact that the resistance generally will decrease when electrolysis is continued after maximum, and most rapidly in the weakest membranes.

As the potential effect as well as the temperature effect corresponds to a nearly constant membrane, we see that, as far as the electric resistance can be considered a criterion of a good membrane, the resistances must be compared at the same temperature and the same potential.

§ 3.

General Remarks as to the Treatment of the Observations.

8. Before going on to describe more minutely the special observations, we shall see which quantities are to be measured. By the term osmotic pressure we shall understand the difference between the hydrostatic pressures on the two sides of a perfect semipermeable membrane when the solution and solvent are in thermodynamic equilibrium. As this pressure is a limiting value for the pressures measurable by our membranes, we shall in the following call it the ideal equilibrium pressure (π_0) and we have :

$$\pi_0 = p - p_0 = \phi(\mathrm{C}, \mathrm{T}, p_0). \quad . \quad . \quad . \quad . \quad (1\,a)$$

The problem to be solved is to determine by experiment the function ϕ. C denotes the concentration defined in one way or other, T the temperature, and p and p_0 the pressure upon the solution and the solvent respectively. In the measurements here given p_0 in the function ϕ can be regarded as a constant, and we have

$$\pi_0 = \phi_0(C, T). \quad \ldots\ldots\ldots \quad (1\,b)$$

There are three quantities to be measured:

(1) The osmotic pressure π_0.
(2) The concentration actually present under the experiment.
(3) The temperature.

On the Calculation of the Osmotic Pressure.

9. As the membranes actually used probably always will admit some solution passing through, the measured apparent equilibrium pressure, π', will be different from π_0. It may be of importance to put the question into a mathematical form, to examine more closely the problem with which we have to deal and to see what would be required for an exact determination of osmotic pressure. To that end we shall consider the velocity of the leak and the velocity of osmotic flow. We shall assume that the velocity of flow as well as the leak is measured by the increase in height of water-level in unit time.

At first we shall make some remarks as regards the leak. The leak may be due to a mere mechanical defect in the membrane. In this case the leak, if it is too small to call forth any motion in the fluids, can be considered as taking place independently of the osmosis. By putting the apparatus up under a certain pressure and measuring the amount of solute that has passed through in a certain time, we should be able to find the velocity of leak by assuming that it has passed through the membrane with the concentration of the solution.

For this kind of leak that will not effect the osmotic activity we shall adopt the name used by Berkeley and Hartley and call it the Solution Leak.

There may, however, be another kind of leak due to the fact that the membrane substance itself, even in the good parts of it, does not give conditions for perfect semipermeability. This leak will be a function of the osmotic process, and the latter will most likely be influenced by the leak. This leak cannot be regarded as a leak of solution, but rather as a leak of solute. This kind of leak we shall call the Osmotic Leak. To get a strict definition of this leak, we shall *assume* that the solute also in this case is connected with so much of the solvent as to give a solution of the same concentration as the solution in the osmometer. This assumption will only cause some difference as to what we understand by the velocity of osmotic flow. The leak defined in this manner will be proportional to the actual leak, and they will both of them disappear simultaneously. When the leaks are defined in this manner we can consider the total leak as a measurable quantity, when we are able to determine the amount of solute that has passed through by a certain pressure in a certain time.

Let us in general assume that the total leak is l and the total amount of solution leak l_0. Further, we shall assume that there are a certain number of leaks $l_1\, l_2 \dots l_n$ which each influence the osmotic flow in its own manner. According to their nature the leaks must be absolute quantities that cannot change their signs, so when $l=0$ all the other leaks must be equal to zero.

The apparent velocity of osmotic flow we shall call λ'. This is the velocity directly examined. The velocity of osmotic flow λ we shall define by the equation

$$\lambda=\lambda'-l. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

In general we must be able to put

$$\left.\begin{array}{l} \lambda=\psi(\pi\, l_1,\, l_2, \dots l_n\, \mathrm{C},\, \mathrm{T},\, k_1 k_2 \dots) \\ l_1=\epsilon_1(\pi\, \lambda\, \mathrm{C}\; \mathrm{T}\, k_1'\, k_2' \dots) \\ l_2=\epsilon_2(\pi\, \lambda\, \mathrm{C}\; \mathrm{T}\, k_1^{(2)}\, k_2^{(2)} \dots) \\ \dots \quad . \quad . \quad . \quad . \quad . \quad . \\ \dots \quad . \quad . \quad . \quad . \quad . \quad . \\ l_n=\epsilon_n(\pi\, \lambda\, \mathrm{C}\; \mathrm{T}\, k_1^{(n)}\, k_2^{(n)} \dots) \\ l_0=\epsilon_0(\pi\, \mathrm{C}\; \mathrm{T}\, k_1^0\, k_2^0 \dots) \end{array}\right\} \quad . \quad . \quad . \quad (2b)$$

π denotes an arbitrary pressure difference between the solution and the solvent; k, $k_1 \dots k_1', k_2' \dots$ &c., are parameters dependent upon the qualities of the membrane and the mechanism of osmotic flow.

In order to find a mathematical expression for the relation between π_0 and π', we must be able to define the ideal equilibrium pressure by means of the quantities in equations 2*a* and 2*b*. This definition we get by fixing the conception of semipermeability. We shall have perfect semipermeability when $l=0$, and λ is a function of π defined as a single-valued function in the neighbourhood of the reversion point, and further we must have $\left(\frac{d\lambda}{d\pi}\right)_{\pi_0}$ different from zero. Then the manipulations necessary for the thermodynamic treatment can be carried out.

For perfect permeability we shall have that the ideal equilibrium pressure is defined by the equation $\lambda=0$.

For all the intervals in which the function ψ has a physical interpretation ψ must, on account of the continuity of nature, be a continuous function with regard to the variables. We shall in general consider the equation

$$\psi(\pi\, l_1\, l_2 \ldots l_n\, \mathrm{C.T}\, k_1\, k_2 \ldots)=0.$$

By this equation the pressure is implicitly given as a function of C.T $l_1 \ldots l_n$ and $k_1\, k_2 \ldots$. This pressure we shall call π_0'. In the interval of physical interpretation π_0' is a continuous and single-valued function of the named variables. But as we cannot produce perfect semipermeability we cannot be sure that the continuity with regard to the leaks will hold quite up to the point $l_1=l_2=\ldots=l_n=0$. If it was not allowed to assume continuity up to this point it would mean that the conception perfect semipermeability, as applied to nature in the case considered, would be an absurdity. It might also be that for certain membranes and solutions the assumption is not allowed, while it is allowed for others. At all events, if we cannot assume continuity up to the point $l=0$, we have no means of combining the ideal equilibrium pressure with the reversion pressure actually measured.

The following development is restricted to those cases for which π_0' can be considered a continuous function of the leaks quite up to the point $l_1=l_2=\ldots=l_n=0$. This condition we can write

$$l-l_0=0.$$

Under these conditions the ideal equilibrium pressure is defined by the equation

$$\psi(\pi l_1 l_2 \ldots l_n \mathrm{CT} k_1 k_2 \ldots)\underset{l-l_0=0}{=0} \quad . \quad . \quad . \quad . \quad (3)$$

With perfect semipermeability π_0 is a function of C and T, provided p_0 is constant, and then we see that if the ideal equilibrium pressure can be defined by equation 3, ψ must be such a function of $k_1 k_2 \ldots k_m$ that for $l-l_0=0$ and $\lambda=0$ the quantities dependent on the membrane must disappear. And consequently, if ψ is continuous with regard to the leaks up to the point of ideality, we must have *that the influence of the membrane upon the reversion pressure actually measured must disappear with the leak.*

Let us, on the other hand, assume that the membrane has such properties that when the leaks diminish the pressure π_0' approaches a value π_0'' where

$$\pi_0-\pi_0''=a,$$

where a is a finite quantity, and as being due to the leaks it would be a quantity characteristic of the membrane, and would necessarily change with the properties of the membrane, and we might expect that a change in the membrane constants would give rise to a change in the reversion pressure of the same order.

If, then, we are able to show that the reversion pressure keeps constant while the qualities of the membrane or the mechanism of osmotic flow in some way are altered, it will give a strong evidence for the correctness of the assumption as to the continuity of π_0' to the point of ideal semipermeability, so the pressure measured by a small total leak must be near to the ideal pressure. We shall later have an occasion to come back to this question.

In general the quantities $k_1k_2\ldots$ &c., even during one experiment, will vary with time. In the following we shall find the properties of the membrane at a certain moment, or, in other words, we shall find the properties under the assumption that $k_1k_2\ldots$ can be kept constant. Further, we shall consider C and T constant. As to the concentration it will change on account of λ and l, but we shall assume that this variation is so small as not to produce any appreciable effect upon the velocities. Then we may write the equations *2a* and *2b*

$$\left.\begin{aligned}
\lambda &= \psi(\pi l_1 l_2 \ldots l_n)\\
l_1 &= \epsilon_1(\pi\lambda)\\
l_2 &= \epsilon_2(\pi\lambda)\\
&\vdots \quad \cdots\cdots\\
l_n &= \epsilon_n(\pi\lambda)\\
l_0 &= \epsilon_0(\pi)\\
\lambda' &= \lambda + l
\end{aligned}\right\} \quad \ldots\ldots \quad (2c)$$

If we put into the functions $\epsilon_1\epsilon_2\ldots\epsilon_n$ the value of λ from the first equation, we get n equations between the $n+1$ quantities $l_1l_2\ldots l_n$ and π. And by this means $l_1l_2\ldots l_n$, and thence λ, can be found in terms of π. From this it follows that we always can put

$$\lambda' = \zeta(\pi)$$
$$l = \eta(\pi).$$

These two functions can be found by experiment. λ' can be found by determining the apparent velocity corresponding to different pressures, and to find $\eta(\pi)$ we should have to analyse the solvent when the solution has been standing for a given time under a certain pressure.

The two functions can be graphically represented by two curves, and the intersection of these two curves would give a point corresponding to a pressure π_0' and a total leak l'. This point will, on account of the last equation in 2*c*, satisfy the condition

$$\lambda=0.$$

The point π_0' will in general be different from π_0. There is only one case in which the point determined in this manner will give the ideal equilibrium pressure. That occurs when the total leak is a solution leak. Then we have

$$l \equiv l_0 \quad \text{and}$$
$$l_1 \equiv l_2 \equiv l_3 \equiv \ldots \equiv l_n \equiv 0.$$

Then we see from equation 3 that the point that satisfies the equation $\lambda=0$ will give the ideal equilibrium pressure.

Thus we see that in the case when the velocity of osmotic flow λ can be considered independent of the leak, it should be possible to determine the ideal equilibrium pressure even with a leak of the same order of size as λ itself. If the leak is not very great, we do not need to determine the whole leak curve; we only need to determine a point corresponding to the apparent equilibrium pressure.

On account of the nature of the leak we must have that l_0 as well as $\frac{\partial l_0}{\partial \pi}$ never can be negative. If, then, for a somewhat large value of π l is maintained fairly low, it seems allowable to conclude that $\frac{\partial l}{\partial \pi}$ is a very small quantity, and for the surroundings of the equilibrium point we can put

$$l=l_{\pi'}=\text{constant}.$$

We shall now treat the general case when we have only osmotic leaks.

In this case the intersection point will not give the ideal equilibrium pressure. If we knew the functions $\epsilon_1, \epsilon_2 \ldots \epsilon_n$ we should by putting $\pi=\pi_0'$ and $\lambda=0$ get a series of values $l_1', l_2' \ldots l_n'$. The pressure π_0' must satisfy the equation

$$\psi(\pi_0' \, l_1' \, l_2' \ldots l_n')=0. \quad . \quad . \quad . \quad . \quad (3b)$$

The ideal equilibrium pressure, however, must satisfy the equation 3:

$$\psi(\pi_0 \, 0, 0 \ldots 0)=0. \quad . \quad . \quad . \quad . \quad (3a)$$

And if the function ψ really varies with the leaks, the solution of equations $3a$ and $3b$ must give different pressures.

As earlier mentioned, as long as in the functions ψ the leaks are different from zero, the quantities dependent on the membrane will not disappear and the pressure π_0' will be a function of the membrane. π_0' is the pressure we should get if the total leak could be regarded as a solution leak not influencing the osmotic flow. This is the pressure which is measured by Berkeley and Hartley.

We see from this that if some of the quantities $l_1 l_2 \dots l_n$ are somewhat great, it may seem as if the pressure π_0' is a property mainly due to the membrane.

We shall find the mathematical expression for the ideal osmotic pressure in the case that the leaks are very small quantities. We have earlier assumed that the function ψ is continuous in the neighbourhood of the point $l=0$. We will now also assume that the first derivates with regard to the pressure and the leaks are continuous.

Then we can apply to the equation $3b$ the formula of Taylor for the neighbourhood of the point $\pi=\pi_0$ and $l=0$, and we get

$$0=\psi(\pi_0' l_1', l_2' \dots l_n')=\psi(\pi_0\,0\,0\dots 0)+\left(\frac{\partial\psi}{\partial\pi}\right)_0(\pi_0'-\pi_0)$$

$$+\left(\frac{\partial\psi}{\partial l_1}\right)_0 l_1'+\left(\frac{\partial\psi}{\partial l_2}\right)_0 l_2'+\dots\left(\frac{\partial\psi}{\partial l_n}\right)_0 l_n'+\omega_2.$$

But according to the definition of π_0

$$\psi(\pi_0\,0\,0\dots 0)=0.$$

If $\dfrac{\partial\psi}{\partial\pi}$ is a finite quantity different from zero, we see that $\pi_0-\pi_0'$ will be a quantity of the same order as the leaks and will disappear with the leaks. ω_2 consists of terms of second and higher order. If we restrict ourselves to terms of the first order we get

$$\pi_0\div\pi_0'=\frac{1}{\left(\frac{\partial\psi}{\partial\pi}\right)_0}\left\{\left(\frac{\partial\psi}{\partial l_1}\right)_0 l_1'+\left(\frac{\partial\psi}{\partial l_2}\right)_0 l_2'+\dots\left(\frac{\partial\psi}{\partial l_n}\right)_0 l_n'\right\}. \quad (4)$$

The pressure π_0' is defined by the equation $\lambda=0$. As we have seen we can put

$$\lambda=\zeta(\pi),$$
$$l=\eta(\pi),$$
$$\lambda'=\xi(\pi).$$

We shall assume what is generally confirmed by experiment, that for a small leak $\frac{d\lambda'}{d\pi}$ and consequently $\frac{d\lambda}{d\pi}$ and $\frac{dl}{d\pi}$ are continuous in the interval

$$0<\pi<\pi_0'.$$

We shall develop the functions λ and l in the neighbourhood of the point $\pi=\pi_0'$. Then we get

$$\lambda=\zeta(\pi_0')+\left(\frac{d\lambda}{d\pi}\right)_{\pi_0'}(\pi-\pi_0')+\alpha_2,$$

$$l=\eta(\pi_0')+\left(\frac{dl}{d\pi}\right)_{\pi_0'}(\pi-\pi_0')+\alpha_2'.$$

But according to the definition of π_0' we have

$$\zeta(\pi_0')=0.$$

And remembering that

$$\frac{d\lambda}{d\pi}+\frac{dl}{d\pi}=\frac{d\lambda'}{d\pi},$$

we get

$$\lambda'=(\pi-\pi_0')\left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'}+\eta(\pi_0')+\alpha_2+\alpha_2'.$$

For the apparent equilibrium pressure we have

$$\lambda'=0 \quad \text{and} \quad \pi=\pi',$$

which gives

$$\pi_0'=\pi'\frac{\eta(\pi_0')}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'}}+\alpha_2''.$$

With the same accuracy as before we can put

$$\alpha_2''=0,$$

$$\eta(\pi_0')=\eta(\pi')=l_{\pi'},$$

$$\left(\frac{d\lambda'}{d\pi}\right)_{\pi_0'}=\left(\frac{d\lambda'}{d\pi}\right)_{\pi'},$$

and

$$\pi_0'=\pi'+\frac{l_{\pi'}}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By addition of equations 4 and 5 and by putting

$$\left(\frac{\partial\psi}{\partial l_1}\right)_0 l_1' + \left(\frac{\partial\psi}{\partial l_2}\right)_0 l_2' + \dots \left(\frac{\partial\psi}{\partial l}\right)_0 l_n' = \Sigma$$

we get

$$\pi_0 = \pi' + \frac{l_{\pi}'}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}} + \frac{\Sigma}{\left(\frac{\partial\psi}{\partial\pi}\right)_0} \quad . \quad . \quad . \quad . \quad . \qquad (6a)$$

When the leaks are very small we can regard $\frac{\partial l_r}{\partial\pi}$ as small quantities in comparison to $\frac{d\lambda'}{d\pi}$, then we can put

$$\left(\frac{\partial\psi}{\partial\pi}\right)_0 = \left(\frac{d\lambda'}{d\pi}\right)_{\pi'},$$

and we get

$$\pi_0 = \pi' + \frac{1}{\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}}(l_{\pi'} + \Sigma). \quad . \quad . \quad . \quad . \qquad (6b)$$

This equation is the most general, it contains also the case when the velocity of osmotic flow is independent of the leak; *e. g.*, if the leak l_1 could be regarded as a solution leak we should have in the sum Σ to put $\frac{\partial\psi}{\partial l_1} = 0$.

Even in the case of a small leak we are, at least with the present knowledge about the osmotic process, unable to find the correction due to that part of the leak which is able to influence the osmotic activity. We can only find the pressure π_0'.

As to the quantity Σ we know at present very little about its actual size. In the case of copper ferrocyanide and sugar solutions we have reason to believe that it will be positive. It is stated by Berkeley and Hartley* that in their experiments the corrected pressure (π_0') generally comes out smaller for a greater leak. It appears from this that as far as the leaks are able to influence the pressure π_0' the latter will be diminished by the leak. This is also confirmed by some experiments that will be described later.

As there probably always will be some osmotic leak we have

$$\pi_0 > \pi_0' > \pi'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

And, as shown by the experiments, $\frac{d\lambda'}{d\pi}$ will be a positive quantity, then

$$\Sigma > 0.$$

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* *Loc. cit.* p. 503.

If this can be considered a general rule it must take place when we have only one kind of leak, then we get

$$\left(\frac{\partial\psi}{\partial l_r}\right)_0 > 0.$$

Remembering that the velocities are positive when the height of water-level is increased, we come to the very reasonable conclusion that the osmotic activity is diminished by the leak.

From (7) we see that by assuming the whole leak a solution leak and finding the pressure π_0', we shall approach the ideal pressure, and in the treatment of the observations we shall use this correction.

The apparent equilibrium pressure is determined by the manometer pressure q, but to this must be added a quantity due to the liquids. For the manometer used at Christiania we get

$$\pi_0' = q - 0{\cdot}44 + 0{\cdot}0104a - p_0 + \Delta\pi \text{ atm.}$$

a is the manometer reading in cm. For somewhat high pressures we can put $p_0 = 1$. $\Delta\pi$ is the correction for the leak regarded as a solution leak. To find $\Delta\pi$ we shall have to find λ' in the neighbourhood of the apparent equilibrium point. Further, we shall have to find the leak corresponding to a pressure near to the equilibrium pressure. Then in the experiments we ought to keep the pressure on an average near to the equilibrium pressure. By analysing the water in the cell and by assuming a constant velocity of leak, the latter can be found.

On the Determination of the Actual Concentration.

10. The concentration difference between the two sides of the membrane in the case of cane-sugar can be altered in three different ways :

(1) By the osmotic flow of water into the solution.
(2) By the leaks.
(3) By inversion.

To determine these corrections the following method was used :—

A possible inversion was tested with Fehling's solution, and in our experiments the first qualitative test gave no measurable precipitate. The change in concentration on account of dilution was found by measuring the angles of polarization α_0 and α before and after the osmosis. The concentration (g)

of the water in the cell was also determined by polarization. If $\frac{\alpha_0-\alpha}{\alpha_0}$ is a small quantity and G is the original concentration, the actual concentration will be

$$C=G\frac{\alpha}{\alpha_0}-g.$$

When the compressor is used we shall generally find $\alpha_0=\alpha$, and in most cases g has been so small as not to be detectable by polarization.

The angle of polarization is measured by Laurent's polarimeter, which enabled me to read with an accuracy of 1 or 2 minutes, when taking the mean of a number of readings. With the tube used it corresponds to a concentration of about 1/8—1/4 gr. in the litre.

[To be continued.]

XX. *On Bessel Functions of Equal Argument and Order.* *By* J. W. Nicholson, *D.Sc., B.A., Isaac Newton Student in the University of Cambridge*[*].

THE solution of many physical problems depends upon a knowledge of the behaviour of the Bessel function commonly denoted by $J_n(z)$, and of other functions associated with it, when the argument z and order n are nearly equal. The only treatment of this question which the author has been able to discover is contained in a paper by Lorenz[†], which only deals with a very special case in which n is half of an odd integer. But even in this restricted investigation, the method employed is highly unsatisfactory, and many of the steps made seem incapable of justification. For example, at one point Lorenz divides a definite integral, involving a Bessel function in the integrand, into two parts, say α and β. In α the range extends from zero to a "small quantity h," and it is shown that to a certain order α may be neglected. The range in β extends from h to a quantity "not small," in fact $\frac{\pi}{2}$. Lorenz substitutes an asymptotic expansion for the Bessel function of zero order in β, but thereby renders the result liable to an error of the same magnitude as the terms retained, for in the lower portion of

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[*] Communicated by the Author.

[†] "Sur la réflexion de la lumière par une sphère transparente," *Œuvres Scientifiques*, i. pp. 435 *et seq.*

the range h to $\frac{\pi}{2}$, the asymptotic expansion does not converge even in its first three terms. The ratio of successive terms it of order ah, where a is large. But unfortunately, Lorenz's argument subsequently compels him to choose the "small quantity h" of order $\frac{1}{a}$, so that ah is comparable with unity. This vitiates the whole argument, and the only apparent means of avoiding the difficulty is to divide the range of integration into three parts, of which the intermediate one passes between the limits h and k, where h is of order $\frac{1}{a}$ as before, and k is such that ak is really of high order. The consideration of this intermediate portion, which must be proved negligible, is very arduous, for no asymptotic value of the Bessel function may be continuously used throughout a range of this character.

But since all these troubles may be avoided by a more direct investigation, it seems desirable to obtain the expansions from the ordinary definite integrals for the Bessel functions. The results may then be found to any desired order of approximation. Moreover, they may be expressed in terms of well-known transcendents whose tabulation, originally made for other purposes, is fairly complete.

The functions to be treated are usually defined in the following manner :—

Whether n be an integer or not, the Bessel function $J_n(z)$ of the first kind is given by

$$J_n(z)=\frac{z^n}{2^n\Gamma(n+1)}\cdot\left\{1-\frac{z^2}{2^2\,.\,\overline{n+1}\,.\,1\,!}+\frac{z^4}{2^4\,.\,\overline{n+1}\,.\,\overline{n+2}\,.\,2\,!}-\dots\right\}, \quad (1)$$

where $\Gamma(n+1)$ is a gamma function becoming identical with $n\,!$ if n be an integer.

With this is associated, when n is not an integer, the function $J_{-n}(z)$, differing from the above by a change of sign of n throughout, or,

$$J_{-n}(z)=\frac{2^n\Gamma(n)\,.\,\sin n\pi}{\pi z^n}\left\{1-\frac{z^2}{2^2\,.\,\overline{1-n}\,.\,1\,!}+\frac{z^4}{2^4\,.\,\overline{1-n}\,.\,\overline{2-n}\,.\,2\,!}-\dots\right\} \quad (2)$$

When n is integral, the first n terms of this series vanish by the factor $\sin n\pi$. An evanescent factor then appears in the subsequent denominators, and evaluating the indeterminate form presented, $J_{-n}(z)=(-)^nJ_n(z)$ in this special case.

Another function must therefore be associated with $J_n(z)$

when n is integral. The one selected is to some extent a matter of convention, so far as an additive multiple of $J_n(z)$ is concerned. We shall choose Hankel's function *, defined by

$$Y_n(z) = \left\{\frac{\partial J_n}{\partial n} - (-)^n \frac{\partial J_{-n}}{\partial n}\right\}_{n=\text{integer}}, \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

$$= -\pi \left\{\frac{J_{-n} - \cos n\pi \,.\, J_n}{\sin n\pi}\right\}_{n=\text{integer}}, \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where n is made integral after the general expressions above have been differentiated.

Expressed in series form, a little reduction shows that

$$Y_n(z) = 2J_n(z) \,.\left\{\gamma + \log\frac{z}{2}\right\} - \left(\frac{2}{z}\right)^n \left\{\overline{n-1}\,! + \frac{\overline{n-2}\,!}{1\,!}\left(\frac{z}{2}\right)^2 \right.$$
$$\left. + \frac{\overline{n-3}\,!}{2\,!}\left(\frac{z}{2}\right)^4 + \ldots\right\} - \left(\frac{z}{2}\right)^n \left\{\frac{1}{n\,!}(S_n) - \frac{1}{1\,!\,\overline{n+1}\,!}\left(\frac{1}{1} + S_{n+1}\right)\left(\frac{z}{2}\right)^4 + \ldots\right\} \quad (5)$$

where

$$S_n = 1 + \frac{1}{2} + \ldots + \frac{1}{n},$$

indicating the behaviour of the function when z is small. When z is positive (or, if complex, when its real part is positive), it may be shown that †

$$J_n(z) = \frac{1}{\pi}\int_0^\pi \cos(z\sin\theta - n\theta)\,d\theta - \frac{\sin n\pi}{\pi}\int_0^\infty e^{-n\theta - z\sinh\theta} \,.\, d\theta \,. \quad (6)$$

for all values of n.

Accordingly, it is also true that

$$J_{-n}(z) = \frac{1}{\pi}\int_0^\pi \cos(z\sin\theta + n\theta)\,d\theta + \frac{\sin n\pi}{\pi}\int_0^\infty e^{n\theta - z\sinh\theta} \,.\, d\theta. \quad (7)$$

The functions so defined are those possessing the asymptotic expansions, when z is very large in comparison with n ‡,

$$\left.\begin{aligned} J_n(z)\left(\frac{\pi z}{2}\right)^{\frac{1}{2}} &= U_n \sin\left(z - \frac{n\pi}{2} + \frac{\pi}{4}\right) + V_n \cos\left(z - \frac{n\pi}{2} + \frac{\pi}{4}\right) \\ J_{-n}(z)\left(\frac{\pi z}{2}\right)^{\frac{1}{2}} &= U_n \cos\left(z + \frac{n\pi}{2} + \frac{\pi}{4}\right) - V_n \sin\left(z + \frac{n\pi}{2} + \frac{\pi}{4}\right) \end{aligned}\right\} \quad (8)$$

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* Hankel, *Math. Ann.* i. 1869.

† *Vide e.g.* Whittaker, 'Modern Analysis,' p. 281.

‡ Hankel, *l. c.*

when n is not integral, and

$$Y_n(z)\,.\left(\frac{z}{2\pi}\right)^{\frac{1}{2}} = -U_n \cos\left(z - \frac{n\pi}{2} + \frac{\pi}{4}\right) + V_n \sin\left(z - \frac{n\pi}{2} + \frac{\pi}{4}\right), \quad (9)$$

when n is integral, provided

$$\left.\begin{aligned} U_n &= 1 - \frac{4n^2-1^2\,.\,4n^2-3^2}{2\,!\,(8z)^2} + \frac{4n^2-1^2\,.\,4n^2-3^2\,.\,4n^2-5^2\,.\,4n^2-7^2}{4\,!\,(8z)^4} - \ldots \\ V_n &= \frac{4n^2-1^2}{1\,!\,8z} - \frac{4n^2-1^2\,.\,4n^2-3^2\,.\,4n^2-5^2}{3\,!\,(8z)^3} + \ldots\ldots \end{aligned}\right\} \quad (10)$$

If $n+\frac{1}{2}$ be written for n, their relations to the forms frequently used in physical problems concerning wave-motion in or about spheres, become apparent. We proceed to obtain an expression for $J_n(z)$, when n and z are nearly equal, and each is fairly large. The more definite limitation required by the last statement will appear later.

If z (or more generally, its real part) be positive, by (6)

$$J_n(z) = \frac{1}{\pi}\int_0^\pi \cos(z\sin\theta - n\theta)\,d\theta - \frac{\sin n\pi}{\pi}\int_0^\infty e^{-n\theta - z\sinh\theta}\,.\,d\theta$$

$$= \frac{1}{\pi}\,.\,I_1 - \frac{\sin n\pi}{\pi} I_2 \quad \text{(say)}. \quad (11)$$

I_1 is the real part of I_3 (if z be real), where

$$I_3 = \int_0^\pi \exp.\,\{\iota z(\sin\theta - \theta) - \iota\,.\,\overline{n-z}\,.\,\theta\}\,d\theta$$

$$= \int_0^\pi \exp.\left\{-\frac{\iota z\theta^3}{3\,!} + \frac{\iota z\theta^5}{5\,!}\ldots\ldots - \iota\,.\,\overline{n-z}\,.\,\theta\right\}d\theta$$

$$= \left(\frac{6}{z}\right)^{\frac{1}{3}}.\int_0^{\pi\left(\frac{z}{6}\right)^{\frac{1}{3}}} dw\,.\,\exp.-\iota\left\{w^3 - \frac{z}{5\,!}\left(\frac{6}{z}\right)^{\frac{5}{3}} w^5\ldots\ldots + \rho w\right\}, \quad (12)$$

where

$$\rho = \overline{n-z}\,.\left(\frac{6}{z}\right)^{\frac{1}{3}},$$

and the variable of integration has been changed by the substitution

$$\theta = \left(\frac{6}{z}\right)^{\frac{1}{3}} w.$$

When n and z are nearly equal, and so nearly that $n-z$ is small in comparison with $z^{\frac{1}{3}}$, then the portion of the exponent (in the integrand) involving w is of less importance than that depending on w^3, and the remaining portions are, in all cases, of even less moment. Neglecting the latter for the present,

$$I_3 = \left(\frac{6}{z}\right)^{\frac{1}{3}} \int_0^{\pi\left(\frac{z}{6}\right)^{\frac{1}{3}}} dw \,.\, \exp. -\iota\{w^3 + \rho w\}. \quad . \quad . \quad . \qquad (13)$$

Thus

$$I_3 = \left(\frac{6}{z}\right)^{\frac{1}{3}} . (I_4 - I_5),$$

where

$$I_4 = \int_0^\infty dw \,.\, \exp. -\iota\{w^3 + \rho w\}, \quad . \quad . \quad . \qquad (14)$$

$$I_5 = \int_\lambda^\infty dw \,.\, \exp. -\iota\{w^3 + \rho w\},$$

$$\lambda = \pi \,.\, \left(\frac{z}{6}\right)^{\frac{1}{3}}.$$

But I_5 has an expansion in powers of the small quantity ρ whose leading term is

$$\int_\lambda^\infty dw \,.\, e^{-\iota w^3},$$

or, by the usual asymptotic evaluation of an integral of this type,

$$\frac{1}{3\iota\lambda^2} e^{-\iota\lambda^3} + \ldots .$$

of order $\frac{1}{z^{2/3}}$ at most. If ρ were not small, the order of I_5 would be higher in $1/z$.

Thus, subject to an error not greater than $z^{-\frac{2}{3}}$, I_5 may be neglected in comparison with I_4, and therefore

$$I_3 = \left(\frac{6}{z}\right)^{\frac{1}{3}} I_4 = \left(\frac{6}{z}\right)^{\frac{1}{3}} \int_0^\infty dw. \exp. -\iota\{w^3 + \rho w\}. \qquad (15)$$

The leading term of the error involved in the expression of I_3 in the form (13) is I_6, where

$$I_6 = \left(\frac{6}{z}\right)^{\frac{1}{3}} \cdot \frac{\iota z}{5!} \left(\frac{6}{z}\right)^{\frac{5}{3}} \int_0^\infty w^5 dw. \exp. -\iota\{w^3 + \rho w\}. \quad . \qquad (16)$$

The integral in this expression has order zero in z, and the error has therefore an order $\frac{1}{z}$, which is again $z^{-\frac{2}{3}}$ relatively to that of the portion retained. Finally, with an error not greater than $\frac{1}{z}$, I_1 is the real part of I_3, where

$$I_3 = \left(\frac{6}{z}\right)^{\frac{1}{3}} \int_0^\infty dw . \exp. -\iota \left\{w^3 + \rho w\right\},$$

in which $\rho = \overline{n-z} . \left(\frac{6}{z}\right)^{\frac{1}{3}}$. . . . . (17)

Now when n and z are great,

$$I_2 = \int_0^\infty e^{-n\theta - z \sinh \theta} \, d\theta$$

is of order $\frac{1}{z}$, and may also therefore be ignored. Thus to order $\frac{1}{z}$, when $\overline{n-z} . \left(\frac{6}{z}\right)^{\frac{1}{3}}$ is not large compared with unity,

$$J_n(z) = \frac{1}{\pi} . \left(\frac{6}{z}\right)^{\frac{1}{3}} \int_0^\infty \cos \left\{ w^3 + \overline{n-z} \left(\frac{6}{z}\right)^{\frac{1}{3}} w \right\} dw, \quad . \quad (18)$$

which is a multiple of Airy's Integral *.

In another connexion, Stokes has considered the properties of this integral in great detail. The tables given by Stokes and Airy may be at once transformed into tables of the Bessel functions whose order and argument are nearly equal. If tables be required to a higher order than this integral will furnish, the necessary correction may be readily made by keeping certain terms ignored in the above discussion, but this will not usually be necessary. We note that to order $\frac{1}{n}$,

$$J_n(n) = \frac{1}{\pi} . \left(\frac{6}{n}\right)^{\frac{1}{3}} \int_0^\infty \cos w^3 . dw$$

$$= \Gamma\left(\frac{1}{3}\right) . 2^{-\frac{2}{3}} 3^{-\frac{1}{6}} \pi^{-1} n^{-\frac{1}{3}}. \quad . \quad . \quad . \quad (19)$$

But this formula, although only formally proved true to this order, has in reality a much wider application in practice, a property shared by the companion formulæ proved in this paper. Thus on comparison with tables †, the expression last written gives $J_7(7)$ correctly to three places of decimals,

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* Airy, Cambr. Phil. Trans. vol. vi. p. 379, vol. viii, p. 595. Stokes, Camb. Phil. Trans. vol. ix; Math. & Phys. Papers, ii, p. 329 *et seq.*

† *E. g.* Gray and Matthews' Treatise on Bessel Functions.

and $J_{10}(10)$ to four places. This indicates that n does not need to be very great for the formulæ to give good approximations, although these approximations rapidly become more valid as n increases.

This comparison made in the case in which the formulæ will necessarily be least accurate, is of more practical value than a refined analysis of the exact validity of the investigation, which would be extremely cumbrous.

By an expansion of (18), it is readily shown that if

$$\rho = \overline{n-z}\left(\frac{6}{z}\right)^{\frac{1}{3}},$$

$$J_n(z) = \frac{1}{3\pi}\cdot\left(\frac{6}{z}\right)^{\frac{1}{3}}\left\{\Gamma\left(\frac{1}{3}\right)\cos\frac{\pi}{6} + \frac{\rho}{1!}\Gamma\left(\frac{2}{3}\right)\cos\frac{5\pi}{6}\right.$$
$$\left. + \frac{\rho^2}{2!}\Gamma\left(\frac{3}{3}\right)\cos\frac{9\pi}{6} + \ldots\right\} \quad (20)$$

when n and z are nearly equal.

The expansion of $J_{-n}(z)$ may be derived in a similar manner from the formula (z positive)

$$J_{-n}(z) = \frac{1}{\pi}\int_0^{\pi}\cos\left(z\sin\theta + n\theta\right)d\theta + \frac{\sin n\pi}{\pi}\int_0^{\infty} e^{n\theta - z\sinh\theta}\,d\theta$$

$$= \frac{I_1}{\pi} + \sin n\pi\,\frac{I_2}{\pi} \quad \text{(say)} \;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (21)$$

But, to the same order as in all the above calculations,

$$I_2 = \int_0^{\infty} d\theta \,\text{exp.}\left\{\overline{n-z}\,\theta - \frac{z}{6}\,\theta^3\right\}$$

$$= \left(\frac{6}{z}\right)^{\frac{1}{3}}\int_0^{\infty} d\theta\,.\,\text{exp.}\left\{-\theta^3 + \overline{n-z}\left(\frac{6}{z}\right)^{\frac{1}{3}}\theta\right\}$$

$$= \frac{1}{3}\cdot\left(\frac{6}{z}\right)^{\frac{1}{3}}\left\{\Gamma\left(\frac{1}{3}\right) + \rho\Gamma\left(\frac{2}{3}\right) + \frac{\rho^2}{2!}\Gamma\left(\frac{3}{3}\right) + \ldots\right\} \;. \quad (22)$$

where ρ has its previous value, and is small.

Again,

$$I_1 = \int_0^{\pi}\cos\left(z\sin\theta + n\theta\right)d\theta$$

$$= \int_0^{\pi}\cos\left(z\sin\theta + n\pi - n\theta\right)\,d\theta,$$

and is the real part of I_3, provided that

$$I_3 \exp. - \iota n\pi = \int_0^\pi d\theta . \exp. \iota . \{z \sin\theta - n\theta\}.$$

Therefore, as in the previous calculation, to order $\frac{1}{z}$,

$$I_3 . \exp. - \iota n\pi = \left(\frac{6}{z}\right)^{\frac{1}{3}} \int_0^\infty dw . \exp. - \iota \left\{ w^3 + \overline{n-z}\left(\frac{6}{z}\right)^{\frac{1}{3}} w \right\};$$

and if ρ is very small, it follows that

$$I_1 = \frac{1}{3} . \left(\frac{6}{z}\right)^{\frac{1}{3}} \left\{ \Gamma\left(\frac{1}{3}\right) \cos\left(n\pi - \frac{\pi}{6}\right) + \frac{\rho}{1!}\Gamma\left(\frac{2}{3}\right)\cos\left(n\pi - \frac{5\pi}{6}\right) - \ldots \right\} \quad (23)$$

On reduction with (22),

$$\begin{aligned} J_{-n}(z) &= \frac{I_1}{\pi} + \sin n\pi \, \frac{I_2}{\pi} \\ &= \frac{2}{3\pi} . \left(\frac{6}{z}\right)^{\frac{1}{3}} \left\{ \Gamma\left(\frac{1}{3}\right) \sin\frac{\pi}{3} \cos\left(n\pi - \frac{\pi}{3}\right) \right. \\ &\quad + \frac{\rho}{1!}\Gamma\left(\frac{2}{3}\right) \sin\frac{2\pi}{3} \cos\left(n\pi - \frac{2\pi}{3}\right) \\ &\quad \left. + \frac{\rho^2}{2!}\Gamma\left(\frac{3}{3}\right) \sin\frac{3\pi}{3} \cos\left(n\pi - \frac{3\pi}{3}\right) + \ldots \right\} \quad (24) \end{aligned}$$

When n is an integer this makes $J_{-n}(z) = (-)^n J_n(z)$ in accordance with the original definition of the functions. We note that to order $\frac{1}{n}$,

$$J_{-n}(n) = \Gamma\left(\frac{1}{3}\right) . 2^{\frac{1}{3}} . 3^{-\frac{1}{6}} . \pi^{-1} . n^{-\frac{1}{3}} . \cos\left(n\pi - \frac{\pi}{3}\right), \quad (25)$$

to which the remarks made on (19) apply.

It follows readily that when ρ is small,

$$\begin{aligned} Y_n(z) &= -\pi \left\{ \frac{J_{-n} - \cos n\pi J_n}{\sin n\pi} \right\}_{n = \text{int.}} \\ &= -\frac{1}{3} . \left(\frac{6}{z}\right)^{\frac{1}{3}} \left\{ \Gamma\left(\frac{1}{3}\right)\left(1 + \sin\frac{\pi}{6}\right) + \rho\Gamma\left(\frac{2}{3}\right)\left(1 + \sin\frac{5\pi}{6}\right) \right. \\ &\quad \left. + \frac{\rho^2}{2!}\Gamma\left(\frac{3}{3}\right)\left(1 + \sin\frac{9\pi}{6}\right) + \ldots \right\} \quad (26) \end{aligned}$$

ρ being $\overline{n-z} . \left(\frac{6}{z}\right)^{\frac{1}{3}}$, to order $\frac{1}{n}$, and in particular,

$$\mathrm{Y}_n(n) = -\Gamma\left(\frac{1}{3}\right) . \, 2^{-\frac{2}{3}} 3^{\frac{1}{3}} n^{-\frac{1}{3}} \quad . \quad . \quad . \qquad (27)$$

with the same criticisms as (25, 19).

When ρ is not small in comparison with unity, the results are best left as integrals to be calculated by Airy's method *.

If

$$\mathrm{F}(\rho) = \int_0^\infty \cos(w^3 + \rho w) dw \quad . \quad . \quad . \quad . \qquad (28)$$

$$f(\rho) = \int_0^\infty \sin(w^3 + \rho w) \, dw \quad . \quad . \quad . \quad . \qquad (29)$$

$$\rho = \overline{n - z} \, . \left(\frac{6}{z}\right)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

Then

$$\mathrm{J}_n(z) = \frac{1}{\pi} \, . \left(\frac{6}{z}\right)^{\frac{1}{3}} \mathrm{F}(\rho) . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (31)$$

$$\mathrm{J}_{-n}(z) = \left(\frac{6}{z}\right)^{\frac{1}{3}} \left\{ \frac{\cos n\pi}{\pi} \mathrm{F}(\rho) + \frac{\sin n\pi}{\pi} f(\rho) \right\}$$

$$+ \left(\frac{6}{z}\right)^{\frac{1}{3}} . \, \frac{\sin n\pi}{\pi} \, . \, e^{\frac{\iota\pi}{6}} \left\{ \mathrm{F}\left(\rho e^{-\frac{\iota\pi}{3}}\right) + \iota f\left(\rho e^{-\frac{\iota\pi}{3}}\right) \right\} \qquad (32)$$

$$\mathrm{Y}_n(z) = -\left(\frac{6}{z}\right)^{\frac{1}{3}} \left\{ e^{\frac{\iota\pi}{3}} \mathrm{F}\left(\rho e^{-\frac{\iota\pi}{3}}\right) + e^{-\frac{\iota\pi}{3}} f\left(\rho e^{-\frac{\iota\pi}{3}}\right) \right\} \, . \qquad (33)$$

These may be proved by the application of contour integration to the integral previously called I_2.

The reduction of the Bessel functions to a dependence on Airy's integral and its associate is important in that it furnishes a means of comparing the results of the ordinary theory of diffraction problems, as developed by Fresnel and others, with those of the electromagnetic theory. The latter has not hitherto led to these integrals, but their connexion, through the Bessel functions to which dynamical theory naturally leads, may now be seen.

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* *Loc. cit.*

XXI. *The Genesis of Ions by Collision of Positive and Negative Ions in a Gas. Experiments on Argon and Helium.*

By E. W. B. Gill, *B.A., Christ Church, Oxford, and* F. B. Pidduck, *B.A., Fellow of Queen's College, Oxford* *.

THE present paper contains an account of some experiments in verification of the theory of ionization by collision of positive and negative ions †, conducted on the monatomic gases argon and helium.

The theory may be summarized as follows:—Let a constant electric force be maintained between parallel plate electrodes, the distance d (in centimetres) being alterable. A number n_0 of negative ions are set free per second by ultra-violet light from the negative plate, and n ions arrive at the positive plate per second. Then if each negative ion produces α ions of each kind, and each positive ion β, in moving through a centimetre under the given force,

$$\frac{n}{n_0}=\frac{(\alpha-\beta)e^{(\alpha-\beta)d}}{\alpha-\beta e^{(\alpha-\beta)d}}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If also X is the electric force in volts per centimetre, and p the pressure in millimetres of mercury,

$$\frac{\alpha}{p} \text{ is a function of } \frac{X}{p}, \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{\beta}{p} \text{ is a function of } \frac{X}{p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (1) the sparking distance a is given by

$$\alpha-\beta e^{(\alpha-\beta)a}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The equations (2), (3), and (4) lead to Paschen's law that the sparking potential depends only on the mass of gas between the electrodes.

On account of the fact that continuous production of new gas was inconvenient, the apparatus previously used was slightly modified. It was arranged so that after an experiment the gas could be pumped up into a reservoir, while the small residue remaining over was pumped out into the air before beginning a fresh experiment. The effect of the small leak of the apparatus (about ·01 mm. in 24 hours) was thus reduced to a minimum.

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* Communicated by Prof. J. S. Townsend, F.R.S.

† For previous experiments on other gases, see papers by J. S. Townsend, Phil. Mag. Nov. 1903; J. S. Townsend and H. E. Hurst, Phil. Mag. Dec. 1904; and H. E. Hurst, Phil. Mag. April 1906.

As usual, the currents produced were measured by means of an induction-balance method with a condenser and high-resistance junction-potentiometer, the electrometer being used only as a detector, or rather to find the proportional part between consecutive junctions.

2. After a number of experiments had been made, the gas was purified in order to see if the small amount of air that got in during an experiment could have affected the results. The purification was carefully carried out by passing sparks through the gas in the presence of oxygen, over a solution of potassium hydroxide, the surplus oxygen being removed by means of copper strongly heated in a hard glass tube. Practically the same results were obtained after the gas was purified and dried. Spectroscopic examination showed the characteristic lines of argon with no trace of the nitrogen bands.

The results of the experiments are given in the following tables. Here q is the observed current for the constant force X for different distances d between the plates. The values of α and β were found so that the numbers n calculated from the formula (1) should coincide as nearly as possible with the currents q.

TABLE I.—Argon, pressure 10 mms.

d...........	·1.	·2.	·3.	·4	·5.	·6.	·9.	1·0.
$X=201$ q.........	1·048	1·090	1·149					
$\alpha=·47$ n.........	1·048	1·099	1·151					
$X=505$ q	1·71	3·26	5·79	10·6	18·5	35·5	284	905
$\alpha=5·88$ $\beta=·010$ n	1·80	3·26	5·89	10·6	19·5	35·5	286	896

TABLE II.—Argon, pressure 4 mms.

d	·2.	·3.	·4.	·6.	·8.	·9.
$X=410$ q	5·26	......	27·6	150	1070	4420
$\alpha=8·29$ $\beta=·00323$ n	5·26	......	27·7	152	1080	5110
$X=610$ q	13·6	54·2	295			
$\alpha=12·95$ $\beta=·0300$ n	13·6	54·2	295			

TABLE III.—Argon, pressure 2 mms.

	d	·1.	·2.	·3.	·4.	·6.
$X=401$	q	2·31	5·67	......	36·2	1140
$\alpha=8{\cdot}61$ $\beta={\cdot}043$	n	2·37	5·67	......	36·2	1140
$X=618$	q	3·51	13·2	66·2		
$\alpha=12{\cdot}53$ $\beta={\cdot}116$	n	3·51	13·2	66·2		

TABLE IV.—Argon, pressure 1 mm.

	d	·1.	·2.	·3.	·4.	·5.	·6.	·7.
$X=309$	q	1·84	3·40	6·24	12·6	24·4	55·2	180
$\alpha=6{\cdot}08$ $\beta={\cdot}058$	n	1·84	3·41	6·39	12·3	24·8	56·5	187
$X=401$	q	2·26	4·78	11·2	26·6	93·0		
$\alpha=7{\cdot}70$ $\beta={\cdot}0934$	n	2·17	4·78	10·9	27·6	96·4		
$X=517$	q	2·21	5·77	14·9	50·1			
$\alpha=8{\cdot}50$ $\beta={\cdot}129$	n	2·36	5·77	15·6	48·0			
$X=615$	q	2·49	6·87	24·4				
$\alpha=9{\cdot}22$ $\beta={\cdot}260$	n	2·49	7·01	24·4				

TABLE V.—Argon, pressure ·66 mm.

	d	·1.	·2.	·3.	·4.	·5.	·6.	·7.
$X=301$	q	1·72	2·96	......	9·75	......	36·6	107
$\alpha=5{\cdot}44$ $\beta={\cdot}0737$	n	1·72	3·00	......	9·51	......	37·0	100
$X=402$	q	1·85	3·47	6·73	14·5	36·8		
$\alpha=6{\cdot}09$ $\beta={\cdot}160$	n	1·85	3·48	6·80	14·4	38·2		

The relation between α/p, β/p, and X/p is shown in the accompanying figures, and it is evident that the points as determined experimentally all lie on one curve.

Fig. 1.—Argon.

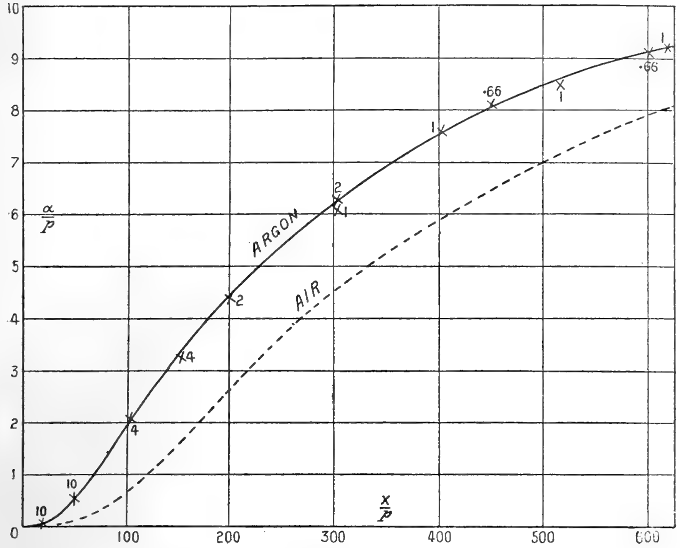
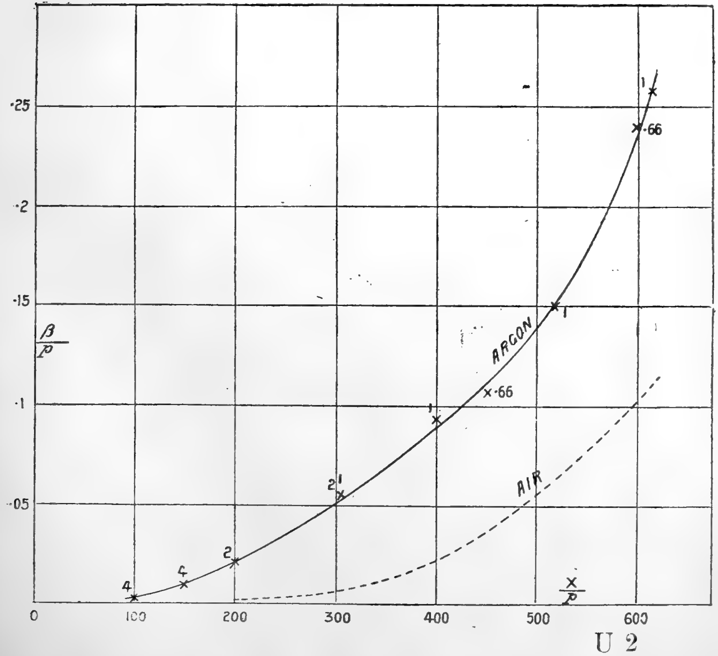


Fig. 2.—Argon.



The corresponding curves for air have been included for comparison, and it will be seen that α and β are both greater for argon under the same conditions of pressure and electric force.

3. The experimental difficulties connected with the manipulation of helium were greater. The first experiments were made on a purchased sample, and on a larger quantity which was kindly given by Professor Ramsay containing at least 98 per cent. of helium.

As the theory holds equally well for mixtures as for pure gases, we give here the results of the experiments. The gas was afterwards purified and similar experiments were made, which gave much higher numbers for β and lower sparking potentials. The experiments on the slightly impure gas are given in the following tables, as they are of interest in showing the effects of small impurities in the case of helium by comparison with the later experiments, and also in showing that the same theory holds good for this gas.

Table VI.—Helium, pressure 13 mms.

d	·2.	·4.	·6.
X=404 q	6·50	44·8	531
$\alpha=9{\cdot}32$ $\beta={\cdot}0179$ n	6·50	44·8	531

Table VII.—Helium, pressure 10 mms.

d	·1.	·2.	·3.	·4.	·5.	·6.
X=101 q	1·13	1·27	1·43			
$\alpha=1{\cdot}19$ n	1·13	1·27	1·43			
X=385 q	2·61	5·84	14·8	38·3	123	503
$\alpha=8{\cdot}95$ $\beta={\cdot}0252$ n	2·45	6·03	15·1	39·2	114	515

Table VIII.—Helium, pressure 8 mms.

d	·2.	·4.	·5.	·7.	·8.
X=305 q	4·04	17·2	34·4	175	8160
$\alpha=6{\cdot}91$ $\beta={\cdot}0206$ n	3·99	16·4	34·3	195	9210

TABLE IX.—Helium, pressure 7 mms.

d …………	·1.	·2.	·3.	·4.
$X=140$ q …………	1·32	1·61	2·33	3·03
$\alpha=2·77$ n …………	1·32	1·74	2·29	3·02

TABLE X.—Helium, pressure 6 mms.

d …………	·1.	·2.	·3.	·4.	·6.	·7.
$X=305$ q ………	1·89	3·73	……	14·0	64·7	226
$\alpha=6·45$ $\beta=·0436$ n ………	1·91	3·66	……	14·0	68·6	216
$X=506$ q ………	2·48	6·55	18·9	82·0		
$\alpha=9·12$ $\beta=·142$ n ………	2·51	6·55	18·9	82·0		
$X=772$ q ………	3·14	10·2	95·0			
$\alpha=10·8$ $\beta=·360$ n ………	3·02	10·6	92·5			

TABLE XI.—Helium, pressure 4 mms.

d …………	·1.	·2.	·3.	·4.	·5.	·6.	·7.
$X=304$ q ………	2·10	3·77	6·95	13·3	25·8	53·0	216
$\beta=5·80$ $\beta=·0740$ n ………	2·13	3·79	6·84	13·7	25·3	51·6	216

TABLE XII.—Helium, pressure 2 mms.

d …………	·1.	·2.	·3.	·4.	·5.	·6.	·8.
$X=304$ q ………	1·54	2·27	3·37	5·07	7·96	13·3	68·5
$\alpha=3·70$ $\beta=·173$ n ………	1·51	2·22	3·28	5·02	7·93	13·4	73·0
$X=402$ q ………	1·60	2·26	3·84	6·05	11·5	29·1	
$\alpha=4·07$ $\beta=·300$ n ………	1·51	2·33	3·72	6·29	11·8	30·4	

The curves giving the values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ in terms of $\frac{X}{p}$

for the unpurified helium are appended. The corresponding curves for hydrogen are given in these diagrams, as this

Fig. 3.—HELIUM.

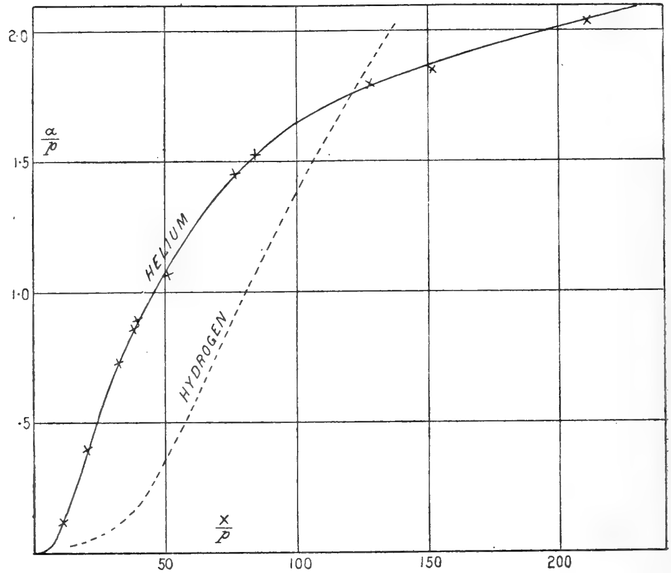
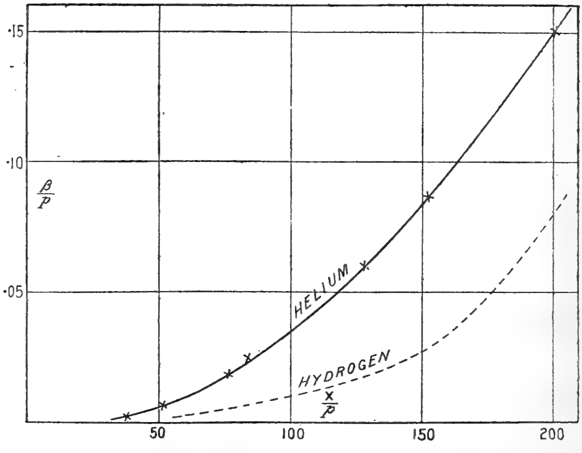


Fig. 4.—HELIUM.



gas most nearly approaches helium in its behaviour in this respect. It is thus seen from these curves that both positive and negative ions ionize the molecules of helium to a greater extent than the molecules of other gases when small electric forces are acting.

4. For those cases in the preceding tables in which more than three currents were measured the agreement of the n and q numbers affords a satisfactory verification of Prof. Townsend's theory. Further confirmation is obtained by calculation of the sparking potential under the given force and its comparison with experiment. In the following tables the sparking distance "a" for the given pressure and electric force was calculated from the formula $\alpha-\beta\epsilon^{(\alpha-\beta)a}=0$. The plates were set at the distance a apart and the sparking potential V determined at the first appearance of a flash in the gas. The increase of V by a volt or two at most was found sufficient to maintain a continuous current. The agreement between V as determined experimentally and the product $a\times X$ may be seen from the following tables.

Table XIII.—Argon, Sparking Potentials.

X.	p.	a.	$a\times$X.	V.
505	10	1·087	549	549
610	4	·471	287	276
410	4	·947	388	380
618	2	·378	234	233
401	2	·618	248	245
615	1	·399	245	248
517	1	·482	249	244
401	1	·580	233	235
309	1	·770	248	237
402	·66	·599	241	248
301	·66	·802	242	238

Table XIV.—Helium (before purification with liquid air), Sparking Potentials.

X.	p.	a.	$a\times$X.	V.
404	13	·674	272	—
305	8	·845	258	262
385	10	·650	250	252
305	6	·781	238	236
304	4	·760	231	234
506	6	·462	234	232
772	6	·326	254	246
304	2	·863	262	262
402	2	·694	279	274

In figures 5 and 6, V and $a \times X$ are shown together as functions of $p \times a$, and Paschen's law is seen to hold. The observed sparking potential is marked with a small circle and the calculated value with a cross.

Fig. 5.—ARGON.

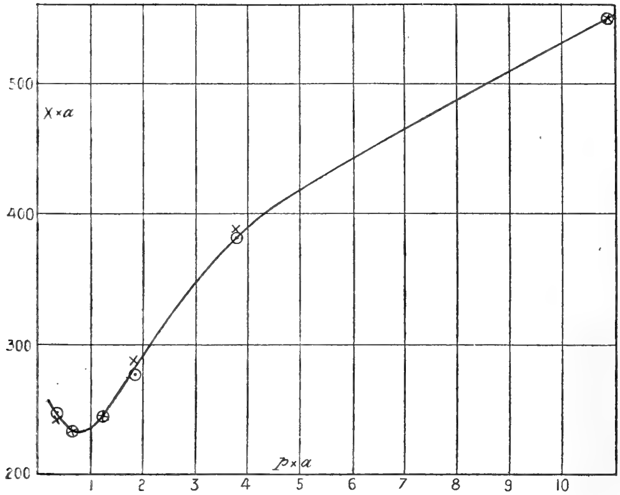
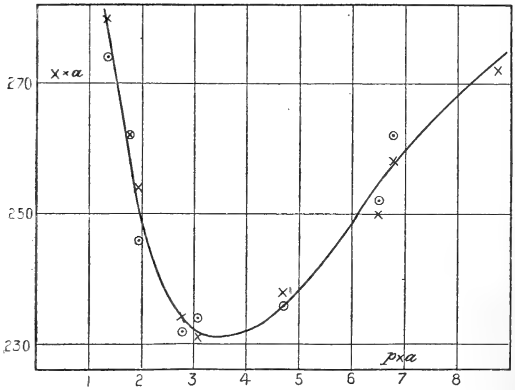


Fig. 6.—HELIUM.



5. After the above experiments were made with helium containing small impurities, it was considered desirable to try some experiments with the gas in as pure a state as it would be possible to obtain. For this purpose the helium was purified by passing it into a tube of charcoal surrounded by liquid air. The tube containing the charcoal was in air-tight connexion

with the rest of the apparatus, so that the experiments on the conductivity could be performed immediately after the gas was purified. All the experiments made under these conditions showed that the sparking potentials were lowered by purifying the gas. A complete set of experiments were not made, but determinations were made at definite pressures and forces to compare the results with those corresponding to the slightly impure gas. All our experiments lead to the conclusion that purification lowers the minimum sparking potential in agreement with the observations of Strutt*. There is, however, no numerical agreement between the two observations. Even with impure helium the minimum sparking potential was found to be 231 volts, as against Strutt's lowest value of 261 volts. After purification, as will be seen later, the most probable value to be expected for this quantity is 201 volts, an error of more than 10 volts either way being improbable.

It was found that after the passage of a spark not only the currents but also the sparking potential was affected, in such a way that an addition of twenty volts was sometimes necessary to spark again just after the first spark had passed. The passage of a spark in the reverse direction facilitated recovery, thus pointing to some polarization or other effect of the spark discharge on the zinc electrodes employed.

For low values of X/p and large values of $p \times a$ the purification did not have very great effect. In the following table the most probable values of α/p for the pure gas are shown for small values of X/p, the corresponding α/p's taken from the mean of observations on the impure gas being shown side by side.

TABLE XV.

$\frac{X}{p}$.	$\frac{a}{p}$ for pure helium.	$\frac{a}{p}$ for impure helium.
10	·12	·12
20	·40	·39
30	·77	·67
40	1·0	·89
50	1·20	1·06
60	1·35	1·21

The values of β/p for such small values of X/p are difficult to determine accurately, but it was clear that the effect of the positive ions is very much increased by purification. Thus for $X/p=40$, β is more than doubled by purification.

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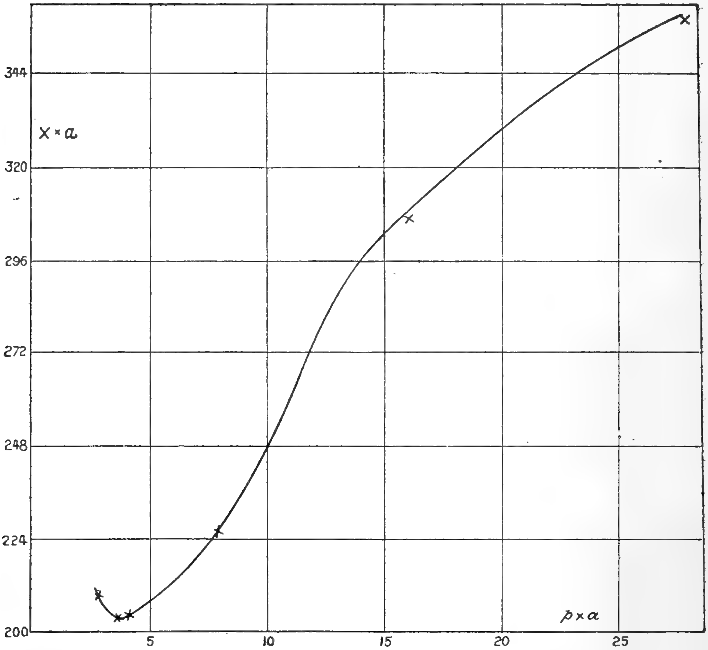
* Hon. R. J. Strutt, Phil. Trans. A, cxciii. p. 377 (1900).

A corresponding provisional table of sparking potential is also given.

TABLE XVI.

$p \times a$.	V for pure helium.	V for impure helium.
2·8	209	234
3·5	203	231
4	205	231
8	226	268
12	274	
16	307	
28	358	

Fig. 7.—PURE HELIUM.



The experiments on helium, particularly at high pressures, were rendered more difficult by an effect analogous to that observed by Prof. Townsend and Mr. Hurst in air and hydrogen, though it was much greater. The elucidation of this effect will shortly be attempted, as we hope to make further experiments when a continuous supply of liquid air will be at our disposal.

In conclusion, we wish to express our best thanks to Prof. Townsend, in whose laboratory the research was conducted, for the facilities he has been ever ready to afford, and for the valuable encouragement and advice he has given us during the work.

XXII. *On the Relative Activity of the Emanation and the Active Deposit from Thorium and from Actinium.* By HOWARD L. BRONSON, *Ph.D.*[*]

MANY important calculations in radioactivity are based on the assumption that each atom of the various radioactive bodies, at each transformation, gives off either one or no α particle. This is the most natural assumption, and, in the case of radium and its transformation products, has the support of many theoretical considerations. It is also supported by the fact that radium, radium emanation, radium A, and radium C, each produces about the same amount of ionization, when the four substances are in equilibrium (Rutherford, 'Radioactivity,' p. 396). This latter point was verified by the writer in the case of radium emanation, radium A, and radium C.

Dr. Boltwood suggested that the writer should investigate this question in the case of thorium and its active deposit, as he had evidence that the results obtained in the case of radium did not hold true in the case of thorium. The results obtained in this investigation entirely confirm Dr. Boltwood's view, and led the writer to investigate the same question in the case of actinium.

Method and Apparatus.

The method adopted was to compare directly the ionization produced by the emanation and the active deposit when the two substances were in equilibrium. This could be easily done in the case of both thorium and actinium, because the transformation periods of their emanations are very short compared with those of their active deposits. The thorium, or actinium, was placed between two layers of filter-paper in a small vessel, and a current of air was drawn through this filter-paper and into the testing vessel by means of a filter-pump. The air current was kept fairly steady by placing between the pump and the testing vessel a large air-chamber, which was connected to the outside air by a mercury trap. After the emanation had been drawn through the testing vessel for a known length of time, or until the active deposit had reached a maximum value, the ionization current due to the sum of the emanation and active deposit was measured. The air current was then cut off and the emanation allowed to decay to a negligible amount, and the ionization current due to the active deposit alone was measured. The difference between these two currents, except

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[*] Communicated by Professor E. Rutherford, F.R.S.

for a very small correction, was a measure of the ionization due to the emanation. If the active deposit had not reached a maximum, it was easily calculated, since the rates of transformation of all the products involved were known.

All the measurements were made by means of an electrometer and "constant deflexion method," and some of them were verified by means of the "rate" method to insure that no serious mistakes were being made. Two cylindrical testing vessels were used. Both were 40 cms. long, and had central electrodes about 0·2 cm. in diameter. The diameters of the testing vessels were 18 cms. and 3·6 cms. respectively. The largest one allowed the α particles of the active deposit on the central electrode to be entirely absorbed in the air, except at the ends. The smaller one made the mean free path of the α particles from the different active substances more nearly equal.

All the experiments were repeated several times under as different conditions as possible. The quantity of thorium and actinium used, the velocity of the air current, and the saturation potential on the testing vessel, were all changed several times. The saturation potential was changed from 80 to 600 volts, and both positive and negative values were used. Thus the active deposit was sometimes deposited on the central electrode and sometimes on the cylindrical surface. In order to make sure of this point for the sake of calculation, the central electrode was removed and tested, and found to have on its surface more than 90 per cent. of the active deposit, when the outside of the testing vessel was connected to the positive pole of the battery. A second testing vessel was put in series with the first one, to make sure that none of the active deposit was drawn through by the air current. No evidence of this was ever detected.

Measurements and Calculations.

Table I. gives a sample set of observations obtained with the thorium emanation in the larger testing vessel.

The time was reckoned from the starting of the emanation through the testing vessel. The maximum value of the active deposit was calculated on the assumption that thorium A decays to half value in 10·6 hours. There are small irregular variations in the ionization currents, which are due to slight changes in the velocity of the air current, and to the humidity, which affects considerably the emanating power of the thorium.

At the end of 88 hours the air current and potential of the testing vessel were changed and another set of measurements taken. Several such changes were made, and the

TABLE I.

Time.	Activities.				
	Th. Emanation +Active Deposit.	Active Deposit.	Calc. Max. of Active Deposit.	Emanation.	Ratio.
0	731	...	...	731	
38	960	248	271	712	·38
45	962	255	269	707	·38
62	990	265	270	725	·37
72	945	260	262	685	·38
87	975	263	264	711	·37

measurements were continued for 10 consecutive days. A similar set of observations was taken with the smaller testing vessel. The experiments with actinium required much less time, because the transformation period of its active deposit is much shorter than that of thorium. In the case of actinium also the experimental conditions were varied as much as possible. As would be expected, the ratio of the ionization due to the active deposit to that due to the emanation was affected by the size of the vessel and the location of the active deposit. None of the other changes in the experimental condition affected this ratio more than a few per cent. Most of these variations could probably be removed by sufficient care, but this was unnecessary for the purpose of the present paper, as the accuracy of the measurements is quite as great as that of the assumptions on which the calculations are based.

Now Hahn (Phil. Mag. June and July 1906) has shown that the active deposit from thorium contains two α ray products, thorium B and thorium C, and that the maximum ranges of their α particles in air are 5·0 and 8·6 cms. respectively. He has also shown that the α rays from these two products produce about the same number of ions per cm. of path. Now if the α particle from thorium emanation, which has a range in air of 5·5 cms., is similar to those from thorium B and thorium C, and if it produces the same number of ions per cm. (when it has the same velocity), then we should expect that the ionization produced by the active deposit would certainly be greater than that produced by the emanation. The exact value of the ratio would, of course, depend upon the mean free paths and the velocities of the different α particles in the given vessel. The results given in Table I. show that the ionization due to the active deposit, instead of being greater, was less than one half that due to the emanation.

Before attempting any explanation of the above results, we will calculate with some degree of accuracy the relative activities that would be expected from the emanation and its active deposit under the conditions of the above experiment. In order to calculate the mean free paths of the α particles from the different substances, certain assumptions were made: first, that the cylinder was infinite in length, that is, the effect of the ends was neglected ; second, that the emanation was distributed uniformly throughout the cylinder ; third, that the α particles were shot off equally in every direction, and therefore that only one half of those from the active deposit produced any ions in the air. For the purpose of this calculation, the first assumption should be approximately true, for the emanation was drawn diagonally across the testing vessel, entering about 5 cms. from one end and leaving the vessel on the opposite side and about the same distance from the other end. There should, therefore, be very little emanation or active deposit near the ends. In any case, any errors introduced into the calculations by this assumption would affect the mean free paths of the α particles from the emanation and active deposit by nearly the same amount, and would therefore have very little effect on their ratio. It is difficult to estimate the accuracy of the second assumption, but the air current was so rapid at the entrance to the vessel that the emanation should have been well distributed. The third assumption is commonly made in all radioactive calculations.

On these assumptions the mean free path, in the larger testing vessel, of the α particles from the active deposit from thorium would be half their maximum range, since one half the α particles were absorbed by the metal and the other half have their maximum range in air. This gives $\frac{5\cdot0+8\cdot6}{2}=6\cdot8$ cms. as the sum of the mean free paths of the α particles from thorium B and thorium C.

In calculating the mean free path of the α particles from the emanation, it was found easier to use a geometrical than an analytical method. On a large sheet of clear mica were drawn concentric circles from 1 to 9 cms. in radius and radial lines cutting these circles every 10°. In order to find the mean free path of α particles shot out from a given point, two sections of the cylinder were taken through this point, one containing the axis and the other at right angles to it. The centre of the concentric circles on the mica was then placed at the given point in each section in turn, and the length of the free path along each radial line was read off directly. The average of the measurements in the two planes, in general, gives a good value for the mean free path of an α particle starting from the given point.

Table II. gives the results of the measurements for the mean free path of the α particle of thorium emanation in the larger testing vessel.

TABLE II.

I.	II *a*.	II *b*.	II.	III.
0·5	5·5	5·5	5·5	2·75
1·5	5·5	5·5	5·5	8·25
2·5	5·5	5·5	5·5	13·75
3·5	5·5	5·5	5·5	19·25
4·5	5·3	5·3	5·3	23·85
5·5	5·1	4·9	5·0	27·50
6·5	4·7	4·5	4·6	29·90
7·5	4·1	3·9	4·0	30·00
8·5	3·3	3·0	3·2	27·20
40·5				182·5

$$\frac{182\cdot5}{40\cdot5} = 4\cdot5 = \text{mean free path.}$$

Column I. gives the distance of the point from the axis of the cylinder. Column II. is the mean of II *a*. and II *b*. which give respectively the mean free paths of α particles in the two perpendicular planes. Since the emanation is uniformly distributed in the vessel, the number of atoms of the emanation at a given distance from the axis of the cylinder is proportional to their distance from the axis. Therefore it is necessary to take the sum of the product of columns I. and II. and divide by the sum of column I. in order to get the mean free path of the α particles for the entire cylinder. The products of columns I. and II. is given in column III.

We have seen that the sum of the mean free paths of the α particles from thorium B and thorium C is 6·8 cms. This value divided by 4·5 cms. gives 1·51, which should be the ratio of the ionization due to the active deposit to that due to the emanation, if an atom of each substance in breaking up throws out one α particle, and if the number of ions produced per cm. by an α particle is the same for each cm. of its path. That the latter assumption is not strictly true has been shown by Bragg, McClung, Hahn, as well as by the writer. This introduces only a small correction, however, and will be discussed later. Now the measured ratio of the activities of the active deposit and the emanation was about

·38 (see Table I.), or almost exactly one quarter of the calculated ratio.

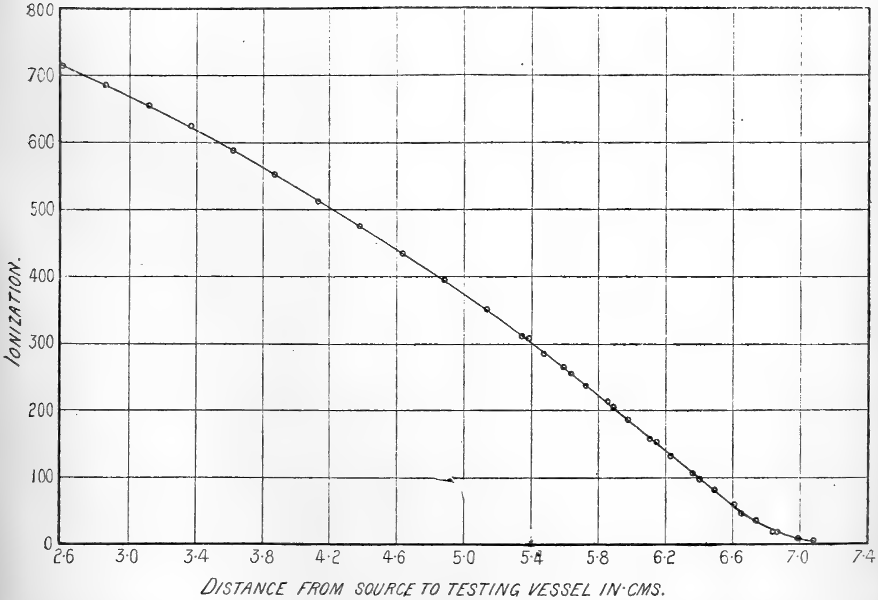
A complete summary of the measurements and calculations for thorium and actinium is given in Table III.

TABLE III.

I. Products.	II. Vessel.	III. Max. range in air.	IV. Mean free path in vessel.	V. Ratio of paths. Active deposit. / Emanation.	VI. Cal. Ratio of ionizations. Active deposit. / Emanation.	VII. Measured ratio of ionizations.	VIII. Measured ratio × 4.
Th. Emanation Th. B ……… Th. C ………	18×40 on central electrode.	5·5 5·0 8·6	4·5 $\frac{5{\cdot}0}{2}$ $\frac{8{\cdot}6}{2}$	1·51	1·48	·38	1·52
Th. Emanation Th. B ……… Th. C ………	18×40 on cyl. surface.	5·5 5·0 8·6	4·5 $\frac{4{\cdot}65}{2}$ $\frac{7{\cdot}75}{2}$	1·38	1·33	·34	1·36
Th. Emanation Th. B ……… Th. C ………	3·6×40 on central electrode.	5·5 5·0 8·6	2·68 $\frac{3{\cdot}14}{2}$ $\frac{3{\cdot}88}{2}$	1·31	1·28	·34	1·36
Th. Emanation Th. B ……… Th. C ………	3·6×40 on cyl. surface.	5·5 5·0 8·6	2·68 $\frac{3{\cdot}68}{2}$ $\frac{4{\cdot}65}{2}$	1·56	1·56	·40	1·60
		………	………	………	………		Measured ratio × 2.
Act. Emanation Act. B ……	18×40 on central electrode.	5·8 5·5	4·8 $\frac{5{\cdot}5}{2}$	·57	·61	·31	·62
Act. Emanation Act. B ……	18×40 on cyl. surface.	5·8 5·5	4·8 $\frac{5{\cdot}1}{2}$	·53	·57	·28	·56
Act. Emanation Act. B ……	3·6×40 on central electrode.	5·8 5·5	2·73 $\frac{3{\cdot}26}{2}$	·60	·65	·33	·66
Act. Emanation Act. B ……	3·6×40 on cyl. surface.	5·8 5·5	2·73 $\frac{3{\cdot}87}{2}$	·71	·81	·41	·82

In calculating the mean free paths of the α particles from the emanation in the smaller vessel, the same method was employed, but it was found to be more accurate to take the two perpendicular planes through the point in such a way that one contained the axis and the other was parallel to it. Also in calculating the mean free path of the α particle from the active deposit on the inner surface of the smaller cylinder, there was such a great difference in the mean free paths in the maximum and minimum planes, that it was found necessary to take six planes at angles of 30° with one another.

The ratios given in column VI. were calculated by taking into account the fact that an α particle does not produce the same number of ions over each cm. of its path. A curve showing the relation between the ionization due to an α particle of radium C and the distance from the end of its ionizing path, was given by the writer in Phil. Mag. for June 1906, and is reproduced here.



This curve gives the ionization for the last 4·5 cms. of the ionizing path of an α particle, and can be extrapolated with little error to cover the last 6 cms. of its path. The extrapolation of the curve to 8·6 cms., which is the maximum ionizing path of the α particle from thorium C, introduces so much uncertainty that the results given in column VI.

are of very little value in the case of thorium. However, in this case the differences between columns V. and VI. are comparatively small.

The following calculation of the ratio at the bottom of column VI. shows the method used. The values of the ionizations are taken from an extrapolation of the above figure.

Activity of the actinium emanation.

Total ionization over the last 5·8 cms. of path = 870
" " " 3·07 " " = 545

" " for average range of 2·73 cms. = 325

Activity of the active deposit.

Total ionization over the last 5·5 cms. of path = 838
" " " 1·63 " " = 308

" " for average range of 3·87 cms. = 530

" " " " $\frac{3\cdot87}{2}$ = 265

$$\frac{\text{Ionization due to active deposit}}{\text{Ionization due to emanation}} = \frac{265}{325} = \cdot81$$

Discussion of Results.

The agreement between the figures in columns VI. and VIII. is surprising considering the nature of the assumptions and calculations. These results could be explained by assuming that there were present other active substances of very short transformation periods. It would require three such products in the case of thorium and one in the case of actinium. Hahn's measurements on the ionization ranges of the products of thorium and actinium give no evidence of this, and it seems very unlikely. A simpler and more satisfactory explanation would seem to be—*that an atom of thorium C, in breaking up, gives off the same number of α particles as an atom of thorium B and that an atom of thorium emanation gives off four times this number; also that an atom of actinium emanation, in breaking up, gives off twice as many α particles as an atom of its active deposit.*

These results raise the very interesting question as to the number of α particles given off when an atom of any radioactive substance breaks up. If the above conclusions are correct, it has been shown that this number is not the same for every active substance. As the measurements in this paper are only relative, no light has been thrown on the question as to the *actual number* of α particles thrown out by an atom of any one of the substances. The writer hopes to continue the present investigation and extend it to other members of the radioactive family. It is possible that light may, in this way, be thrown on the question of the actual number of α particles thrown off by atoms of the different active substances.

Former Results with Radium.

The results in the case of radium are added here for the sake of comparison. They were obtained from curves of the rise and decay of the active deposit from radium. These curves were obtained by the writer in 1905, while investigating the transformation periods of the different products of which the active deposit from radium is composed. Table IV. is similar to Table III., but gives only a single set of results. These results indicate, as was said at the beginning of the paper, that the same number of α particles are thrown off by the disintegration of an atom of either radium emanation, radium A, or radium C.

Table IV.

I. Products.	II. Max. range in air.	III. Mean free path in vessel.	IV. Ratio of paths. $\frac{\text{Emanation.}}{\text{Active deposit.}}$	V. Cal. ratio of ionization $\frac{\text{Emanation.}}{\text{Active deposit.}}$	VI. Measured ratio of ionizations.
Ra. Emanation...	4·3	2·60			
Radium A	4·8	$\frac{3\cdot28}{2}$	·63	·62	·63
Radium C	7·1	$\frac{3\cdot76}{2}$	·72	·55	·51
Radium A+C	4·8+7·1	$\frac{3\cdot28}{2}+\frac{3\cdot76}{2}$	1·35	1·17	1·14

The vessel used had a diameter of 4·8 cms. and a length of 20 cms. The active deposit was on the central electrode, and in making the calculations the actual length of the vessel was taken into account.

Macdonald Physics Building,
McGill University, Montreal,
April 27th, 1908.

XXIII. *Experiments with the Radium Emanation.* (1) *The Volume of the Emanation.* *By* E. RUTHERFORD, *F.R.S.*, *Professor of Physics, University of Manchester* *.

THE amount of radium emanation to be obtained from one gram of radium in equilibrium is a definite quantity, and is equal to q/λ where q is the rate of production of emanation per second and λ is the radioactive constant of the emanation. Taking the half period of the emanation as 3·75 days, the value of λ is 1/468000. I have on different occasions † calculated the volume of the emanation (at normal pressure and temperature) to be expected from one gram of radium from the radioactive data at our disposal. As the simplest and most probable assumption, it is supposed that one atom of radium in breaking up emits one α particle and then becomes an atom of the emanation. On the assumption that each α particle carries the ordinary ionic charge e of $3{\cdot}4 \times 10^{-10}$ electrostatic unit, it was calculated that the volume of the emanation from one gram of radium should be 0·8 cubic millimetre. Later work ‡ indicated the probability that the α particle carried the charge $2e$. This reduces the calculated volume of the emanation to one-half of the above value. Recently, in conjunction with Dr. Geiger, the number of α particles expelled per second from one gram of radium has been accurately determined, and also the charge carried by each α particle. From these data, we have calculated that the volume of the emanation is 0·57 cubic mm.— a value about intermediate between the other two values §.

The first experiments to measure directly the volume of the emanation were made by Ramsay and Soddy ‖. The emanation after suitable treatment was condensed in a glass tube surrounded by liquid air. The residual gases were pumped off, and the emanation after volatilization was forced by raising the mercury into a capillary tube where its volume was measured. From the volume of the collected gas observed after two days, they concluded that the volume of the emanation was about 1·2 cubic mm. Later a number of systematic observations of the volume of the emanation by a similar method have been made by Ramsay and Cameron ¶.

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* Communicated by the Author, having been read before the Academy of Sciences of Vienna, July 2, 1908.

† 'Radioactivity,' 2nd edition, p. 288.

‡ Rutherford, Phil. Mag. Oct. 1906.

§ An account of this work was given to the Royal Society, June 18, 1908.

‖ Proc. Roy. Soc. lxxiii. p. 346 (1904).

¶ Journ. Chem. Soc. p. 1266 (1907).

They conclude that the volume of the emanation is about 7·07 cubic mms., and suggest that the smaller value initially obtained by Ramsay and Soddy was due to the greater part of the emanation being pumped off during the experiment. The volume of the emanation (7·07 cubic mms.) obtained in their experiments is of quite a different order from the calculated volume (0·57 cubic mm.). It is of importance to determine the cause of this wide discrepancy between theory and experiment. If the experimental value proves correct, it would indicate that much of the radioactive data and of the theory on which the calculations are based is seriously in error. Apart from the interest attaching to the comparison of theory with experiment, the separation of the radium emanation in a pure state is now of the highest practical importance. Not only is pure emanation required in order to study carefully the physical and chemical properties of this remarkable gas, but it is also required in the experiments similar to those initiated by Ramsay and Cameron [*], where the radium emanation is added to different solutions and the resulting products determined.

By the generosity of the Academy of Sciences of Vienna, I was recently loaned a preparation of radium containing about 250 milligrams of radium. Experiments were immediately begun in order to purify the emanation produced by it, and to determine its volume. In all, a large number of experiments have been made, but for brevity I shall here only indicate the general results obtained in these investigations.

Separation of the Emanation.

There are two general methods of obtaining the emanation from preparations of radium, viz., by heat or by solution. Both of these methods have been used. In the earlier experiments, the radium preparation was placed in a thin quartz tube which was enclosed in a larger quartz tube. The latter was heated to the desired temperature by means of an electric furnace. The emanation is practically all released at the temperature of fusion (about 830° C.) [†] of barium-radium chloride. After the preliminary heating, a very small quantity of intensely radioactive gas was released, the volume of which was so small that it was found necessary to add a small quantity of hydrogen or oxygen in order to pump off the emanation completely. In later experiments, the radium preparation was in solution in a quartz tube. The emanation

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[*] Journ. Chem. Soc. p. 1593 (1907).

[†] See paper by L. Kolowrat, *Le Radium*, Sept. 1907.

was pumped off together with a large quantity of hydrogen and oxygen formed in solution. After the method employed by Ramsay and Cameron, this was sparked down and a small quantity of oxygen added in order to reduce the excess of hydrogen. The emanation, mixed with about 1 cc. of hydrogen, was then collected over mercury in a small burette in which was placed a piece of caustic potash in order to absorb any carbon dioxide present. The apparatus for purification of the emanation and measurement of its volume is shown in fig. 1. The measuring apparatus consisted essentially of a Macleod gauge. A capillary tube, 15 cms. long and 0·58 mm. diameter, was attached to a long glass tube of volume about 25 cubic cms. By raising the reservoir with the stopcock A closed, the gas in the tube E was forced into the capillary tube F and its volume measured. A mercury trap R was used to avoid the entrance of any gas which crept along the surface of the glass. The general method of purification of the emanation is best seen from a description of an experiment *.

The whole apparatus was first exhausted to a low vacuum by means of a mercury pump. The emanation, conveyed with about 1 cc. of gas, was transferred over mercury into the reservoir C. The stopcocks A and B were closed, and the emanation was forced by raising the mercury reservoir through the stopcock H along the tube D, coated with caustic potash, into the U-tube T. The U-tube, of volume about 1·5 c.cms., was surrounded by liquid air in order to condense the emanation. The whole emanation was condensed by successively raising and lowering the mercury in the reservoir. The stopcock B was then opened into the pump and the uncondensed gases completely pumped off. The mercury was then lowered in the tube D to the position of the dotted line in the figure. The liquid air was then removed. The emanation after volatilization was left some hours in contact with the caustic potash in the tube D to remove the last trace of carbon dioxide. The U-tube was then surrounded by a vessel filled with pentane, which was cooled down by liquid air to a temperature between the temperature of condensation of the emanation (−150° C.) and the temperature of liquid air (−186° C.). The whole apparatus was then completely exhausted again by the mercury pump, a portion of the emanation being volatilized during the process and removed by the pump. Finally, when a very low vacuum was

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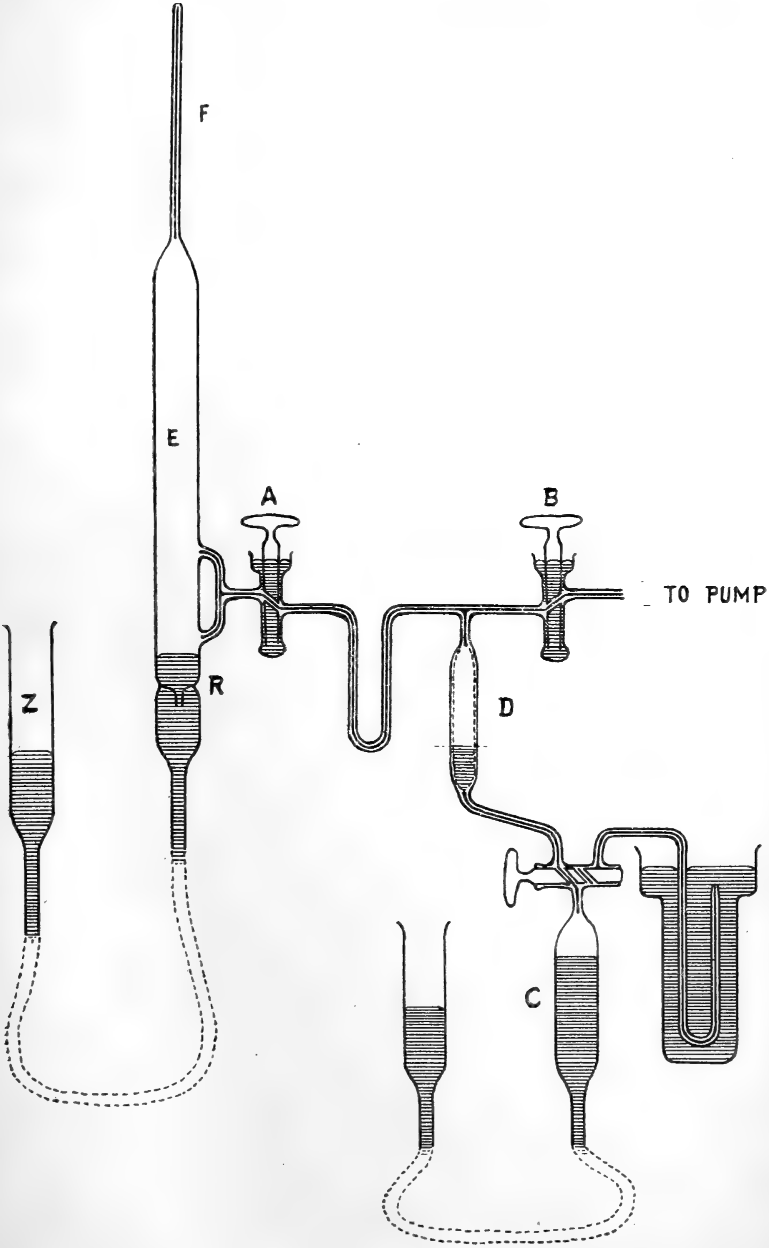
* In this work, I have found the methods developed by Ramsay and others for manipulating small quantities of gases of great assistance. See Travers, "Study of Gases."

Fig. 1.



obtained, the liquid air was removed, the stopcock B closed, and the emanation after volatilization was allowed to expand into the tube E. Since the volume of the U-tube was small compared with the tube E, the greater part of the emanation after volatilization expands into the tube E. The experiments were made in a darkened room, so that the moment of almost complete volatilization of the emanation could be observed by the sudden phosphorescence of the tube E due to the entrance of the emanation. The stopcock A was then closed and the emanation forced into the capillary, where its volume was measured at regular intervals.

Activity measurements.

In this type of experiment, it is of importance to determine accurately the amount of emanation in the capillary where the volume is measured. This was done by comparison of the γ ray activity due to the emanation in the capillary with that due to a standard sample of radium bromide which gave a heating effect of 110 gram-calories per gram per hour. When the emanation had been forced into the capillary, the residual emanation in the U-tube and connexions was completely pumped out and all sources of γ rays removed to a distance. A small closed lead electroscope was placed at a distance of 76 cms. from the emanation in the capillary, and the rate of discharge observed about three hours after the introduction of the emanation. The γ ray activity compared with a standard is then a measure of the amount of emanation expressed in terms of the equilibrium quantity present in one milligram of pure radium. Measurements were made daily of the γ ray activity of the emanation. Experiment showed that the highly concentrated emanation compressed into a small volume had the usual rate of decay, viz. half period in 3·75 days. Measurements of this character are essential if any accuracy is required. It is not sufficient to assume that all the emanation formed in a certain interval of days is pumped off from the radium solution. Moreover a small part of the emanation is left behind in every operation of transferring the emanation from one vessel to another. It may be mentioned that in most of the experiments the amount of emanation whose volume and activity were measured was equivalent to the equilibrium quantity from 60 to 140 milligrams of radium. Usually the amount of emanation pumped off during the experiment corresponded to 20 or 30 milligrams of radium.

Discussion of Experiments.

Preliminary experiments showed that the volume of the emanation was certainly much lower than that found by Ramsay and Cameron; the purity of the emanation was examined spectroscopically in the capillary itself without the use of electrodes. Some tinfoil was wound round the upper and lower part of the capillary and a discharge produced in the capillary by means of a small induction-coil. The spectrum was examined by a Hilger spectroscope, by means of which the wave-length of the lines could be read off directly. In the preliminary experiments, the spectrum observed was the ordinary band spectrum ascribed to carbon dioxide with some of the mercury lines and occasionally a few other very faint lines. Precautions were then taken to get rid of the carbon dioxide. Phosphorus pentoxide instead of tap grease was used to lubricate the stopcocks. The emanation was always left in the presence of solid caustic potash some time before its introduction into the U-tube. In addition the emanation after the uncondensed gases were pumped off was left in contact with the tube D which was coated with a layer of caustic potash. Notwithstanding all these precautions it was found at first impossible to remove the last traces of carbon dioxide. Attempts were made to remove the greater part of the residual CO_2 by fractional distillation, using the pentane bath for temperature adjustment, but with only partial success. There appears to be some evidence that the emanation prefers to condense with the CO_2 which is present, and is released with it when the temperature rises. Finally, after a large number of experiments, it was found essential to allow the emanation after purification from other gases to remain five or six hours, preferably 24 hours, in the presence of the caustic potash tube D. When this was done, it was found that the volume of the gas obtained in the capillary was much reduced and the carbon-dioxide spectrum became much fainter. The reason why such a long time of exposure to caustic potash is required is not at all clear. It may be due to the very slow absorption of the last traces of carbon dioxide by caustic potash. It is possible, however, that the spectrum ascribed to CO_2 is in reality due to carbon monoxide in the presence of oxygen. There is considerable difference of opinion among spectroscopists on this point. If the disturbing gas is CO it must first be converted into CO_2 in the presence of oxygen by the action of the emanation before absorption by the caustic potash. This would account for the long time required for complete absorption. As far as my experience has gone, the essential conditions for the purification of the emanation depend upon the pumping off the residual gases at a temperature below the temperature of volatilization of the emanation and considerably above the temperature of liquid air; and the long exposure of the emanation to caustic potash. By the former method practically all the known inactive gases would be pumped off. I think the high value of the volume of the emanation obtained by Ramsay and Cameron must be ascribed to the presence of other gases besides the emanation, which are condensed at the temperature of liquid air.

Changes in Volume.

Ramsay and Cameron (*loc. cit.*) have given a number of examples of the changes in volume observed in their experiments to measure the volume of the emanation. The volume of the gas in the capillary usually diminished with time rapidly during the first two hours to about half value and then more slowly. I have observed very similar effects in my experiments, using impure emanation. In some cases the volume diminished in the course of several hours to less than half value, but after this preliminary decrease little change was observed in the volume over the further interval of a week. In other experiments, the volume increased instead of diminishing in the course of a few hours, sometimes increasing to twice the initial volume, followed later by a slow decrease with time. The expansion or contraction of the volume has in many cases no direct connexion with the volume changes of the emanation itself, for the true volume of the emanation present was in some experiments certainly not more than 20 per cent. of the total *. It is difficult to explain these expansions and contractions except on the supposition that the gases mixed with the emanation either combine or dissociate under the influence of the powerful radiation from the emanation. Until experiments are made with some known gas or gases added to pure emanation, we can only speculate upon the nature of the gases present and the combinations or dissociations which are effected. There is another possibility which may prove to be an important factor in the volume changes, especially with nearly pure emanation. It is believed that the positive and negative ions produced in a gas at

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* Ramsay and Cameron explained the decrease of volume observed in their experiments on the assumption that the emanation changed from a monatomic to a diatomic gas. Since the volume in these experiments certainly contained less than 20 per cent. of emanation, the explanation is inadmissible.

ordinary pressure have a cluster of molecules attached which move with them. Since the emanation itself and the gases associated with it are intensely ionized, it is possible that the effective volume may be decreased due to the production of a large number of these aggregates. On this view, the decrease of volume observed during the first two hours may be partly due to the increase of the number of these aggregates consequent upon the increase of the radiation from radium C.

Experimental Results.

We shall now give some typical examples out of a number illustrating the initial changes in volume. The capillary tube used in all the experiments was of Jena borosilicate glass of very uniform bore, 0·58 mm. in diameter. The capillary correction was equal to 14 mm. of mercury. The tube was slowly coloured brown by the emanation. By heating the tube to the temperature of thermo-luminescence, the glass again became quite clear. The capillary was heated at the beginning of each experiment to drive off residual gases. The gases in the capillary in all cases obeyed Boyle's law over the range examined within the limit of experimental error.

Experiment I.—This illustrates the increase of volume observed for very impure radium emanation. The amount of emanation in the capillary, determined by direct measurement, corresponded to 67 mgrs. of pure radium.

Time after introduction of the emanation into capillary.	Volume of gas in capillary at standard pressure and room temperature.
2 minutes	0·154 c.mm.
6 ,,	·169 ,,
17 ,,	·201 ,,
28 ,,	·235 ,,
41 ,,	·260 ,,
50 ,,	·270 ,,
64 ,,	·280 ,,
71 ,,	·291 ,,
81 ,,	·297 ,,
3·9 hours	·346 ,,
21 ,,	·355 ,,

At the end of 24 hours the spectrum of the gas was examined in the capillary. The carbon dioxide spectrum was prominent. In addition to the mercury lines, a few others were observed which were not identified with certainty. The initial volume, 0·154 c.mm., corresponded to 67 mgs. radium, consequently the initial volume corresponding to one gram of radium was 2·3 c.mm. The final volume after 21 hours corresponds to 5·2 c.mm. per gram. As the spectrum indicated, the emanation in this case was very impure, containing probably a large proportion of CO or CO_2.

Experiment II.—We shall now give an example of the contraction of volume. In this case the emanation was far purer than in experiment I. The emanation was left four hours in the presence of caustic potash before introduction into the capillary. The amount of emanation in the capillary corresponded to 130 mgs. radium.

Time after introduction of the emanation into capillary.	Volume of gas in capillary at normal pressure and room temperature.
2 minutes	0·171 c.mm.
5 ,,	·169 ,,
10 ,,	·165 ,,
18 ,,	·158 ,,
26 ,,	·150 ,,
37 ,,	·135 ,,
56 ,,	·126 ,,
70 ,,	·120 ,,
91 ,,	·106 ,,
5·9 hours	·097 ,,
17 ,,	·069 ,,
44 ,,	·075 ,,
92 ,,	·079 ,,
161 ,,	·080 ,,
185 ,,	·119 ,,
209 ,,	·125 ,,
257 ,,	·125 ,,

The initial volume for the emanation from one gram of radium corresponded to 1·32 c.mm. Correcting for the decay of the emanation, the volume at the minimum after an interval of 17 hours was equal to 0·59 c.mm. per gram of radium. It will be observed that the volume sank to about 0·4 of its initial value after 17 hours. After passing through a minimum, the volume increased again, though not very regularly. At the conclusion of the experiment, *i.e.* after the emanation had remained nearly 11 days in the capillary, the spectrum of the gas was examined in the capillary as described above. *A brilliant spectrum was obtained showing all the lines of helium.* The spectrum of CO_2 was also observed, although weak in intensity compared with that of helium. In addition to the mercury lines, a few unidentified bright lines were noted. This result is a confirmation of the well-known experiment of Ramsay and Soddy, who found that the spectrum of helium appeared after some time in a tube containing radium emanation. The cause of the increase of volume after the minimum is now clear. Assuming that the α particles are atoms of helium, the helium would at first be fired into the glass. After a time part of it gradually escaped and added its volume to the emanation and other gases present. It is difficult to be certain how much of the helium was retained in the glass of the capillary. If we take the initial volume of the emanation to be about that observed at the minimum volume, viz. ·059 c.mm., the volume of helium to be expected is about three times this amount. This is on the assumption that each α particle expelled is a helium atom. The final volume observed after 11 days was ·125 c.mm., and was probably mainly due to the helium.

Experiment III.—In this case the emanation was very carefully purified, after standing for 18 hours over caustic potash. The amount of emanation present corresponded to 130 mgs. radium. The initial volume of the emanation was ·097 c.mm. This corresponds to a volume of 0·80 c.mm. per gram of radium. No certain change in volume was observed over an interval of 15 minutes. The emanation was then recondensed in the U-tube, which was pumped out again using a pentane bath. On introducing the emanation into the capillary again, very nearly the same initial volume as before was observed. In order to test the purity of the emanation, the spectrum of the gas in the capillary was examined. A new spectrum of bright lines, certainly due to the emanation itself, was observed. Some of the bands of the carbon dioxide spectrum were observable. Observations were at once begun to determine the wave-lengths of the new lines with accuracy. Before this was completed, most of the lines due to the emanation suddenly ran out, and the carbon dioxide spectrum became more prominent. The volume of the gas in the capillary was also found to have considerably decreased. It was then observed by the phosphorescence that the emanation was adhering to the walls of the capillary, and only a part of the emanation was free in the gaseous state. The emanation remained fast to the walls for two days, and was only removed finally by a vigorous heating of the tube. It appears that the emanation must have been driven into the walls of the tube or occluded in it under some condition due to the passage of the discharge.

Experiment IV.—In this case the emanation, after the initial purification, was left five hours over caustic potash. After introduction the initial volume was ·126 c.mm. The volume remained nearly stationary for 20 minutes and then slowly diminished, reaching a value of ·076 c.mm. after 17 hours. The amount of radium emanation initially present was 130 mgs. radium. The initial volume of emanation thus corresponded to 0·97 c.mm. per gram of radium, and the lowest volume, allowing for the decay of the emanation in the interim, corresponded to 0·66 c.mm. per gram.

Experiment V.—The emanation used in experiment IV. was again condensed in the U-tube and then left for 24 hours in the presence of caustic potash. The emanation after further treatment was admitted into the capillary. The initial volume was ·083 c.mm. As in the case of experiment IV., the volume remained nearly stationary for 20 minutes and then slowly decreased. The volume after 4 hours was ·046 c.mm. The amount of radium emanation in the tube was equal to 79 mgs. radium. Consequently the initial volume of the emanation per gram was 1·05 c.mm., and the volume after 4 hours 0·58 c.mm. The spectrum of the gases in the capillary was then examined. As before the carbon dioxide spectrum was seen together with a number of new lines due to the emanation, the wave-lengths of which were measured. No trace of the hydrogen lines was observed in this or in the other experiments. After the discharge had passed at intervals for two hours, most of the lines due to the emanation disappeared. The greater part of the emanation was then found to be sticking to the surface of the capillary, as in the previous experiment. The prominence of the carbon dioxide spectrum cannot I think be ascribed to the presence of a considerable amount of this gas mixed with the emanation before the discharge passed, but rather to the production of this gas by the discharge, due probably to the presence of a trace of some organic matter at the surface of the mercury. The correctness of this view was confirmed by the observation that the spectrum of carbon dioxide was unaltered in brightness, after practically all the residual gases and emanation had been removed by the pump[*]. I hope in a later paper to give a more detailed account of these and other experiments to determine the spectrum of the radium emanation. In these investigations the spectrum has been obtained incidentally in the course of testing the purity of the emanation in the capillary.

Summary of Results.

For convenience, the results of experiments II. to V. on the volume of the emanation are collected below:—

Experiment.	Initial volume of emanation per gram of radium.	Final volume of emanation per gram of radium.
II.	1·32 c.mm.	0 59 c.mm.
III.	0·80 „	
IV.	0·97 „	0·66 „
V.	1·05 „	0·58 „

The volumes here given are at normal pressure and room-temperature (about 16° C.). If corrected to standard temperature, the volumes will be about 5 per cent. smaller. A small undetermined correction should also be applied for the heating effect of the emanation. We have already seen that the calculated volume at normal pressure and temperature is 0·57 c.mm.

From the above table it is seen, that the smallest initial volume of the emanation observed is 0·80 c.mm. per gram of radium, and the smallest volume after contraction 0·58 c.mm. The volume before contraction, observed by Ramsay and Cameron, was 7·07 c.mm. per gram. It was observed that the emanation was not appreciably absorbed in the capillary during the first few hours, provided a discharge was not passed, and was all released on lowering the mercury. For these reasons, it seems probable that the volume after contraction is to be taken as the true volume of the emanation rather than the volume in the beginning. On this view, there is as good an agreement as could be expected from the nature of the experiments between the final volumes,

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[*] Later observations have confirmed the correctness of this explanation. The emanation purified after the manner described was introduced in a spectrum-tube with platinum electrodes. No trace of the band spectrum of carbon dioxide has been observed in the spectrum produced by the discharge. (See accompanying paper "On the Spectrum of the Radium Emanation.")

viz. 0·59, 0·66, and 0·58 c.mm., and the calculated volume, viz. 0·57 c.mm.

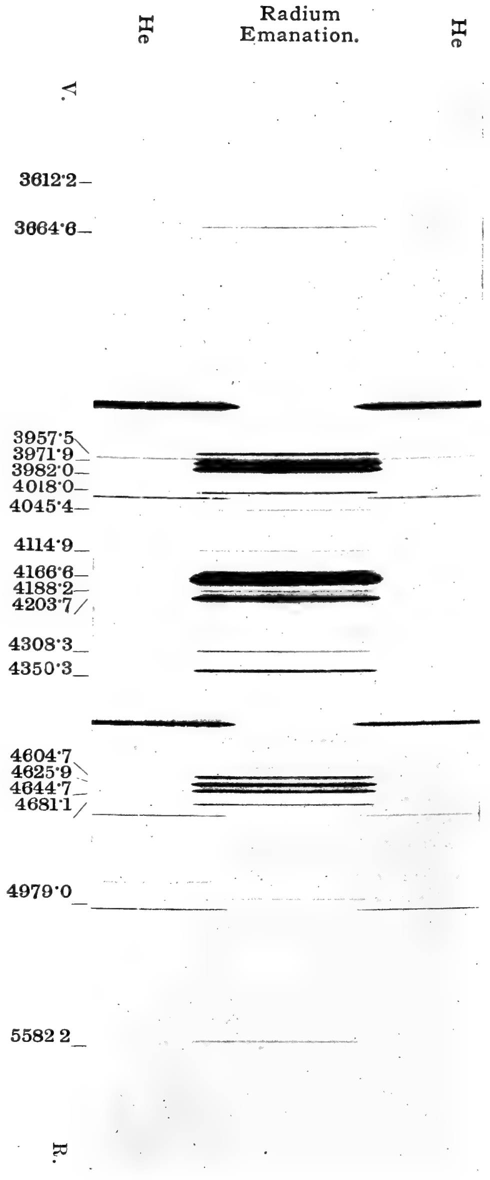
We have already seen that it is difficult to offer a satisfactory explanation of the initial contraction. Before this can be done, a large number of further experiments will be required. The work outlined in this paper is merely preliminary, and it is hoped in a later paper to give the results of a more complete examination of the volume of the emanation and of the changes it undergoes.

Remarks on the Condensation of the Emanation.

When the emanation was obtained in a nearly pure state, it condensed exceedingly rapidly at any point cooled below the temperature of condensation (−150° C.). If the emanation were contained in the U-tube (fig. 1), the slow approach of the liquid air to the bottom of the tube caused the condensation in some cases to take place over an extremely small area, probably at a point where the tube was thinnest. A brilliant phosphorescent speck was then observed, and it almost appeared as if one could see the liquid emanation in the form of a flat globule condensed over an area of less than half a square millimetre. This effect was often observed and is very striking. After a few minutes the emanation, even at the temperature of liquid air, gradually diffuses, and the area of distribution becomes much larger. Ramsay has observed that the emanation condensed at the temperature of liquid air can be partly removed by continual pumping, indicating that it has an appreciable vapour-pressure at that temperature. This effect, however, becomes far more noticeable when using a pentane bath whose temperature is not more than 10° or 20° C. below the temperature of condensation. Every stroke of the pump then removes a not inconsiderable fraction of the total emanation. There is another effect observed which is very striking. Suppose that the nearly pure emanation contained in the U-tube is condensed over a small area by applying the liquid air only to the bottom of the U-tube. If the U-tube is then fully immersed in liquid air, in the course of about ten minutes it will be observed by the phosphorescence that the emanation is distributed throughout the tube, even though the U-tube is not connected with the pump. In addition, a part of the emanation has condensed above the level of the liquid air. Such experiments bring out clearly that the emanation has a sensible vapour-pressure far below the temperature of condensation. There is continual volatilization of the emanation in one part of the tube and condensation in another part.

I desire to thank Mr. T. Royds, M.Sc., who very kindly assisted me in many of these experiments.

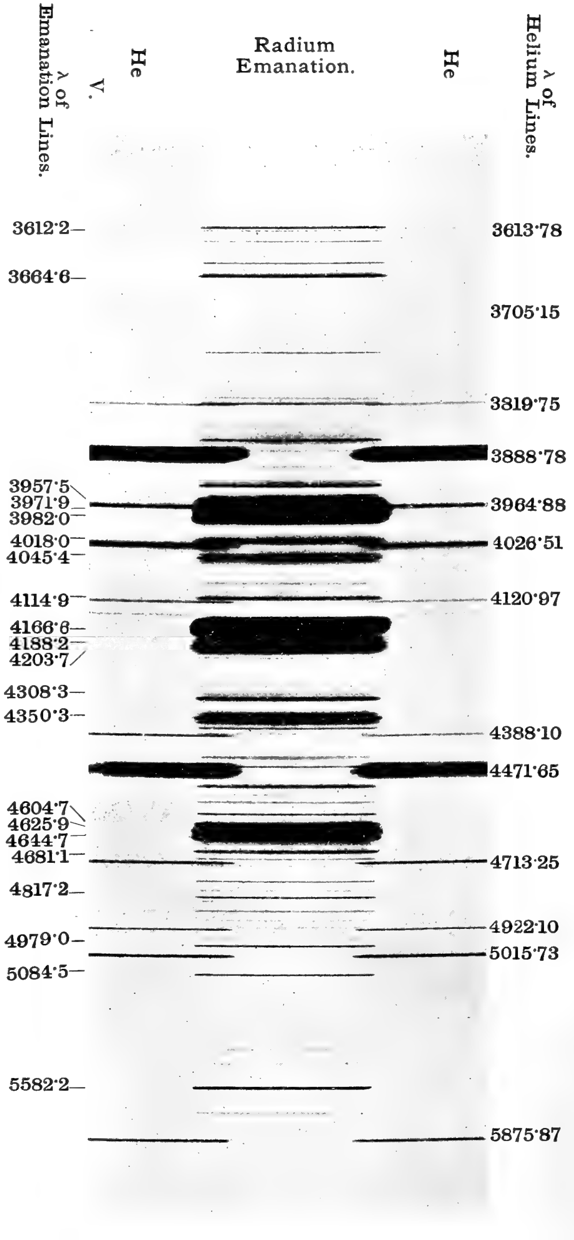
University, Manchester.



Strongest Lines in the
SPECTRUM OF RADIUM EMANATION.

RUTHERFORD.

Phil. Mag. Ser. 6, Vol. 16, Pl. XI.



SPECTRUM OF RADIUM EMANATION.

XXIV. *Spectrum of the Radium Emanation.* *By* Prof. E. RUTHERFORD, *F.R.S., and* T. ROYDS, *M.Sc., Beyer Fellow, University of Manchester* [*].

[Plates X. & XI.]

THE first determination of the spectrum of the radium emanation was made in 1904 by Ramsay and Collie [†], who obtained visual observations of the wave-lengths of eleven lines. They stated that the emanation was a bright line spectrum similar in general character to that observed for other monatomic gases. Since that time, no further information on this important subject has been forthcoming. In a previous paper [‡], one of us has given an account of methods employed in purification of the emanation and determination of its volume. In order to test the purity of the emanation, an electrodeless discharge was passed in the capillary tube in which the volume of the emanation was measured, and visual observations of the wave-lengths of the main lines were made by means of a direct reading Hilger spectroscope. We have observed the spectrum of the radium emanation in this way on four different occasions during the past two months. It was evident that a number of new lines were present, which were not recorded in the initial observations of Ramsay and Collie. As soon as the measurements of the volume had been completed, arrangements were made to photograph the emanation spectrum in order to determine the wave-lengths of the lines with more accuracy than is possible with visual observations. For this purpose, a quantity of radium emanation was purified as completely as possible by the methods outlined in the last paper. The emanation was first condensed in a U-tube surrounded by liquid air, and the uncondensed gases completely pumped off. The emanation was then left for three hours in contact with a tube coated with caustic potash to remove the last traces of carbon dioxide. Finally, the U-tube was surrounded by a pentane bath cooled down by liquid air, and the uncondensed gases pumped off at a temperature above that of liquid air. In order to obtain the spectrum, a small vacuum tube of capacity about

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[*] Communicated by the Authors. A preliminary account of this work was published as a letter in 'Nature,' July 8, 1908.

[†] Proc. Roy. Soc. lxxiii. p. 470 (1904).

[‡] See Rutherford, "Volume of Emanation," Phil. Mag. Aug. 1908.

50 c.mms., provided with fine platinum electrodes, was used. This was sealed to the connexion leading to the pump and completely exhausted, a discharge being passed to free the electrodes of hydrogen. When the emanation had been purified as completely as possible in the manner outlined, it was condensed in the spectrum-tube by dipping a side tube connected with it in liquid air. When the greater part of the emanation had been condensed, the spectrum-tube was sealed off and removed for observation.

Measurements of the γ ray activity showed that the amount of emanation in the tube corresponded to 130 milligrams of radium. Now the volume of the emanation per gram of radium is ·57 cubic mm. Consequently, the volume of the pure emanation in the spectrum tube was ·074 cubic mm. Since the volume of the spectrum-tube was 50 cubic mms., this would give a pressure of emanation in the tube of 1·1 mms. of mercury. In order to photograph the spectrum, a spectrograph with a glass prism of two inches base was used. The length of the spectrum on the plate between λ 5000 and λ 4000 was 1·5 cms. Arrangements were made so that visual observations of the wave-lengths could be made by the Hilger spectroscope while the plate was being exposed. Two photographs were taken before the emanation spectrum ran out. The first (photograph 1) showed about thirty of the more intense emanation lines. The second (photograph 2), which had a much longer exposure, showed over a hundred lines. A helium tube was used for comparison purposes, and its spectrum obtained above and below the emanation spectrum. The plates were measured up with the aid of a Kayser's measuring machine. The wave-lengths were deduced with the aid of the Hartmann dispersion formula.

Remarks on Spectrum.

The colour of the discharge through the emanation was bluish and not so intense as the helium tube. The spectrum observed visually was a brilliant one of bright lines. The most noticeable lines were a number of strong lines in the green and another group in the violet. The mercury and hydrogen lines were also observed. In order to be sure that the lines were due to the emanation, the side tube attached to the spectrum-tube was immersed in liquid air. At the moment of condensation, which was readily noticed by the increased brilliancy of the phosphorescence of the glass, practically all the lines except those due to hydrogen vanished. The colour of the discharge then completely changed to a pale rose, and the tube became harder. At the moment of volatilization the emanation lines flashed out again.

The hydrogen lines came out more strongly when the emanation was condensed. In previous experiments with the electrodeless discharge, the hydrogen lines had been absent. Their occurrence in the present experiment was without doubt due to the liberation of hydrogen from the platinum electrodes when a strong discharge was passed. This is borne out by the results of another experiment recorded later. The emanation was momentarily condensed at intervals during the experiment in the side tube. From observations of the brilliancy of the phosphorescence at condensation, it was noted that the amount of the free emanation in the tube gradually diminished with increasing time of discharge, while the intensity of the emanation spectrum decreased relatively to that of hydrogen. The emanation lines, however, persisted to the close of the experiment, when practically all the emanation had been driven into the walls of the tube. From observations of the phosphorescence, it was evident that the emanation was approximately uniformly distributed along the line of discharge. As the discharge had been reversed at intervals during the experiment, it was difficult to be certain whether there had been any considerable absorption of the emanation by the electrodes. The occlusion of the emanation had been observed previously on several occasions in the capillary tube using the electrodeless discharge (see previous paper). It seems probable that the emanation is in some way driven into the walls of the tube by the discharge. This effect is no doubt similar to that recorded by Campbell Swinton for ordinary gases. It is difficult to remove such occluded emanation even by strongly heating the glass.

After three days, the tube was very much darkened by the emanation, and it was necessary to get rid of the blackening by heat in order to observe the spectrum. The main helium lines were observed, but were faint in comparison with the hydrogen lines.

After a week's interval, the spectrum-tube was again attached to the pump and thoroughly heated above the temperature of thermo-luminescence in order to make the glass as transparent as possible. The spectrum-tube was exhausted, care being taken by heating the tube and by passage of a strong discharge to get rid of most of the hydrogen from the electrodes. About the same quantity of pure emanation as in the first experiment was condensed in the tube. After sealing off the tube, the spectrum was photographed, visual observations being made at the same time.

The same general effect as in the first experiment was observed when the emanation was condensed on the side tube. In this case, however, the hydrogen spectrum was relatively much feebler. On condensing the emanation, the tube became very hard and showed the characteristic green coloration of the cathode-ray vacuum. It was thus clear that the methods employed had been fairly successful in getting rid of the hydrogen from the electrodes. The photograph of the spectrum in this case (photograph 3) showed only the hydrogen line H_β, although H_α also was observed visually. In the second photograph, already referred to, the stronger lines of the compound line spectrum of hydrogen had been photographed*. The photograph 3 is reproduced in Plates X. and XI., magnification 3·7 times. Plate X. was exposed to bring out clearly the strong lines of the spectrum only. It will be seen that the stronger lines in Plate XI. are somewhat overexposed in order to bring out some of the less intense lines in the spectrum. This photograph is somewhat better for reproduction purposes than photograph 2, but does not show quite the same number of faint lines.

The measurements of the wave-lengths of the lines common to the two plates agreed within the limits of experimental error. We shall consequently only give the measurement of photograph 2, since the hydrogen lines present in this spectrum serve as an indication of the accuracy of the measurements. It will be seen that the error of measurement is certainly not greater than half an Ångström unit. The lines given in the Table are common to both photographs. It has not been thought necessary to give the weaker lines observed, for the identity of these with the emanation spectrum requires further confirmation.

In the Table the lines observed visually are given in a separate column. In photograph 3, when the hydrogen was far less prominent, the relative intensity of some of the emanation lines differed from that observed in photograph 2.

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* No trace of the carbon-dioxide spectrum was observed in either experiment. The occurrence of this spectrum in the electrodeless discharge in nearly pure emanation (see paper, *loc. cit.*) was without doubt due to a trace of organic matter on the surface of the mercury.

Wave-lengths of the Emanation Lines.

Visual.		Photograph.		Remarks.
Inty	λ.	Inty	λ.	
0	6079			
1	5976			
1	5945			
1	5829			
1	5765			
3	5718	1	5715·0	
5	5582	8	5582·2	
0	5395	0	5392·4	
0	5372			
1	5257			
2	5120			
10	5087	4	5084·5	
2	5060			
10	4985	4	4979·0	
1	4964	0	4965·6	
1	4955	00	4949·4	
1	4917	00	4914·6	
1	4895	0	4889·5	
	4865		4861·3	Hβ 4861·49
0	4831	1	4827·8	
2	4820	4	4817·2	
0	4798	1	4796·7	
1	4772	3	4767·9	
1	4726	5	4721·5	Inty 1 in photo. 3.
0	4705	2	4701·7	
5	4685	10	4681·1	Does not quite disappear when emanation condensed.
		1	4671·8	
		1	4659·3	
5	4650	10	4644·7	
6	4631	8	4625·9	
1	4614	7	4609·9	Inty 4 in photo. 3.
3	4608	4	4604·7	,, 6 ,,
1	4581	7	4578·7	,, 4 ,,
0	4550	1	4549·9	
1	4511	9	4509·0	,, 4 ,,
		2	4504·0	
0	4460	10	4460·0	,, 2 ,,
		2	4440·6	
0	4439	8	4435·7	Inty 2 in photo. 3.
		3	4384·0	
		4	4372·1	
3	4351	15	4350·3	
		7	4340·9	Hγ 4340·66. Absent from 3rd photo.
1	4310	10	4308·3	
		2	4225·8	
1	4202	10	4203·7	
		5	4188·2	
1	4169	20	4166·6	
		7	4114·9	
		6	4102·2	Hδ 4101·85. Absent from 3rd photo.
		2	4088·4	
		1	4055·7	
		2	4051·1	
		4	4045·4	
		1	4040·2	
		10	4018·0	
		12	3982·0	
		9	3971·9	Not Hε 3970·25.
		7	3957·5	
		3	3952·7	
		3	3933·3	
		1	3927·7	
		2	3905·7	Inty 0 in photo. 3.
		4	3867·6	
		2	3818·0	
		0	3811·2	
		10	3753·6	Inty 3 in photo. 3.
		1	3748·6	
		7	3739·9	,, 1 ,,
		2	3690·4	
		1	3679·2	
		10	3664·6	
		0	3650·0	,, 3 ,,
		2	3626·6	
		1	3615·4	
		6	3612·2	

None of the emanation lines have been identified in any stellar spectra.

Manchester University.

XXV. *Telescopic Vision.*

By G. JOHNSTONE STONEY, *M.A.*, *Sc.D.*, *F.R.S.*[*]

PART I.—THE NECESSARY APPARATUS.

[Plate XII.]

CHAPTER 1.

A cosmical apparatus which, if it could be realised, would give the information we seek.

In this paper:—

1. A wavelet will mean a luminous wave *of infinitesimal intensity.*
2. An undulation will usually mean a *simple* undulation, that is a complete train of *similar* waves or wavelets.
3. u f w is employed as a short way of writing *undulation of flat wavelets* of light, of infinitesimal intensity.
4. Similarly, u f W will mean an *undulation of flat waves* of light, of finite intensity.
5. A *sheaf* of undulations will mean all the undulations that fulfil some condition which will be stated. The term is often used of u f w's travelling nearly in the same direction—or, more precisely, whose guide lines (lines perpendicular to the wavelets) are parallel to lines drawn within a very acute cone, from its vertex.

1. THE opposition of Mars in September 1909 will occur when Mars is near perihelion and the earth near aphelion: when, also, the planet will be sufficiently high in the sky for convenient observation from all the observatories of the southern hemisphere, and from most of those in the northern. Accordingly not far short of the best conditions for observing the surface of the planet will then present themselves, and an even nearer approach to the best possible conditions for observing the terminator of the planet when slightly gibbous will occur in August. Mars will on the 13th of that month reach perihelion and exhibit the degree of gibbosity which will then exist, with the advantage that the planet will be almost at the shortest distance from the observer which is compatible with its being in that degree gibbous. Moreover, the position of the planet in September will give an opportunity of scrutinising its southern circumpolar regions under exceptionally favourable conditions.

These considerations, and a desire that there shall be time for adequate preparation before the summer of next year, have induced the writer of this paper to publish somewhat prematurely one part of an inquiry respecting the process by which nature forms those images which we find in optical instruments or on the retina, although (being the part of the inquiry which concerns the telescope) it would more naturally have come after another unpublished part of the investigation

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[*] Communicated by the Author.

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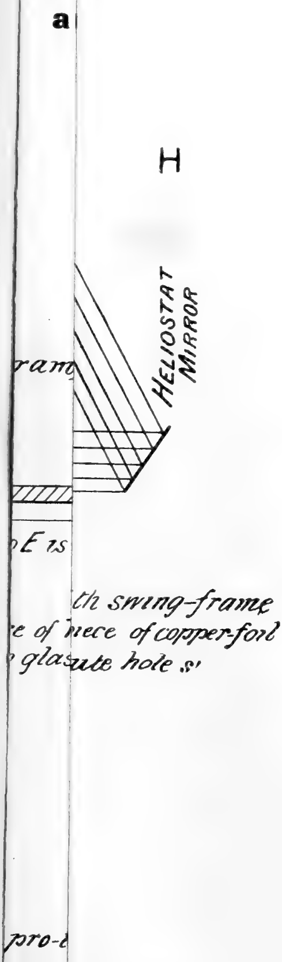
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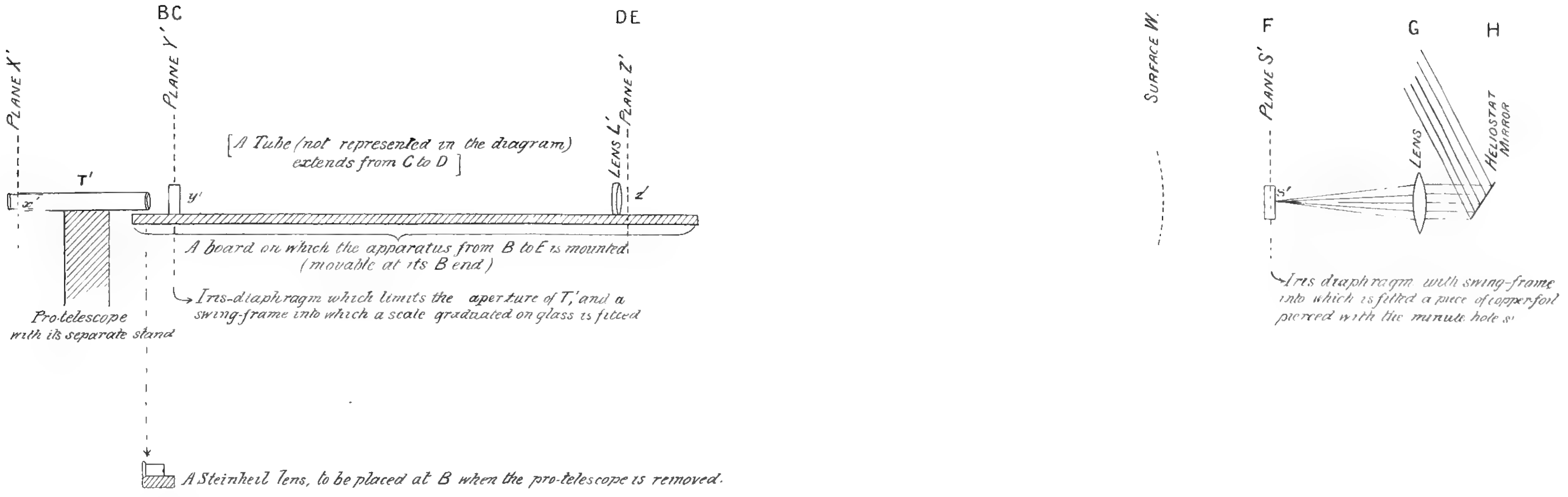

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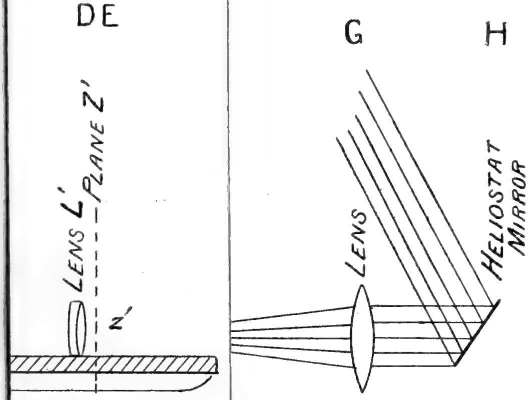

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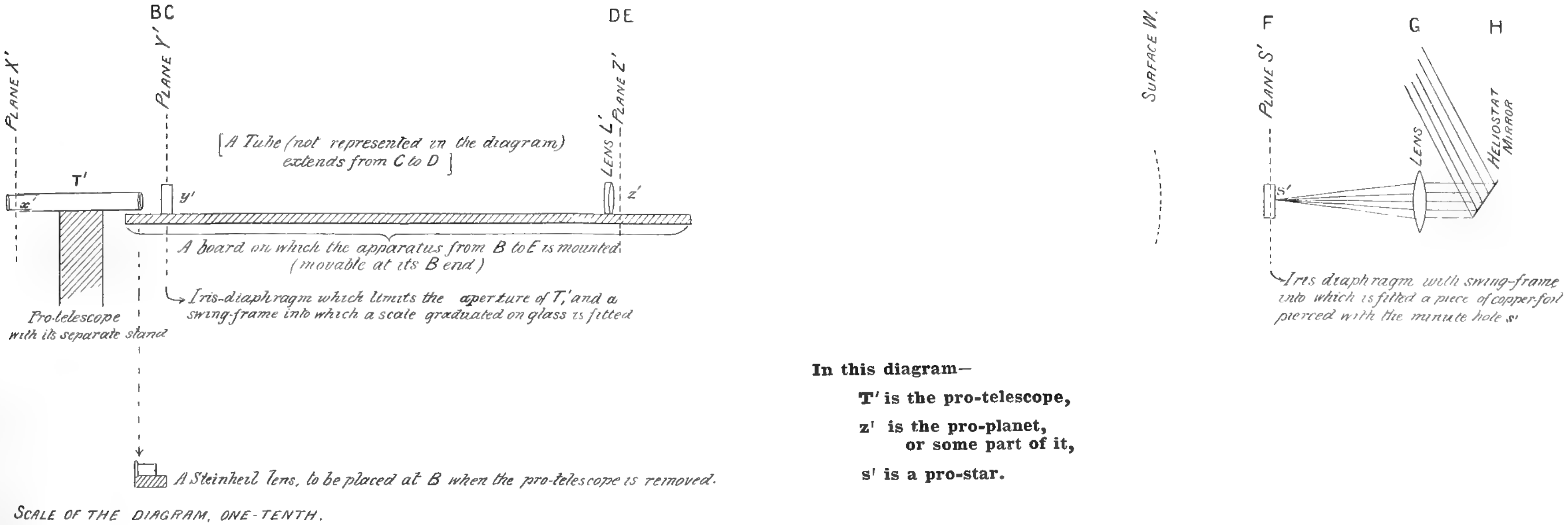

In this diagram—

T' is the pro-telescope,

z' is the pro-planet, or some part of it,

s' is a pro-star.

in which almost all inferences arrived at deductively admit of satisfactory verification at almost every step, by experiments with the microscope—an instrument which permits a greater range of useful conditions to be secured than are available with the telescope.

2. In the experimental verifications, which are what we shall be chiefly concerned with here, we have to consider specially the relation in which two images stand to one another. One of these is the familiar image of the celestial object presented by the telescope to the eye. Either the whole or a part of the other (which we shall find it appropriate to call the *Concentration* Image) can in all cases be formed by the same identical light but is an entirely different image, as will presently be explained. The advantage of introducing this concentration image arises from the circumstance that the method of analysis which has proved to be the most efficient in tracing out how images are actually formed by nature, is the analysis of the light within any space occupied by a uniform medium into its constituent u f w's (undulations of flat wavelets)—an analysis which can be shown to be always possible and legitimate however complex the light traversing that part of the medium may be. These undulations are innumerable, each consisting of wavelets of infinitesimal intensity, each undulation to be thought of as pervading the whole of the medium when the medium is pictured as extended in all directions without limit, and being of such a kind that its wavelets are equidistant, alike, and uniform throughout their whole extent in regard to wavelength, intensity, and state of polarization *. Moreover, one such undulation and one only needs to be recognized as travelling in each direction in which light traverses the medium. It is by the interferences of these innumerable undulations with one another when they, as it were, pour down simultaneously upon the place where the image is formed—it is by these interferences that the image is called into existence however intricate it may be.

3. This is by no means the only way in which light can be resolved. In fact the number of ways in which light may legitimately be resolved has no limit; and any one of the numberless legitimate resolutions, *if only we were able to follow out its consequences*, would guide us to the same ultimate interference effect—in other words, to the same image; but among them the resolution into undulations of absolutely uniform and absolutely flat wavelets recommends itself as the one by which the student of nature can best appreciate

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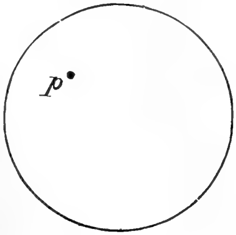
* See Phil. Mag. for April 1905, p. 594, Appendix.

the actual progress of events and can, with least difficulty, succeed by deductive reasoning in foreseeing the optical effects that will arise.

4. However, in making observations and experiments, it is somewhat different: and we shall find it often convenient to resolve the light in some other way that is legitimate; *e. g.*, (when dealing with singly refracting media) into undulations of spherical wavelets which within a limited volume situated at a sufficient distance from the centres of the spheres, will, within that space, be undulations of nearly though not quite flat wavelets. Among events of this kind light which reaches the earth from a star is by far the nearest approach to light consisting of flat waves that is available when we want to make actual experiments with it.

5. In treating of vision with the telescope it is found most convenient to resolve the light before it enters the telescope into a very special system of undulations of spherical wavelets, viz. into spherical undulations the centres of which shall be the several points of a plane perpendicular to the optic axis, situated just in front of the objective of our telescope. This plane we shall call plane Y, and the circular disk of it in front of the objective we may call disk y, the diameter of which will be A, the "Aperture" of the telescope. The centres of the undulations, being the points of plane Y, are so remote from the object—suppose Mars—that the light waves as they leave the planet to converge towards those centres are very nearly flat waves in the vicinity of the planet; and, inasmuch as the centres towards which they converge are upon a plane close to the objective, *they indicate at once which of these spherical undulations can and which cannot enter the objective.* Obviously those converging towards points lying within disk y enter the telescope, while all the others whose centres are at other points of plane Y cannot enter it. Let us fix our attention upon that one of the spherical undulations which has its centre at the point p of disk y. Between Mars and p, the part of this undulation



Disk y.

with which we are concerned is an enormously long cone of light with its base upon Mars and its vertex at p, and consists of that portion of the whole spherical undulation converging towards p, which happens to lie within the geometrical cone we have indicated. After passing p, this portion of the undulation becomes a small diverging cone which enters the objective, and (unless the axis of the cone is already on the optic axis) the little cone in passing through the objective is bent so that the light advances towards a certain tiny patch where we shall find an image of Mars, if a suitable screen, which we may call screen X, be set up perpendicularly to the optic axis at the principal focus of the objective. Upon that little patch, which we may call patch x, the part of the spherical undulation which has travelled within the cone falls, and would there produce a uniform illumination over the whole of that patch if it were the only light admitted to the telescope. Similarly the portions that happen to lie within the corresponding cones of the undulations which converge upon the other points p', p'', &c. of disk y, will after entering the telescope be made to fall upon the same tiny patch x, and would each of them simply illuminate it uniformly, if they could be isolated from one another. But as they are all present together upon patch x, they interfere with one another, and *it is by their interferences that the complex image of Mars is formed.*

6. It is of importance to keep in mind that in looking at such an object as Mars, the differences of distance from the observer of the features seen upon different parts of the surface of the planet, are of no optical account. Screen X may therefore be practically treated as a simple plane perpendicular to the optic axis, and all parts of the image will be simultaneously in focus upon it. This is an advantage which the telescope has over the microscope.

7. In the rest of this Chapter we shall request the reader to picture to himself apparatus which in fact is unattainable, but which if it existed would enable man to make what we may call cosmical experiments; and we shall invite him to consider what would be the optical effect of bringing that apparatus into operation if such a thing were possible. In the next following chapter we shall describe how to repeat these experiments with apparatus that is under our control, and shall show how by employing it we need no longer be content with merely conceiving, but can actually see the results.

8. We shall begin by asking the reader to permit us to effect a simplification which will be a help to us in our

inquiry, and which is based on the circumstance that it is legitimate to conceive any change to be made at the Mars end of our series of events which will preserve the image in our telescope without sensible alteration. One such change would be if Mars were removed and a pro-Mars substituted for it, this pro-Mars being a flat transparent disk set up close to Mars and perpendicular to the line of sight from us to Mars. We may conceive it to be of the same size as the great circle upon Mars which bounds our vision of the planet. Upon this disk are to be delineated in transparent paints—*i. e.* in paints visible by transmitted light—all the details upon the planet which an artist placed upon the disk would see perpendicularly under him if he moved over the disk from place to place. We may now conceive Mars to be removed and this picture illuminated from behind to be substituted, since the painting would then present to the terrestrial observer precisely the same appearance as Mars does. Both the planet itself and this pro-Mars would obviously contain an enormous quantity of more minute detail than any that can be seen from the great distance of our earth.

9. The light from behind which we are to suppose illuminating the pro-Mars, like every other transmission of light through a medium, is susceptible of being resolved into undulations of flat wavelets; and it is possible to determine the effect which any one of these would have if it acted alone, by picturing to ourselves the pro-Mars as illuminated from behind by a single bright star properly situated, and by considering what the optical effect would then be. If this state of things could be realised, the light incident upon the pro-Mars from behind would behave as a single undulation of flat waves of light; and this in passing through the pro-Mars would—because of the details upon that object—develop into a sheaf of innumerable u f w's travelling forwards in definite directions, one of which may be called the direct light and the others the diverted lights associated with it. If by any contrivance the proper parts of all these undulations could be combined, by being made to fall upon a single disk after having occupied identical times in their several journeys, they would exhibit on that disk by their mutual interferences an *optimum* image of the pro-Mars, i. e. *the best image which the light emitted by the pro-Mars is competent to produce at that distance.*

10. In order to make the transmission forwards of these undulations compatible with the formation of the Concentration Image upon plane Y which we shall need to assist us in our further study, we may conceive a lens L of immensely

long focus and of vast aperture to be introduced perpendicularly to the optic axis and immediately in front of the pro-Mars, the focal length of this lens being the whole distance from lens L to disk *y*, which latter stands immediately in front of our astronomical telescope. It is legitimate to introduce this lens, inasmuch as such a lens situated close to the planet, or to the pro-planet, would not have any sensible effect upon an image of either of those objects formed at a distance, such as the image in our telescope. Again, if both Mars and the pro-Mars were removed from behind the lens, an image of the distant star would be formed by lens L upon disk *y*. This stellar image, which we may call the *star-burst* produced by the light that has come from the star through a lens, would present that appearance of a spurious disk and surrounding rings which Airy investigated, and the size of which for light of each wave-length would be, as appears from his investigation, directly proportional to the distance from lens L to the earth and inversely proportional to the diameter of lens L. Now as there is nothing to limit our conception of the size of lens L, it is legitimate for us to imagine it of such immense aperture that the spurious disk and rings, which are the image of the star, shall shrink into being a mere speck upon disk *y*. Let us next conceive our pro-Mars to be restored to its position behind lens L. Light from the star is now incident upon the farther side of the pro-Mars, and this single undulation of flat waves in passing through the pro-Mars changes into a sheaf of u f w's which are what advance towards our telescope. Each of these innumerable undulations will by lens L be concentrated into a speck on plane Y; and *those of them, and those only, which produce specks that fall within disk y* will be the undulations emitted by the pro-Mars that will be caught by our telescope. As these will be only some of the entire sheaf of undulations transmitted forward by the pro-Mars, the image they can form in our telescope will fall short of being the best which the light emitted by the pro-Mars would be competent to form, in other words, it will fall short of being the optimum image.

11. It is possible, at this stage, to get some insight into the true character of the image presented in our telescope. Let us call the light from the planet which is *admitted* into the telescope, light A, and the light *excluded* from it, light E; and let us imagine another body of light identical with E, except that all the component undulations of wavelets of which it consists travel half a wave-length behind those of E. This imagined light we may call −E. Then if +E and −E

were both introduced they would simply cancel one another. Therefore we are justified in regarding the telescopic image as formed by the light A + E − E, since the addition of both + E and − E leaves matters unchanged. But it is also permissible to view the matter otherwise, and this we shall now do. The light A + E, if it could all be made use of, would form what we have called the optimum image, meaning that it is the best image of the planet which the light emitted by the planet is capable of yielding. Hence what we see in the telescope is this optimum image with light − E superimposed upon it. What the full effect of this superposition will be we do not know, but we can at all events see that light − E, consisting as it does of ufw's more inclined to one another than any of those of light A, may introduce additions and defects into the optimum image, *some of which may be smaller than any* of those parts of the telescopic image *which can represent detail really existing* upon the planet. Thus—as we shall find farther on—the minute dark specks which have been detected upon the image of Mars and to which has been given the name of oases under the impression that they represent something on the planet, are probably optical markings arising in the way described above. Misleading appearances of this kind are familiar to microscopists, who sometimes speak of them as 'Intercostal Markings.' They may perhaps be more appropriately termed Phenāko-spiles, or misleading markings upon the image presented by the telescope, as they are a semblance of detail which has no existence upon the object.

It thus appears that what is seen by the Astronomer in his telescope represents the celestial object imperfectly; and what we have to aim at in this inquiry is to study the excesses and defects in the image, with a view to learning how to minimise them and how to detect and measure and make allowance for those that continue outstanding.

12. We may call the image directly formed by the objective the primary telescopic image. It is usually on too small a scale for the eye to see in it the whole of the detail which the objective, if good, can exhibit. It has therefore to be magnified by an eyepiece, and we shall use the term *eikon* to signify the resulting larger image which is what is actually seen by the observer. The eikon will then be, not the primary telescopic image, but an enlargement of it. Again, let us use the term *eidolon* to signify the object which *seems* to the observer to be what he is looking at—in other words, the eidolon is a model of the planet, of such a size and with such additions imperfections and blurring together of details,

as would cause it to have, if viewed by the naked eye from the distance of most distinct vision, *exactly the same* appearance as the image seen in the telescope. We shall assume, in accordance with the usual convention, that the average eye finds it most convenient to scrutinise an object critically when placed in front of it at a distance of 10 metric inches, which is the same as a quarter of a metre. This then is the distance from which we are to conceive the eidolon to be viewed and criticised by the unassisted eye of a person with good sight. The astronomer should never lose sight of the fact that what he sees in his telescope is this eidolon and *not the distant object* ; and it behoves him very carefully to discriminate between those features on the eidolon which he may rely on as representing somewhat similar details upon the planet, and those others which are due to a very different cause.

13. It is advantageous to the observer to be readily able to form a correct estimate of the actual size of the eidolon, or object which appears to be what is seen in his telescope. Its size can be easily computed from a number which is recorded in the Nautical Almanac for each day, viz.: the number of seconds of angle in the apparent semidiameter of the planet on that day. Let ρ'' be the number of seconds in the semidiameter of any planet, and M the magnifying power we are using upon our telescope. Then the angular diameter of the eikon, the image of the planet we see in the telescope, will be $2M\rho''$; and the diameter of the eidolon, the object which will then seem to be presented to us, will be

$$2M\rho d \times \frac{48481.36811}{10^{15}}$$

where $\frac{48481,36811}{10^{15}}$ is the value of $1''$ in circular measure, and d stands for the average distance of most distinct vision. We may adopt the usual convention and assume d to be 250 millimetres. Introducing this value we find

$$\text{Diameter of eidolon} = \frac{M}{412\cdot53}\,\rho \text{ millimetres.}$$

Hence if we arm our telescope with an eyepiece which will make M, the magnifying power of the telescope, $= 412\cdot53$, we shall have the extremely convenient relation that the resulting eidolon of the planet will have the number of millimetres in its diameter the same as the number entered in the Nautical Almanac as the number of seconds in the apparent semidiameter of the planet for the day on which the observation is made; so that every half-millimetre anywhere on the eidolon will exactly represent 1″ upon the corresponding part of the planet. Partly for this reason and partly because a power of about 400 is (under favourable atmospheric conditions) the best, as we shall see farther on, for bringing out the full capabilities of the telescope of 12-inch aperture which the author was in the habit of using, he made a practice for several years of regarding 412 as a standard of magnification, with which he compared the various magnifying powers he had occasion to employ. Thus, when using an eyepiece giving magnification 140, he would think of this as not far from one-third of his standard, and that accordingly each half-millimetre on the smaller eidolon of the planet which it would furnish would correspond to a length at the distance of the planet subtending 3″. This was very convenient. But other considerations of much weight have since convinced the author that it would be still better for astronomers to adopt a magnification of 400 as a standard unit, and to make a practice of estimating the various powers they use as multiples or fractions of that number. The reason for this recommendation will be explained farther on. Meanwhile it may be useful to call attention to the use which may be made of the new standard, viz. 400, in estimating magnitudes. The eidolon of a planet which results from using a power of 400 is slightly smaller than the eidolon which would be yielded by 412·53. The reduction in size, however, is little more than 3 per cent., and does not hinder its being useful for the observer to keep in mind that each 1″ on the planet will now be represented by *slightly less* than half a millimetre on the eidolon, where 'slightly less' means roughly speaking 3 per cent. less, or more nearly in the ratio of 32 to 33, or, if extreme accuracy is required, in the ratio of 2″ to 2″·062648—the latter angle being the angle whose circular measure is exactly 0·00001. This last mentioned angle, viz. the angle 0·00001, is of special and frequent use to the observer and we shall call it angle ϵ; and the length which at the distance of the planet would subtend angle ϵ, we may call the length e. It is this length upon the planet which each mm. on the standard eidolon *exactly* represents.

14. Let us apply this way of regarding events to what will happen next year. Mars will come closest to the earth on 1909, Sept. 18. On that day its semidiameter will have become 12″·02. Accordingly, when nearest and examined with a power of 400, the diameter of its eidolon will be about 3 per cent. less than 12·02 millimetres, *i.e.* it will be 11·8 mm. in diameter.

Now, under the circumstances described, and at the centre of the disk, a millimetre on the eidolon corresponds to nearly 10 of the geographical degrees annexed to the maps of the so-called 'canals' upon Mars. To appreciate this, get a small marble somewhat less than 12 mm. in diameter, and view it from a distance of ten inches; for it is on to such a tiny sphere that we must conceive the details recorded in the maps of Schiaparelli and Lowell to be crowded, in order to have a just idea of what it was that those skilful observers succeeded in glimpsing on this minute scale, occasionally, at favourable moments, and with difficulty. Many years ago, after the second of Schiaparelli's maps appeared, the writer of the present paper took advantage of a good opposition of Mars to study what could be seen when the state of the atmosphere was favourable, upon the eidolon of the planet which was presented to him by a good reflecting telescope of 12-inch aperture, exceptionally well adjusted *. The author also derived specially useful instruction from making careful control observations upon the Moon when nearly full *under equivalent optical conditions* to those which he employed upon Mars. These will be described in the last Chapter of this paper, and he can recommend a frequent recourse to control observations upon the nearly full Moon to all astronomers who have occasion to make it their aim to become serious students of Mars.

But before describing these comparative observations, we have first to inquire under what conditions certain typical

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* The author's telescope was adjusted by the special Collimator for completing the Adjustments of Reflecting Telescopes, described at p. 30 of the Report of the Cheltenham Meeting of the British Association in 1856, with the addition that the line of collimation of the tube which carries the eyepieces (into which the collimator is to be placed) was made movable through a small range by three screws acting against springs; and that the adjustment was completed, not by disturbing the adjustments of either of the mirrors, but by a slight motion of this tube, thus altering the line of collimation of the eyepieces. This was found to be optically sufficient and rendered it extremely easy to make the adjustment—so easy that it could be made if necessary before each observation. An electric spark, made by that kind of replenisher sold for lighting gas, furnished the light at the focus of the collimator.

The instrument was made for the author by Sir Howard Grubb, F.R.S., and when employed upon a sufficiently good telescope was found to add materially to the excellence of the image that could be secured by the usual methods of adjusting the two mirrors.

The adjustments of the mirrors were in the first instance made with care in the usual way. This was sufficient to bring the image of the spark well within the field of view of the collimator, and the image of the spark was then brought into coincidence with the sparks by the three adjusting screws mentioned above.

features upon a planet can be adequately seen through a telescope, and what modification their appearance will undergo when those conditions can be only partly secured. In prosecuting this inquiry an efficient working model of the cosmical apparatus described in the foregoing pages, will be found exceedingly useful. This, accordingly, we shall next describe.

CHAPTER 2.

How to construct an adequate working model of the apparatus described in the last Chapter, with which the necessary experiments can be made.

15. In the preceding pages the reader has been asked to consider what optical effects would follow if a lens L could be placed close to the object which the astronomer is examining through his telescope. If we are content to confine ourselves to the *deductive* treatment of telescopic vision, the intrusion of this imaginary lens may be dispensed with, since the conclusions arrived at can be reached without that machinery. It would be legitimate and sufficient to resolve the light emitted by the planet directly into undulations of spherical wavelets subjected to the condition that the centres of these spherical undulations shall be the several points of any assumed unfolded* surface of one sheet enveloping the whole of that aspect of the object which is turned towards us. This would be a legitimate procedure; and would answer our purpose. But the conceptions which the investigator must be able to form in order to prosecute the inquiry in this way can, perhaps, most easily be grasped after he has pictured to himself the intervention of lens L, which he may think of as placed either immediately in front of or immediately behind the pro-Mars; and at all events this imagined lens suggests and serves as an introduction to a valuable piece of apparatus whereby the steps of the process by which the telescopic image is formed can, so far as is necessary, be submitted for our inspection. The steps of that process can no doubt in many cases be ascertained, and the details of it computed, by the deductive method of treatment; but it is in some respects perhaps even more instructive and it is certainly much more impressive actually to see them. On this account, and as in this paper deductive reasoning is avoided as much as possible, the reader will be invited to direct his attention for the most part to those verifications of results which are brought within his reach by the apparatus

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* By the term "unfolded" is meant that no vector outwards from the planet will pierce the surface more than once.

about to be described in the present chapter—an apparatus easily put together and which the author ventures to suggest ought to be an adjunct of every astronomical observatory which is occupied with the study of what can be seen upon celestial objects of visible size, whether sun, or moon, or planet, or comet, or nebula.

16. The essential parts of this apparatus, the ease with which it can be constructed, and the many convenient arrangements that can be secured in using it, will be understood from a description of the specimen which the author was able to set up for his own use out of materials that happened to be at at hand. The apparatus as a whole may be designated an Observatory-experiments Apparatus, or OE Apparatus, or, still more briefly, OEA. The essential parts are represented in the diagram on Plate XII.

The proposed apparatus is a working model of the Cosmical Apparatus described in the last chapter, and of so efficient a kind that all the experiments that could be made with the Cosmical Apparatus, if the Cosmical Apparatus were available, can be made with our model of it. In the Cosmical Apparatus we may distinguish four planes, two of which have already been mentioned :—(1) The plane X within the telescope, erected perpendicular to its optic axis and at the principal focus of the objective ; (2) and (3) planes Y and Z, perpendicular to the line from the telescope to z, the object on the planet which is under examination—Y being a plane erected perpendicular to this line at its nearer end and Z the plane perpendicular to it erected at its farther end. Finally, (4) a plane that we may call plane S, to be located at the star s that we have asked the reader to imagine behind the planet, and which is to be the plane through that star perpendicular to the line from z to s. All of these are represented in the experimental apparatus by screens or planes which are indicated upon the diagram in Pl. XII. by the letters X′Y′Z′ and S′.

17. T′ in the diagram is the pro-telescope, which means that it is a small telescope which in our apparatus can be made *adequately* to exhibit the optical performance obtainable from any astronomical telescope, T, up to telescopes of two-metre aperture. This, moreover, it does with the great added advantage that provision is made whereby we are enabled to study the Concentration Images which are associated with the telescopic image, and can ascertain from them the causes of the effects produced by varying the apertures of telescopes ; and so learn with what classes of objects an increase of aperture will give improved vision as well as how much and of

what kind, and with what other classes of objects the improvement will be too slight to be valuable.

The pro-telescope in the author's apparatus is a small laboratory telescope of one-inch aperture and eight-inch focal length, intended for reading scales upon instruments without having to go close to them, but here used to view the object z', placed at E. We make use of the letter z to signify any feature we picture as possibly existing on the planet, and the conditions for seeing which satisfactorily we want to investigate. The z' in our apparatus is a pro-z, that is an object at E of the same shape as z, and of the size which will in the experimental apparatus correctly represent the dimensions of z upon the planet. It can easily be made of this size, inasmuch as such dispositions have been made in setting up the apparatus that one millimetre at z' represents length e upon the planet, viz.: the length upon the planet which subtends standard angle ϵ as seen from the earth. We already know that this length is also represented by one millimetre upon the standard eidolon of the planet, viz.: the eidolon furnished by an astronomical telescope magnifying 400 times. When, as usually happens, the object z upon the planet is one of which we only expect to see the outline, it will be sufficiently represented by a hole in copper-foil at z' of the proper shape and size, illuminated by light coming from beyond. When this light is diffused light such as that from a sheet of white paper or from the reflexion of a cloud, and when the aperture of the pro-telescope T′ has been adjusted to correspond to the aperture of the astronomical telescope, which it will be when the one aperture is made the hundredth part of the other, then will the vision of z' which we shall obtain through the pro-telescope be precisely *the same* as that which the astronomer can, *at best*, secure of the corresponding object z if it exists upon the planet. By "at best" is meant if the three following conditions are secured:—

1. If the "seeing" is perfect;
2. If a magnifying power which corresponds to that on the pro-telescope (viz.: a magnifying power 100 times that employed on the pro-telescope) can be with advantage employed on the astronomical telescope;
3. If z upon the planet is as adequately illuminated as z' in the experimental apparatus.

The pro-telescope is mounted upon a separate stand easily removed from before the rest of the apparatus, so as to allow the observer to examine an iris-diaphragm at B, which is what limits the aperture of the pro-telescope, and a scale behind it at C, which enables him to adjust the iris-diaphragm. These observations are conveniently made through a Steinheil lens magnifying about 7 times mounted on a small piece of wood so as to be readily placed in its position before B. The scale at C to be read through this lens is an ordinary eyepiece micrometer scale—a centimetre graduated into 100 parts upon glass ; and both it and the iris-diaphragm are mounted on an ordinary substage apparatus belonging to a microscope, the eyepiece micrometer being sufficiently tightened by a slight caulking of soft twine into the swing-frame intended for the microscope's sub-stage stops. The swing-frame enables the observer to turn the scale out of the line of sight when using the pro-telescope. This has to be done, since the glass on which such scales are graduated is not sufficiently good to be left in front of the pro-telescope.

18. It is here also, and through the Steinheil lens, that observations are to be made upon the concentration images which will be brought to their focus upon plane Y′, the representative of plane Y of the cosmical apparatus. We are to regard the plane at C perpendicular to the optic axis as plane Y′. The concentration images will then, when focussed upon this plane, coincide with the graduated scale —an arrangement which enables details upon the concentration images to be conveniently measured. Provision was made when setting up the apparatus whereby each *millimetre on the concentration image* as measured in the experimental apparatus corresponds to *one decimetre on the concentration image* that would be formed in front of the astronomical telescope if the imaginary lens L could be placed before the planet. In fact all measures made on the concentration image as seen in the experimental apparatus have only to be multiplied by 100 to arrive at what the corresponding measures would have been in the cosmical apparatus, if the cosmical apparatus could have been made available.

19. Another very useful numerical relation furnishes us with the means of dealing with spectra, and is often of service because the concentration images which render us most assistance are images consisting of spectra. If we could set up the cosmical apparatus described in Chapter 1, these images would present themselves on plane Y, and measures upon the spectra which would be there seen are most conveniently expressed in terms of a standard length *b*, which symbol stands for λ/ϵ, where λ is the wave-length of

the light whose optical effect is under consideration. Since $\epsilon = 0{\cdot}00001$, b or $\lambda/\epsilon = 100000\,\lambda$. Hence b on plane Y is the same fraction of a *decimetre* as λ is of a *micron*, which is convenient inasmuch as wave-lengths are in modern science always recorded as fractions of a micron.

What corresponds to this in the experimental apparatus is that the concentration image seen at C through the Steinheil lens, will in each case be identically the same concentration image as would be formed on plane Y in the cosmical apparatus, but on a scale 100 times smaller. Hence in measuring the details of its spectra we are to use a b' (or pro-b) which shall be the hundredth part of b. Accordingly $b' = 1000\,\lambda$ and is the same fraction of a *millimetre* as λ is of a micron. This enables us to read off directly upon the scale at C the length, corresponding to each wave-length, of any required multiple of b'.

20. To secure these convenient numerical relations and other advantages of a like kind the following arrangements were made. D, the distance of the planet from the earth varies from day to day, but has to be represented in our apparatus by a D′, or pro-D, which shall not vary. *This fixed distance is made* 1 *metre*. Again, e, the length which at the distance of the planet subtends the angle ϵ at the earth, and which is therefore $= \epsilon D$, will vary in the same ratio as D, but in the experimental apparatus is to be represented by a fixed length at z'. *This length has been made* 1 *mm.*, so that $e' = 1$ mm. With these conventions, since $\epsilon = e/D$, ϵ' (the pro-ϵ or representative of ϵ) must $= e'/D'$, *i. e.* 1 mm./1 metre, which $= 0{\cdot}001$. Hence the standard angle ϵ' of the experimental apparatus is exactly 100 times the standard angle ϵ of the astronomer.

To attain these convenient results the distance D′ upon our apparatus will need to be not directly the distance from y' at C to z' at E, but that distance when corrected by making allowance for the optical effect upon it of lens L′. For the distance has to be made such that 1 mm. at z' shall subtend the angle ϵ' or $0{\cdot}001$ at y', and this requires that the distance from y' to the optical centre of lens L′ shall be slightly more than one metre. In the author's apparatus it is made $1^{m}{\cdot}005$, and the object z' when pushed into its place is some 4 or 5 millimetres to the right of the optical centre of lens L′. When these arrangements were made, what we may call the optical distance of z' from y' became one metre.

21. The lens L′ is to be a pro-L, that is a lens which shall function in our apparatus in the way in which we have asked

the reader to imagine an immense lens placed in front of the planet as functioning. L′, the pro-L, is a two-inch objective of only 55 cm. focal length. A longer focal length, something near a metre, would have been preferred, as it would have made L′ function more exactly like L in the cosmical apparatus. But the shorter focal length of L′ in the author's apparatus works well enough: it only necessitates the substitution in one instance of a resolution into spherical undulations with the centres of the spheres the several points of surface W, where in using the cosmical apparatus the resolution would have been into flat undulations.

22. The whole of the apparatus from B to E is mounted upon a board, made movable at its B end under sufficiently delicate control, both sideways and up and down. This is in order to be able to change at will the inclination of the optic axis of the part of the apparatus to the left of E, relatively to the position of the optic axis of the apparatus to the right of E, which latter remains in one fixed position. When the pro-telescope is used it is to be set up before B, and its optic axis is to be adjusted to coincide with that of the apparatus attached to the board.

23. The next part of the apparatus to be noticed is the pro-star at *s*′. This is a clean round hole, $\frac{1}{3}$ of a millimetre in diameter, made by a very fine needle in copper-foil. It is to be set up as far off as convenient to the right of *z*′, the pro-planet, and this distance in the author's apparatus is about $1\frac{1}{2}$ metre, which was found to be sufficient. Beyond it again is a simple lens G and the heliostat H. The heliostat reflects a sunbeam horizontally, and lens G condenses this into an image of the sun upon the sheet of copper foil S′, at the place where the minute hole *s*′ has been made in it. The light which then passes will produce the same optical effect upon a sufficiently small object at *z*′, as would *a single undulation* of flat luminous waves reaching that object. As this is a very important optical statement, and as upon its being true depends the working of our apparatus, we shall give in an appendix to the present Chapter an exceptionally simple proof of it; and will add some observations which will it is hoped help the student of this branch of Nature's work, to judge correctly how far the conditions he produces in his experiments may be trusted to represent the process pursued by Nature.

24. Attempts to use artificial light focussed by a lens upon *s*′, instead of the sunbeam, have been more or less unsatisfactory. The Nernst lamp is not sufficiently intense, and the arc light, while abundantly bright, produces an unsteady

image when focussed on the copper-foil S′, which it is difficult to keep on the small hole. Nevertheless these artificial illuminants have sometimes been used, when sunshine was not available.

25. In making our observations two images have to be studied—the telescopic image of z' as presented by the pro-telescope T′, and the concentration image *produced by the same light* at y', which is to be examined through the Steinheil lens. When the sun is the source of light, the concentration image is usually seen in great perfection, but the telescopic image is apt to be too bright for the eye. When this is the case, a dark glass may be put either before the eye, or close beyond z', or near s'; in any of which positions moderate imperfection in the dark glass will not spoil the image. The author usually hangs the dark glass just beyond s'; where also another dark glass is mounted through which to view the inconveniently bright image of the sun formed by lens G when adjusting the heliostat to throw the sun's image where the hole s' is.

When setting up the apparatus the two following dispositions have to be attended to. D′ is to be one metre; and the object z' has to be pushed into its proper position. It has already been explained how to secure that D′ shall be a metre. To get z' into its place the procedure described below was found convenient.

26. The objects at z' are usually openings of various shapes and sizes made in small pieces of copper-foil. The copper-foil is about $\frac{1}{10}$ mm. thick, and has been softened by heating it red-hot in a Bunsen's burner. Round and triangular holes, to represent objects upon the planet of those shapes, can be conveniently made by ordinary and glovers' needles. For rectangular and other polygonal openings the author crosses pieces of the softened foil out of which strips have been cut with a small pair of scissors. The objects z', whether of this kind or any other, are brought into position by the following contrivance. A small piece of board is fastened to the steel blade of an ordinary carpenter's square, and two pieces of the copper-foil about $2\frac{1}{4}$ inches square are screwed to one edge of the wood so that when the carpenter's square is made to slide along the board on which the apparatus is mounted, it will push the squares of foil up against lens L′. A round opening about half an inch across is provided in both the squares of copper, opposite to the middle of lens L′. The strip of copper or glass holding whatever is to be viewed at z' is to be slipped between the squares of foil, and the object itself is to be brought to the middle of the half-inch

opening. The object *z′* will then come into its proper position when the carpenter's square is simply slid up against lens L′.

27. The copper-foil used at *s′* is of the same kind as that used at *z′* and is softened in the same way. It is then possible to pierce it with the thinnest needle that can be procured, with which a clean round hole about $\frac{1}{3}$ mm. across can be made. This small hole, which subtends less than 1′ of angle at *z′*, furnishes the opening at *s′* which is to admit the light that is to be our pro-star. The copper-foil at *s′* is fitted into the swing-frame of a substage apparatus belonging to a microscope similar to that employed at BC, and like it fitted with an iris-diaphragm. The swing-frame allows the copper-foil with the small hole to be turned aside, and the iris-diaphragm can then be brought into action to limit diffused light incident upon *z′*, in the way which is required for one of the experiments which are about to be described.

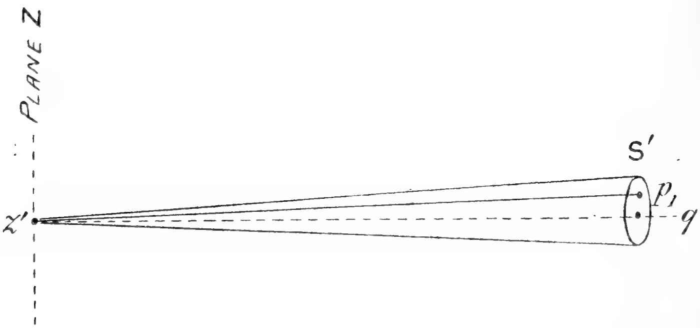
28. One other appliance remains to be mentioned. One of the eyepieces provided for the pro-telescope is armed with an eyepiece micrometer in its focus. By using this, and varying the aperture of the pro-telescope by the iris-diaphragm at B, it is easy to measure the changes in magnitude and in appearance which small objects seem to undergo when examined through telescopes of different apertures—a very important matter for the astronomer to become acquainted with. This completed the arrangements in the apparatus which the author put together.

Our main task in the second part of this paper will be to find out by the use of this apparatus the actual process by which images in the astronomical telescope or in the pro-telescope are brought into existence by nature; and incidentally we shall learn what that familiar but very remarkable optical phenomenon, a beam of light, really is.

APPENDIX TO CHAPTER 2, § 23.

29. In our experimental apparatus light from the sun has been admitted through the pro-star *s′*, a hole about $\frac{1}{3}$ mm. in diameter, and allowed to fall upon small objects *z′*, usually less than $1\frac{1}{2}$ mm. in diameter, which are placed at a distance of $1\frac{1}{2}$ metre from *s′*. The part of this light which is of wave-length λ will be treated as a single u f W (undulation of flat waves) where it falls upon those small objects, and we have to show that it is legitimate so to regard it.

Let *s'* represent diagrammatically the minute hole through which the light has been admitted and let the point *z'* be



the middle point of the small object *z'* upon which the transmitted light is incident. Then the light of any one wave-length λ, which reaches point *z'* through the hole is resolvable into innumerable u f w's (undulations of flat wavelets) to which the lines p_1z', p_2z', p_3z', &c. will be normals—p_1, p_2, &c. being the several points of the circular disk *s'*. Consider one of these undulations, suppose that which has p_1z' for its normal, and which we shall call undulation P_1. Next imagine two other u f w's, $+Q_1$ and $-Q_1$, to be transmitted along the dotted line qz' which stands for the axis of the acute cone which is figured in the diagram. Of these, $+Q_1$ is to be exactly like P_1 in every respect except that it is to advance in the fixed direction qz' instead of in the inclined direction p_1z' ; and let $-Q_1$ be an undulation identical with $+Q_1$ except that it follows it half a wave-length behind. $+Q_1$ and $-Q_1$ will then be everywhere of equal intensity but in opposite phases, and will simply cancel one another. Accordingly their introduction has been legitimate, since it has made no optical change. We may, however, take another view of what has been done. The undulations P_1 and $-Q_1$ if acting alone would be competent to produce on plane Z' a ruling of alternate bright and dark bands, the point *z'* being situated in the middle of one of the dark bands where the illumination is zero, while at situations so close to *z'* that they are within the darker parts of the dark band, the illumination due to the presence of P_1 and $-Q_1$ will be faint. It follows from this that the resultant effect within this small range of the three undulations $P_1, -Q_1$ and $+Q_1$ will be practically undistinguishable from the effect which would be produced by $+Q_1$ acting alone. It thus appears that if we only need to deal with what happens to a small object z', we may regard P_1 as suppressed and substitute $+Q_1$ for it, without sensibly altering the optical effect upon that small patch. In like manner, we may withdraw the other undulations P_2 P_3 &c. which reach z' from the other points of disk s', and substitute undulations similar to them, $+Q_2$, $+Q_3$, &c., travelling in the fixed direction qz'. We have now no undulations but the Q's outstanding, and since these all travel in the same direction and are of one wave-length, they may be combined (by a known theorem) into a single resultant undulation which we shall call Q_0, travelling in that direction. Moreover it follows from the theorem referred to, that the undulations Q_1 Q_2 &c., which yield this single resultant, may differ to any extent from one another as regards intensities, phases, and states of polarization ; the only property that they must have in common being that their wave-lengths must be the same.

A similar treatment is to be applied to the light of other wave-lengths admitted through the minute hole s', so that what we finally learn is that the numberless u f w's which reach the small object z' from the pro-star s'—that this whole sheaf of undulations, travelling in slightly differing directions, may be replaced by a single u f W (undulation of flat waves) for each wave-length, travelling in the one definite direction qz' ; always provided that we have no concern except with the effect that will be produced in the neighbourhood of the point z'. Observe that the word 'waves' must be here used instead of wavelet, since the intensity of the *resultant* undulation Q_0 need not be infinitesimal.

30. By far the most remarkable instance of such light is the light reaching the solar system from a star, which, though it arrives from all parts of half the surface of an immense body, and in all varieties of phase intensity polarization, &c., nevertheless comes to any point z' upon the earth in directions passing through that point which form such an excessively acute cone that the size of the patch in the neighbourhood of z' throughout which it is legtimate to regard the whole of the light of each wave-length as a single undulation of flat waves, is so large as to be dozens of metres in diameter.

31. *Light of various wave-lengths.*—In the foregoing pages we have only taken into consideration light of one wave-length. Now in nature light of one wave-length never visibly presents itself unaccompanied by light of neighbouring wave-lengths. The nearest approach to light of one wave-length that we know of is the light which furnishes a thin line in the spectrum of a gas, but, however narrow the line,

it always has some width—in other words, it consists of light of wave-lengths ranging between limits which may be close but cannot be coincident. What happens under these circumstances is discussed in the Phil. Mag. for Feb. 1903, p. 275 *et seq.*, from which discussion it appears that it is permissible to divide the wave-lengths of the light which issues from the minute hole s', into little groups within each of which the wave-lengths shall vary between narrow limits; and we may then substitute light of one wave-length for each of these. This resultant, however, is not the simple kind of u f W of which we have hitherto been thinking, for the luminous undulations which occur in nature always have, at any given station, fluctuations in intensity of the same nature as beats in acoustics, which however need not be so simple as to be periodic but will occur in whatever manner may be the outcome of the conditions—probably molecular conditions—that have prevailed in the parts of the source from which the light has come. Abrupt changes of phase may also take place, of the same nature but not of the same simple kind as the reversals of phase that occur when there are beats in music. And also alterations of the state of polarization.

We have referred to these complications* in order to have an opportunity of pointing out that though the result will be one of immense complexity which it is impossible to simplify in any experiments man can make, it nevertheless is of such a character that the fluctuations which take place do not prevent portions of light derived from any single one of these *complex* u f W's from being capable of interfering with one another and furnishing that *persistent* kind of interference upon which we shall find that the formation of visible

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* A resolution of light into undulations of flat waves of finite intensity however small, is only legitimate when dealing with what happens within a limited volume of space and a limited duration of time. [See Phil. Mag. for February 1903; Theorem X. p. 274, and Theorem XIII. p. 279; see also § 4 on p. 265.] All such undulations are more or less affected by the complications referred to in the text—more, if the number of the components is moderate and their intensities considerable; less, when the number of components is increased and their separate intensities correspondingly lowered. During this process the volume within which the resolution is available increases. But, as the mathematical reader will understand, it is only *at the limit*, when the number of components has been increased indefinitely and their intensities fall to being infinitesimal—when in fact wavelets take the place in the undulations of waves, and when the range of wave-lengths for which each λ stands has become an infinitesimal range—it is only at this limit, unattainable in practice, that the components are entirely devoid of the above-mentioned complications and become undulations of waves that are absolutely alike. The resolution would then become what would be true of all space and all time, if in a uniform transparent medium of infinite extent.

images in telescopes depends. By persistent interference, is meant an interference which lasts for a time sufficiently long for the human eye to take note of it, that is which lasts for a vast æon of time if compared with the durations we have to consider when treating of the molecular events which determine the great bulk of the interference effects that occur in light.

The reason of this persistence is that the fluctuations that occur in a complex u f W are functions of the time only, so that although consecutive waves will in some parts of the undulation differ, yet every wave will be absolutely the same throughout all parts of its own extent; and this is the condition which renders a lasting interference effect possible.

Thus when a wave of the complex u f W which issues from the pro-star s' reaches the object z', which is usually a small opening of some definite shape in the sheet of copper Z', a part of this wave and its successors are allowed to advance through the hole, and are scattered into different forward directions in a way which will be explained in the next Chapter. These scattered portions or some of them will enter the pro-telescope and by its objective be made to converge upon a small space at x', and it is *in consequence of their being capable of interfering with one another* that they will produce there an image of the opening at z'.

This u f W will produce at x' an image of some kind of object z', and this image is one of the partials of the complete image which will be formed when diffused light instead of only one u f W is allowed to operate as the light incident upon z'.

It is well here to observe that no two of the u f W's need be so related to one another that the light of the one can produce visible interference effects with the light of the other; and accordingly the image we see in the pro-telescope when we employ diffused light, consists of our seeing, as it were, superposed upon one another, the images *formed independently of one another* by u f W's into which the diffused light can be resolved. Thus the partials, as they exist on disk x, are light superposed upon light under the condition that they can produce no interference effect one with another. They accordingly furnish at each point of disk x an illumination which is the simple sum of the intensities of them separately at that point. It is in this way that a telescopic image is formed.

In the second part of this paper it is proposed to go fully into this subject, and into others allied with it.

[To be continued.]

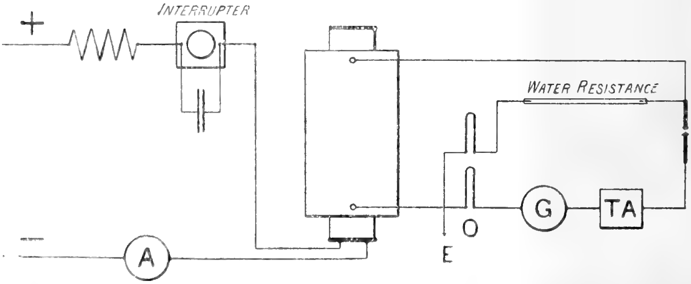
XXVI. *Short Spark Phenomena.*
By W. Duddell, *F.R.S.*[*]

[Plates XIII.-XV.]

In connexion with some measurements of the current in the secondary circuit of an induction-coil, I have noticed two curious effects, which are probably well known but which I do not remember having seen described anywhere.

The apparatus in use consisted of a 12-inch Newton induction-coil which was supplied from the 200 volt direct-current mains. A large resistance was placed in series with the primary of the coil to limit the current, and the current was interrupted by means of a mercury-jet interrupter; the connexions are shown in fig. 1. The secondary circuit contained a galvanometer G to measure the mean current and thermo-ammeter T. A. to measure the root-mean-squared current.

Fig. 1.



The galvanometer was specially constructed for the purpose so as to have a sufficiently low sensibility without using a shunt. It was of the moving-coil type and was well insulated from earth by means of porcelain insulators. The sensibility was such that 1 milliampere gave a scale-deflexion of 200 divisions (1 division equals 1/40 in.). The thermo-ammeter had a resistance of about 101·5 ohms and gave its full scale-deflexion for about 70 milliamperes R.M.S. value.

By breaking the current through the primary by means of a switch, the direction of the deflexion of the galvanometer corresponding to breaking the primary current was determined. A deflexion, in this direction I will call, in what follows, a positive deflexion, and a deflexion in the opposite direction, that is corresponding to the make of the primary current, I will call a negative deflexion.

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[*] Communicated by the Physical Society: read April 10, 1908.

P.D. and Current Wave-Forms of Short Sparks.

Fig. 3.—Spark-length equals zero.

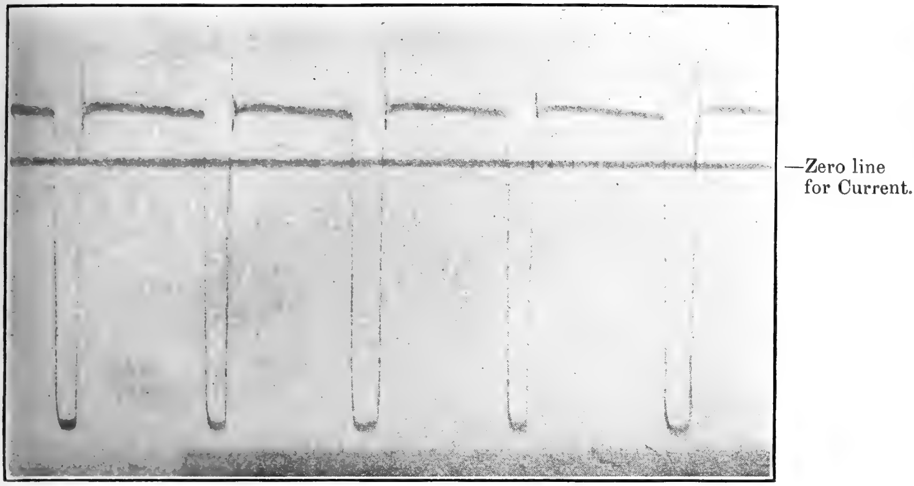
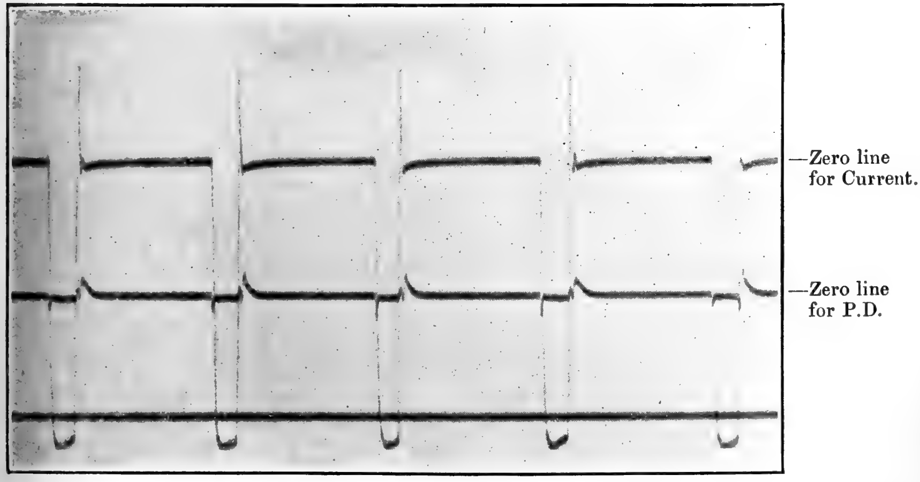


Fig. 4.—Spark-length 1 mm.



P.D. and Current Wave-Forms of Short Sparks.

FIG. 5.—Spark-length 5 mm.

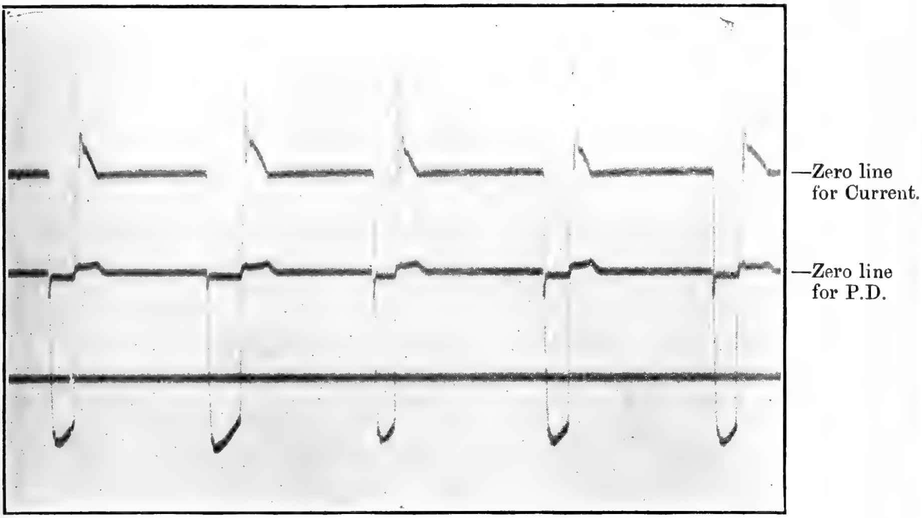
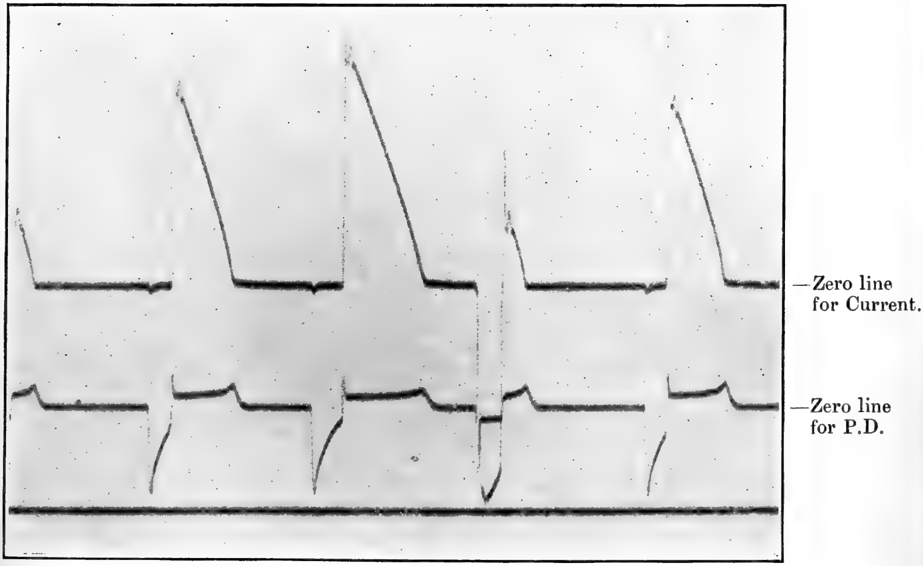
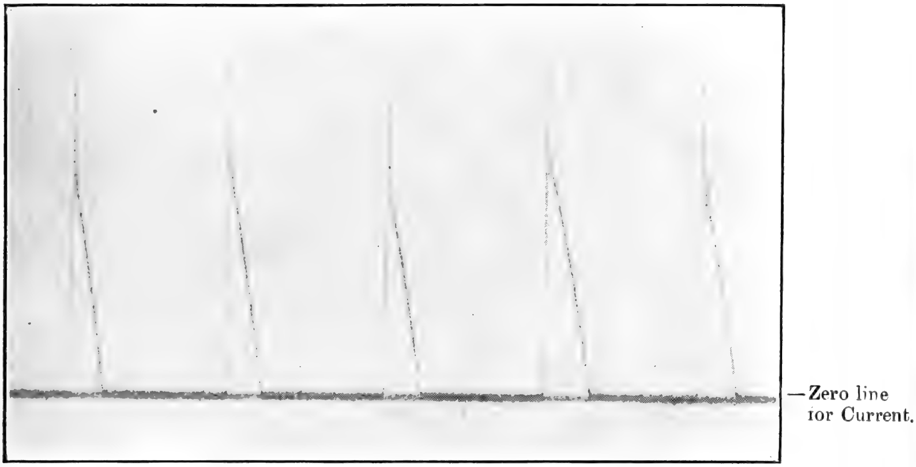


FIG. 6.—Spark-length 15 mm.



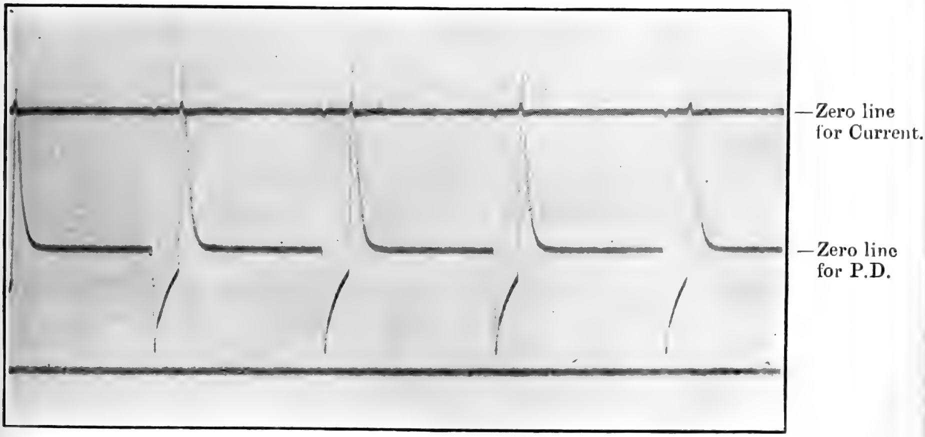
P.D. and Current Wave-Forms of Short Sparks.

FIG. 7.—Spark-length 30 mm.



P.D. Wave-Form not recorded.

FIG. 8.—Distance between electrodes too great for sparking to take place.

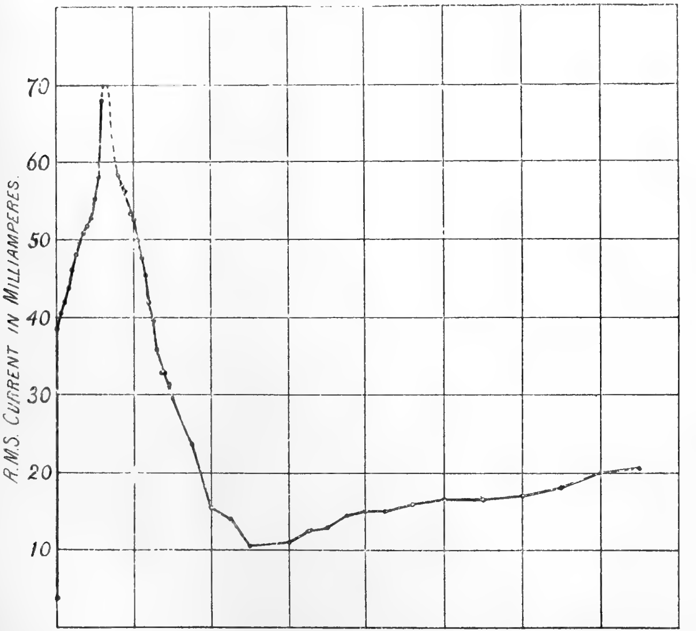


When there was no spark-gap in the secondary circuit and the coil was in action, the mean current, as read by the galvanometer, was zero, as it should be, and the root-mean-squared current had a value of about 3·8 milliamperes.

If now a microscopic spark-gap, say between two aluminium points, is introduced into the secondary circuit two curious effects take place. Firstly, the R.M.S. current enormously increases in value; and secondly, a very large deflexion is produced on the galvanometer, reading the mean current, and this deflexion is in the *negative* direction, that is to say, in the direction corresponding to making the primary circuit. I will consider these two effects separately.

In order to give an idea of the magnitude of the increase in the R.M.S. current produced by introducing a very small spark-gap into the secondary circuit of the coil, I have plotted in fig. 2 the R.M.S. current corresponding to various

Fig. 2.



lengths of spark between 0 and 15 mm. In making these observations the resistance in the primary circuit of the coil and the frequency of the interrupter of the primary current were kept constant, the resistance being 137 ohms and the frequency 75 interruptions per second. The current through the primary of the coil was about 1/4 ampere.

A large number of points were taken and are plotted on the curve. They do not give very consistent results, so it is difficult to draw a smooth curve through them; but the general appearance of the phenomenon can be seen. On introducing a spark-gap 1/10 mm long the root-mean-squared current instantly rose from 3·8 to 38·5 milliamperes, and continued to increase with increasing spark-length until it reached a maximum at a spark-length somewhere in the neighbourhood of 1·4 mm. The exact point is slightly uncertain owing to the R.M.S. current just exceeding the range of the instrument that was in use. From 1·6 to 5 mm. spark-length the R.M.S. current gradually fell in value and attained a minimum value of $10\frac{1}{2}$ milliamperes. Further increase in spark-length produced a gradual increase in the R.M.S. current up to the maximum length of 15 mm. that was used in the experiments.

There is no doubt in my mind as to the cause of this effect. It is due to very high frequency oscillations being set up in the wires connected to the secondary circuit of the coil when a spark-gap is introduced. The magnitude of the oscillations will depend on the voltage between the terminals of the spark-gap just before the spark passes and on the resistance that the spark-gap offers. Now the P.D. between the terminals of the spark-gap will increase with increasing length and so will the resistance, so that on increasing the spark-length we have two conflicting agencies at work, one tending to increase the magnitude of the oscillatory current, and the second tending to decrease the magnitude. I think that it is due to this differential action that the curve is such a curious shape.

The presence of the oscillations in the secondary circuit can easily be made evident by taking a well insulated metal plate and touching various points in the secondary circuit with it. The effect of this plate will be to largely increase or decrease, generally increase, the value of the R.M.S. current. The practical aspect of this question from my point of view was that, owing to the unexpectedly large value of the R.M.S. current, I burnt up several thermo-ammeters before I discovered the cause of the trouble.

I have obtained the effect with brass, iron, zinc, and aluminium electrodes and it probably takes place with all other metals. I think that, so far, the best metal to show the effect has been aluminium.

The large deflexion in the negative direction observed on the galvanometer was investigated by recording the wave-forms of the P. D. and the current by means of an oscillograph. The sensibility of the oscillograph was adjusted so that 1 mm. deflexion equals 1 milliampere for the current wave-forms. To obtain the P.D. wave-forms a water resistance of about 1 megohm was placed in series with the second moving system of the oscillograph so that 1 mm. equals about 1000 volts. The speed of the plate on which the records were taken was 1500 mm. per second. For this series of tests, the frequency of interruption was 75 per second and the resistance in series with primary of the induction-coil was 37 ohms.

Records were made for a series of spark-lengths between aluminium-point electrodes. I have selected from these some typical results which are shown in Plates XIII.–XV. figs. 3, 4, 5, 6, 7, 8.

Fig. 3 is the current wave-form when the spark-gap is short-circuited, length 0. The straight line across the centre of the figure is the true zero line. Deflexions above this zero line represent current in the positive direction and below the zero line represent current in the negative direction. It will be noticed that the maximum current in the positive direction (14·5 milliamperes) is much less than the maximum current in the negative direction (35 milliamperes), but the length of time that the negative current lasts is much shorter than that which the positive current lasts; so that the areas of the two sides of the zero line are equal and the mean current zero.

The smallest gap that I could make in this circuit between the aluminium electrodes, at once changed the wave-form to the type shown in fig. 4, which is for spark-length 1 mm. In this figure, the straight parts of the curve along the centre of the figure are in the position of zero current. This was carefully checked by taking records with a fixed datum-line at the zero of the curve. The line was afterwards moved to the lower part of the figure in order not to hide small details of the curve near the zero. The effect of introducing the spark-gap of 1 mm. is, while leaving the maximum current on the two sides of the zero at practically the same value, to reduce the area of the curve on the positive side of the zero line nearly to zero, so that instead of the areas on the two sides being equal there is a large excess of area on the negative side causing a large mean current in the negative direction.

On increasing the length of the gap a small area on the opposite side of the zero line again begins to form, which increases with increasing length of gap, until the condition shown in fig. 6 is reached. In this figure, the spark is sometimes rectifying or stopping the current flowing round the circuit in the negative direction altogether. We have in this figure the large triangular current wave-form which corresponds to the current flowing in only one direction round the circuit, and the smaller triangular current pulses accompanied by a large current in the negative direction at make.

Further lengthening the spark-gap brings it into the normal condition of long sparks; the current wave of this is shown in fig. 7. The datum-line across the centre of the plate, in this case, is true zero line.

It was necessary in order to obtain the wave-form of these longer lengths to disconnect the circuit for recording the P.D. wave-form, as the leak which it formed, having a resistance of only 1 megohm, prevented the sparks passing across the gap.

Fig. 8 shows the P.D. wave-form with so long a spark-gap that the spark could not jump across it. This is the normal wave-form given on the secondary of the induction-coil when supplied from a high voltage direct-current circuit.

It will be noted that the voltage induced in the circuit at the break is about 23,000 volts and at make about 13,500, so that the make voltage exceeds one half of the break voltage. Also, the voltage induced at the make dies away less rapidly than that induced at the break. It may be enquired how it is possible, if the make voltage is less than the break voltage, for the current to be larger at make than at break. I think that this question must be answered by noting that during the make period the primary of the induction-coil is connected to the supply mains so that the energy may be directly transferred from the primary to the secondary circuit by magnetic induction; that is to say, as long as we maintain a steadily increasing flow of current into the primary, we can continue to take energy from the secondary. During the break period, however, things are very different. The whole of the energy that we can get out of the secondary is that stored up in the magnetic field which is linked with the secondary winding. The greater part of this magnetic field will pass through the core. The magnetization of the core will depend upon the resultant magnetizing ampere-turns which is equal to the primary ampere-turns less the secondary ampere-turns. At the moment of break the current in the secondary is at a value of say 35 milliamperes, and the current in the primary cannot have exceeded $\frac{200 \text{ v.}}{37 \text{ ohms}}$ or 5·4 amperes.

I do not know the exact ratio between the numbers of turns on the primary and on the secondary of this induction-coil, but it is probably of the order of 100, so that the 35 milliamperes flowing in the negative direction in the secondary would correspond to a demagnetizing current of about $3\frac{1}{2}$ amperes in the primary, which would leave a comparatively small margin of resultant magnetizing ampere-turns.

If this is the case, the energy that can be got out of the secondary on break is very limited, which would account for the rapid dying away of the current to zero when even a very small spark-gap is introduced in the circuit. Directly the length of the spark-gap is sufficient to prevent the current flowing in the negative direction round the secondary circuit, the whole of the demagnetizing effect of the secondary current is done away with, and under the conditions of the experiment the magnetizing current in the primary is mainly limited by the large resistance in the circuit; hence, we get a very much larger amount of energy available directly the secondary current is prevented from flowing in the negative direction. This I think accounts for the large difference in the size of the current waves in fig. 6, and shows the great importance of preventing any current from flowing round the secondary circuit in the negative direction at make when using the induction-coil on a high voltage supply.

I made certain that the phenomenon was not due to any want of symmetry in the points of the spark-gap by reversing the electrodes of the gap and also by interchanging the connexions to it. The material of the electrodes did not seem to appreciably affect the results, but the shape of the electrodes was important in so far that the spark-length at which the galvanometer deflexion changed sign depended on the shape. Thus with two spheres the galvanometer deflexion changed sign at a shorter length than with points.

I have brought these two observations forward in the hope that in the discussion either my views as to the explanations may be confirmed or that better ones may be suggested.

XXVII. *On some Physical Relations affecting Matter in Diverse Stages of Subdivision.* *By* Dr. S. TOLVER PRESTON [*].

THE phrase "Continuity" is employed here in respect to certain physical qualities, in actual practice as efficacious as *if* continuity in an absolute sense existed. We refer, for instance, to the capacity to maintain a sensibly equable

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[*] Communicated by the Author.

pressure about a small object (say a sphere * of finite radius) by the simplest kinetic medium composed of particles of matter or "corpuscules" in a normal state of motion. The absence of a universal agreement as to the ultimate constitution of Matter, does not prevent the deduction of certain physical relations rigorously resulting from given premisses.

The more the material constituting our physical agent (sometimes termed "medium") diffused in space is subdivided, the more equable evidently will the pressure (kinetic) about the said finite small sphere become, until, in the limit, by progressive subdivision of the material, the pressure comes to rival in steadiness that of a perfectly *continuous* fluid. Yet, at the same time, the medium might represent a Vacuity far surpassing that of any "Vacuum" artificially obtainable, in regard to relatively small proportion of material contained in the medium, compared with the total (pervaded) space.

In this way, by simple subdivision, a single molecule of gross matter might be imagined capable of pervading the range of the visible Cosmos,—with minute "corpuscules" in close proximity (reckoned from centre to centre). It may possibly be well to realize that there is no assignable limit (practically speaking) to this procedure, in conception at least: and thus dimensions actually measured or calculated may possibly be easier brought within mental grasp, in connexion with the Corpuscular view of Matter.

"Continuity" may (additionally) refer to that sensible physical continuity, in reference to the impossibility of directly detecting any trace of *structure* anywhere in our medium, on account of its dimensional properties eluding direct appreciation by the senses; so that the appearance is presented of the continuity of a fluid. Thus the extremes of Vacuity and of Continuity may be said "to meet,"—in a certain physical signification.

That the "mean length of path," by this process of subdivision of material, also diminishes continuously in the same

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* Given a normal velocity for the constituent particles, the sensible uniformity of the pressure of a medium [say our atmosphere] upon a small body immersed therein, evidently does not depend on the *size* of the impinging air-particles, which maintain the pressure, but on their proximity (from centre to centre), or on their number in unit of volume. Hence, by simple subdivision of the material, we observe that any degree of Continuity combined with Vacuity [*i. e.*, optionally small collective volume of material compared with the total volume of space pervaded]—may be practically achieved, capable of serving useful ends. The so-termed "small" body evidently must not be so reduced that its dimensions become comparable to the mean distance [relatively inferior] of the component particles of the medium, in which it is located.

ratio as the other dimensional elements, may not possibly appear so evident at first sight.

An ideal case, although not exactly applicable in nature, may, as *approximately* applicable, often be of practical utility to illustrate closely natural facts. Thus actually, by diverse stages of aggregation of material into grosser clusters, interstices exist between the component corpuscules which constitute the cluster, and that even if the component corpuscules be supposed to possess some elasticity [adaptation of shape to pressure], or imagined to be in actual contact. Our object here is to consider the ideal case where the interstices eliminate themselves.

The electron theory of the corpuscular constitution of Matter is taking a foremost place in philosophical thought in the present day. May it not be conceivable that in certain regions of the universe these corpuscules part with their motion (whether by transference &c.) If so, then under central forces such as gravitation &c. the corpuscules, if elastic, could aggregate into masses practically *continuous* [comparable to a continuous fluid], without interstices, excepting possibly near the exterior confines of the masses. The very high intensity of motion of corpuscules, observed by us, may well only exist in a relatively small proportion of the universe, namely in those (probably exceptional) regions where Life, as known to us, prevails.

While physical consequences or relations in their ideal exactness may of course have a permanence not unlike mathematical truths, they may at the same time apply to possible realities of Nature with sufficient approximation to merit that realization which makes knowledge productive.

Let us consider the in some respects ideal case of a perfect fluid in diverse stages of subdivision into spherical globules, and where, under assumed central forces, the globules [however small by subdivision, or however large, by aggregation, they may become] automatically resume the spherical form when left to themselves.

On the above premisses, we observe it to be readily demonstrable that a progressive subdivision of material to stages finer and finer, has the consequence that the radii of the (globular formed) corpuscules thus set free, their mean distance, reckoned from centre to centre, with their " mean length of path,"—these dimensional properties (of the medium thus constituted), although changing absolutely, are *relatively* unalterable by this process of subdivision of the material and consequent multiplication of available parts, but remain as constant as the quantity of material itself.

We may notice then that the "mean length of path" of an ideal stellar mass (generated by inverse aggregation out of corpuscules) would be the same multiple of the radius of the stellar mass, as the mean length of path of a corpuscule was (beforehand) of *its* radius. Nevertheless, in view of the familiar phrase "sparsely scattered stars," the first case would be considered as illustrative of Vacuity, while the second exemplifies the Continuity of some medium where the dimensional elements elude our direct powers of measurement. Yet in *both* cases, the dimensional elements (as we may note) may actually be similar.

By supposed progressive subdivision of the material under the conditions cited, we may observe the globular corpuscules thus set free gradually approaching each other (as to their geometrical centres) asymptotically, without assignable limit as to proximity :—all the dimensional properties of the medium thus constituted [including length of mean path] diminishing in a like proportion. The recognized Relativity of the results reached does not exclude the possibility of *practical* or useful consequences in connexion with the economy of Nature, which mental realization may go further to develop.

Elementary illustrative methods (wherever possible), may be not without their value. If we suppose a cubical element of space, with portions of material in spherical form situated at the eight corners of this cube, and, for the concept of ready subdivision into parts, suppose the material to be a continuous or perfect fluid, with a central force acting to maintain any portion thereof globular when set free : then it becomes evident (illustratively) that when by the subdividing process, the radius of a fluid globe is reduced to one half, eight times as many then become available ;—permitting eight times as many cubical space-elements to be furnished with portions of material at their corners. Then, by the simple subdivision of our material, (obviously) the *side* of each cubical space-element [representing the distance of the portions of material from centre to centre], becomes exactly halved.

Clearly, in this way, by a progressively finer stage of subdivision of material, we have reached an exactly *similar* configuration (geometrically), in regard to relative radii of the globules [corpuscules], relative distances, reckoned from centre to centre, &c. as those with which we started :—this continuing to hold true if the process of subdivision of material were carried out without assigned limit.

Accordingly we may observe that whatever multiple of the radius of a globule [or globe] the mean length of path was at the commencement, it will remain that same multiple, however far the process [whether of subdivision or of inverse aggregation] be conceived to be carried. In some relational sense, in respect to small scale, we might even speak of an ætherial medium, or, in respect to big scale, of a stellar medium.

Somewhat in correlation with the present subject—in 'Nature,' September 28, 1893, p. 517, I ventured critically to comment a view of M. Delbœuf, given in *Bulletin de l'Académie de Belgique*, No. 6, 1893, who contests Laplace's conclusion as to the *Relativity* of all dimensions, velocities, &c., in regard to the visible universe. In the abstract of M. Delbœuf's paper, Laplace's view is quoted as follows :—

"According to Laplace, if the dimensions of all the bodies in the universe, their mutual distances and velocities were to increase or diminish in a constant proportion, these bodies would describe the same curves as they do now. The appearances presented to observers would be the same, and independent of the dimensions assumed. Hence the only facts we are able to appreciate are ratios." ('Nature,' August 24, 1893, p. 406.)

It is added (in the abstract in 'Nature') that considerations pursued by M. Delbœuf into directions other than concerning dimensions alone, "go to show that real space is different from geometric space, and that the dimensions of the universe are absolute" (p. 406).

But surely Laplace must have implied that not only velocities, but forces &c. were supposed to vary in correspondence, so as to maintain the previous state of equilibrium undisturbed. For if equilibrium were upset, there would be no fair test possible of the power of observation to detect a change of *dimensions* accomplished,—which is *the* point of debate.

In my communication to 'Nature' of the above date, under the same title as that chosen by M. Delbœuf—"*Megamicros*,"—I offered as an illustrative case a human being grasping a metrically graduated staff equal in length to his own height.

By any supposed reduction in size, simultaneously with the dimensional scale of *our* universe (in extent conceived * radially finite), there would be nothing positive to indicate that a change of size had effected itself, while the metrical staff grasped by the observer would still be the same length as

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* Without necessarily postulating any particular limit to the Cosmos, we may perfectly well suppose the above modifications to be confined to *our* universe, *i. e.* to the known, within the range of telescopic vision, —leaving the unknown entirely out of consideration.

himself,—and that if dimensions oscillated between the infinites. We seem in this way to bridge the infinite (so to say) in extremes of thought.

To connect dimensions (if only in one isolated instance) with our idea of the indestructibility of Matter, we might imagine the metrical standard of the "Conservatoire" to have *alone* remained unaltered in length, when the accomplished reduction (or increase) of size of everything else would then become obvious,—by comparison with the metrical standard left over as the sole test-relic of the previous state of Relativity. Such modification of dimensions of *our* universe would evidently imply a proportional "creation" or (respectively) "annihilation" of Matter, with the concomitant shortening (or lengthening) of the radius of extension of the whole system affected. And if these changes of dimensions be imagined to be instantaneous, the conservation of the memory-mechanism (itself independent of scale, and united with a psychological side), would secure the unbroken recognition of undisturbed Relativity.

In order to reason effectively on some questions, we may fitly make certain preliminary assumptions, which do not abate the logic of the conclusions.

The catastrophic change of absolute size (by unaltered relative dimensions of internal constituents) of our cosmos, with variation of radius of extension, implied in the passage from one state of Relativity to another,—must be imagined for the purpose of our argument) to be perfectly instantaneous.

It appears, however, that the fact of a physical catastrophe being involved in such changes, goes to demonstrate that there *is* such a thing as *absolute size*, or that this phrase has a meaning within the domain of Physical Science. Indeed, in the absence of the concept of "absolute size," as a basis to rest on, it seems that the abstract idea of infinite extension oscillates hither and thither in uncertainty (as if its logical justification were in question).

Only "absolute size" appears to possess this peculiarity, that any imagined fluctuations of its value [in exact parallelism with that of the metrical standard—by the conservation of Relativity], would elude our observation, even under the implied retention of memory throughout. For the independence of the most elaborate mechanisms on absolute, and their unique dependence on relative scale of parts,—is an obvious and accepted fact in Engineering design.

Gross Flottbek, bei Altona, Germany,
Dec. 1907—April 1908.

[*Added June* 11, 1908.]—It may be noticed that under the radial (central) action of its own gravitational forces, a mass of matter, by mere increase of size,—becomes elastic. The forcible recovery of the spherical form, under the radial stress, amounts substantially to a power of elastic restitution.

Let us suppose a nebula, instead of consisting of those smaller fragments of material to which we apply the name "meteorites," after disintegration in our atmosphere,—to be constituted of masses more comparable to the earth in size [small in relation to the solar dimensions]:—these energetic bodies automatically setting up that equilibriated movement among themselves characteristic of the (minuter) particles of a gas. Then such gravitationally-elastic portions of material constituting an attenuated nebula, and surviving without encounters for lengthy time-periods, would strive to conserve the natural globular form [vibrating about the same], conditioned by the powerful radial stress of gravity in each case: but coalescence into larger masses (spherical) now and then, by relaxation of the translatory motion, is of course not excluded.

An inert mass of (say) the solar diameter, if we suppose broken up by a quick encounter, would then, even if cold and solidified throughout, resolve itself into globular fragments, and not into portions of irregular shape,—excepting those splinters below a certain limit of size.

And this would doubtless be the essential primary stage of such a cosmic encounter :—a truly gaseous nebula demanding time to constitute itself. It appears, accordingly, that the translatory energy of the encounter would at first continue mainly as mass-motion :—passing more gradually into the finer motion of molecules.

XXVIII. *Notices respecting New Books.*

A Treatise on Hydraulics. By William Cawthorne Unwin, LL.D., F.R.S. London: A. & C. Black. 1907.

THIS book may in a sense be regarded as a new edition of the valuable article contributed by Professor Unwin to the *Encyclopædia Britannica* more than thirty years ago. Certain paragraphs and many of the diagrams are simply reproduced, but the omission of much of the former detail and the substitution of more recent data, with a complete recasting of many essential parts, make the treatise an altogether new work. To one familiar with the article of 1867, a glance through the book will reveal many similarities; but a careful inspection will show that there are many more differences, and that Professor Unwin has spared no pains to bring his work up to date. A complete chapter on the distribution of water-supplies takes the place of a few paragraphs in the Encyclopædia article; and the discussion of the flow of compressible fluids is considerably extended. There is, however, in the book no chapter corresponding to the former section on Hydraulic Machinery which occupied nearly one third of the whole. There can be but one opinion as to the value of this Treatise. It is the outcome of more than forty years' continued study of the subject on the part of one of our most distinguished teachers of engineering science.

XXIX. *Intelligence and Miscellaneous Articles.*

REMARKS ON THE PAPER OF HANS GEIGER: "THE IRREGULARITIES IN THE RADIATION FROM RADIOACTIVE BODIES." BY DR. EDGAR MEYER, UNIVERSITY OF ZÜRICH, AND DR. ERICH REGENER, UNIVERSITY OF BERLIN.

IN the Philosophical Magazine of April 1908 Hans Geiger has published a paper bearing the above title. At the end of his communication he adds a note, in which he refers to a paper of ours entitled "Ueber Schwankungen der radioaktiven Strahlung und eine Methode zur Bestimmung des elektrischen Elementarquantums" (paper read before the Deutsche Physikalische Gesellschaft, December 13, 1907, published in the *Verhandlungen der deutschen physikalischen Gesellschaft*, x. p. 1, 1908, and also recently in the *Annalen der Physik*, xxv. p. 757, 1908).

Geiger says in this note: "Further, they [the authors] state that by measuring the error ϵ [the average oscillation of the radiation from a radioactive body] and the saturation current i, the charge of an ion may be determined. But the calculation involves the number of ions produced by an α particle, and this number was determined by Rutherford under the assumption that the charge of an α particle is identical with the charge of an ion. This, however, is still an unsettled question."

In relation to this remark we have to say that we were fully aware of the fact, that in our calculation we assumed the charge of an α particle to be identical with the charge of an ion. This follows clearly from the fact that in our paper (§ 10 in the *Verhandlungen*, § 14 in the *Annalen*) we have also given a new method of determining in a simple manner, whether an α particle carries one or two charges of an ion under the assumption of a known value of the charge of an ion.

Geiger in his note also gives a method of determining the number of α particles emitted per second by a given radioactive substance. Perhaps we may be permitted to point to the fact that the same method has been already applied in our research.

Zürich and Berlin, May 1908.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

SEPTEMBER 1908.

XXX. *The Kinetic Energy of the Negative Electrons emitted by Hot Bodies.* By O. W. RICHARDSON, *Professor of Physics, and* F. C. BROWN, *Experimental Science Fellow, Princeton University*[*].

THAT the carriers of negative electricity emitted by hot metals are electrons was first proved by the experiments of J. J. Thomson[†] on their deflexion in a magnetic field. This result alone did not compel any definite view of the origin of this ionization. Somewhat later one of the authors[‡] showed that the phenomena then known were such as would arise if the electrons originate in the metals, from which they were able to escape when their velocity normal to the surface exceeded a certain value. This method of looking at the question was found to give a particularly satisfactory account of the thermal relations of the phenomena which were then accurately investigated for the first time. In Richardson's method of developing the subject (*loc. cit.*) the assumption is justified by theoretical considerations, that the translational kinetic energy of the electrons inside the metal has the same value as that of the molecules of a gas at the same temperature as that of the metal. From the principles there laid down it also follows that the translational kinetic energy of the electrons outside the metal possesses the same value. This equality applies not only to the average value,

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[*] Communicated by the Authors.

[†] Phil. Mag. [5] vol. xlviii. p. 547 (1899).

[‡] O. W. Richardson, Camb. Phil. Proc. vol. xi. p. 286 (1901); Phil. Trans. A, vol. cci. p. 497 (1903).

but to the way in which the energy is distributed among the different electrons as well. Although a knowledge of the kinetic energy of the emitted electrons is of obvious importance, no attempt appears to have been made to determine it. The present paper embodies the results of an investigation of the portion of the kinetic energy which depends upon the component of the velocity normal to the emitting surface. What is determined is the value of $\frac{1}{2}mu^2$, where m is the mass of an electron and u is its component of velocity perpendicular to the surface from which it is emitted. Both the average value of this portion of the energy and the law according to which it is distributed among the different particles given off are examined. The method employed gives no information about the part of the energy which depends on the component of velocity parallel to the surface of emission: the sideways energy will form the subject of another communication by one of the authors.

Theory of the Method.

Stated briefly the method used consisted in measuring the rate at which an insulated plate A charged up when a portion of another plate B parallel to A consisted of metal sufficiently hot to emit ions. It is clear that as the metal in B emits negative ions the plate A will become negatively charged, so that a difference of potential will be established tending to stop the flow of electricity. From the way in which the current between the two plates varies with the time or with the difference of potential between them the desired information can be obtained.

Consider two parallel planes of indefinite extent perpendicular to the axis of x. The lower plane, determined by $x=0$, has a small portion of its central region heated so that it is emitting ions. The potential of this plane is maintained at zero. The potential of the upper plane, determined by $x=x_0$, has the value V at the instant considered. Consider an ion whose charge is e and mass m situated at a point between the planes whose coordinates are x, y, z. Its equation of motion will be

$$m\frac{d^2x}{dt^2}=-e\frac{dV}{dx}, \quad m\frac{d^2y}{dt^2}=m\frac{d^2z}{dt^2}=0. \quad . \quad . \quad (1)$$

From these equations it follows (see Phil. Trans. A, vol. cci. p. 499) that the electron will only arrive at the upper plate provided

$$\tfrac{1}{2}mu_0{}^2 \geqq Ve, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where u_0 is the initial velocity perpendicular to the plate, and V is the difference of potential between the two plates. There is no reason why all the ions should be emitted from the hot metal with the same velocity. If we consider a sufficiently great number the velocity or energy will be distributed among them according to some regular law. Out of any large number of ions emitted by the plate let us denote the fraction having velocity components between u_0 and u_0+du_0 by $F(u_0)du_0$, those between v_0 and v_0+dv_0, and w_0 and w_0+dw_0 by $f(v_0)dv_0$ and $f(w_0)dw_0$ respectively. Here v_0 and w_0 are the initial components of velocity parallel to y and z respectively; if the planes are of sufficient extent the condition that the ions should reach the upper plane will be independent of these components of velocity. If n is the total number of ions emitted by the lower plane per second the current i to the upper plane is clearly

$$i=c\frac{dV}{dt}=ne\int_{\sqrt{2\frac{e}{m}V}}^{\infty}F(u_0)du_0\int_{-\infty}^{\infty}f(v_0)dv_0\int_{-\infty}^{\infty}f(w_0)dw_0, \quad (3)$$

where c is the capacity of the system.

Circular Plate.

In practice it is impossible to use planes of indefinite extent, so that it is important to determine the effect of the finite size of the two plates. In the experiments the plates were circular, the lower being somewhat larger than the upper one. The upper plate was surrounded by a guard-ring. The hot metal could be treated with sufficient approximation as a point at the centre of the lower plate. We shall now calculate the number of ions which reach the upper plate, everything being supposed to be symmetrical about the axis of the two circles. Consider a charged particle whose distance from this axis is ρ, and whose distance from the lower plate is x. Its equations of motion are

$$m\frac{d^2x}{dt^2}=-e\frac{\partial V}{\partial x} \quad \text{and} \quad m\frac{d^2\rho}{dt^2}=0. \quad . \quad . \quad . \quad (4)$$

Integrating these subject to the conditions that when

$$t=0,\ x=0,\ \frac{dx}{dt}=u_0,\ \rho=0,$$

and

$$\frac{d\rho}{dt}=W,$$

we get

$$\left.\begin{aligned} mx &= +\tfrac{1}{2}Xet^2 + mu_0 t \\ \rho &= Wt \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $X = -\frac{\partial V}{\partial x}$ is supposed to be constant.

The equation to the path is thus

$$\tfrac{1}{2}Xe\frac{\rho^2}{W^2} + m\frac{u_0}{W}\rho = mx. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If x_0 is the distance between the two plates and ρ_0 the radius of the upper one the condition that the particle should just reach the boundary of the upper plate is

$$mx_0W^2 - mu_0\rho_0W = \tfrac{1}{2}Xe\rho_0^2. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If the value of W considered as a function of u_0, x_0, and ρ_0 is $\overset{=}{<}$ that given by equation (7) the particle will reach the upper plate, provided u_0 also satisfies the inequality (2), otherwise it will either be returned to the lower plate or it will reach the guard-ring. Solving the quadratic equation we see that the particle will just reach the edge of the plate if

$$W = \tfrac{1}{2}\frac{\rho_0}{x_0}\left(u_0 \pm \sqrt{u_0^2 - 2\frac{e}{m}V}\right),$$

when

$$V = 0, \quad \frac{W}{\rho_0} = \frac{u_0}{x_0},$$

so that the positive sign is the one to take. Hence for the particle to reach the upper plate W must lie between the limits 0 and $\frac{1}{2}\frac{\rho_0}{x_0}\left(u_0 + \sqrt{u_0^2 - 2\frac{e}{m}V}\right)$, whilst u_0 must lie between ∞ and $\sqrt{2\frac{e}{m}V}$. If the fraction of the ions emitted whose velocity parallel to the plates lies between W and W + dW is F(W)dW, the current received by the upper plate will be

$$i = ne\int_{\sqrt{2\frac{e}{m}V}}^{\infty} F(u_0)du_0 \int_0^{\frac{1}{2}\frac{\rho_0}{x_0}\left(u_0 + \sqrt{u_0^2 - 2\frac{e}{m}V}\right)} F'(W)dW. \quad . \quad . \quad . \quad . \quad (8)$$

Particular Case of Maxwell's Law of Distribution.

If we assume tentatively that the law of distribution of velocity among the emitted ions is the same as that among the molecules of a gas which start from any surface bounding it or within it, then the above functions may be calculated by the methods of the kinetic theory of gases. They are

$$\left.\begin{aligned} F(u_0)du_0 &= 2km\,u_0\,\epsilon^{-kmu_0^2}du_0,\ f(v_0)\,dv_0=\sqrt{\frac{km}{\pi}}\,\epsilon^{-kmv_0^2}dv_0 \\ f(w_0)dw_0 &= \sqrt{\frac{km}{\pi}}\,\epsilon^{-kmw_0^2}dw_0 \text{ and } F'(W)dW=2kmW\epsilon^{-kmW^2}dW \end{aligned}\right\}, \quad (9)$$

where $\frac{3}{4}k$ is the average energy of translation of a molecule at the temperature of the hot body. It is to be borne in mind that the above functions are expressed as fractions of the total number of ions leaving an element of area perpendicular to the axis x in unit time, and not in terms of the number in unit volume as is usually done.

If we substitute these values of the functions in the preceding formulæ and carry out the integrations, we shall obtain the current to the upper plate as a function of the potential-difference, provided the law of distribution of velocity among the emitted electrons is Maxwell's law. Under these circumstances, in the case where the planes are of indefinite extent, the current to the upper plate becomes

$$\left.\begin{aligned} i &= n\,e\,\frac{2(km)^2}{\pi}\int_{\sqrt{2\frac{e}{m}V}}^{\infty} du\,u\,\epsilon^{-kmu^2}\int_{-\infty}^{\infty}dv\,\epsilon^{-kmv^2}\int_{-\infty}^{\infty}dw\,\epsilon^{-kmw^2} \\ &= ne\epsilon^{-2kVe} = i_0\,\epsilon^{-2kVe} \end{aligned}\right\}(10)$$

if i_0 is the value of the current at the initial instant when $V=0$. Since $k=\dfrac{1}{2R_1\theta}$ where R_1 is the constant in the gas equation $pv=R_1\theta$, calculated for a single molecule, and θ is the absolute temperature, we have, taking logarithms

$$\log_\epsilon\frac{i}{i_0}=-\frac{Ve}{R_1\theta}=-\frac{\nu e}{\nu R_1\theta}V=-\frac{\nu e}{R\theta}V, \quad . \quad . \quad (11)$$

where ν is the number of molecules in 1 c.c. of gas at 0° C. and 760 mms. pressure, and R is the constant in the equation $pv=R\theta$ taken to refer to the quantity of gas occupying unit volume under these standard conditions. Assuming what is now fairly well established, that the charge e on an electron is equal to that carried by a monovalent ion during electrolysis, νe is equal to the quantity of electricity required to liberate half a cubic centimetre of hydrogen in a water voltameter under standard conditions of temperature and pressure, since hydrogen is a monovalent element having a diatomic molecule in the gaseous state. Thus on this view both ve and R are well known physical constants.

The preceding relations may be used to determine the way in which the potential of the upper plate varies with the time t, during which the current from the hot body has been flowing. If C is the capacity of the upper plate and its connexions we have

$$\mathrm{C}\frac{d\mathrm{V}}{dt} = i = i_0 \epsilon^{-\frac{ve}{\mathrm{R}\theta}\mathrm{V}},$$

so that

$$\epsilon^{\frac{ve}{\mathrm{R}\theta}\mathrm{V}}\, d\mathrm{V} = \frac{i_0}{\mathrm{C}}\, dt;$$

integrating this, subject to the condition that $\mathrm{V}=0$ when $t=0$, we have

$$e^{\frac{ve}{\mathrm{R}\theta}\mathrm{V}} = 1 + \frac{ve}{\mathrm{R}\theta}\frac{i_0}{\mathrm{C}}t,$$

or

$$\mathrm{V} = \frac{\mathrm{R}\theta}{ve}\log_\epsilon\left(1 + \frac{ve}{\mathrm{R}\theta}\cdot\frac{i_0}{\mathrm{C}}t\right), \quad . \quad . \quad . \quad . \quad (12)$$

and

$$i = \mathrm{C}\frac{d\mathrm{V}}{dt} = i_0 \Big/ \left(1 + \frac{ve}{\mathrm{R}\theta}\cdot\frac{i_0}{\mathrm{C}}t\right). \quad . \quad . \quad . \quad (13)$$

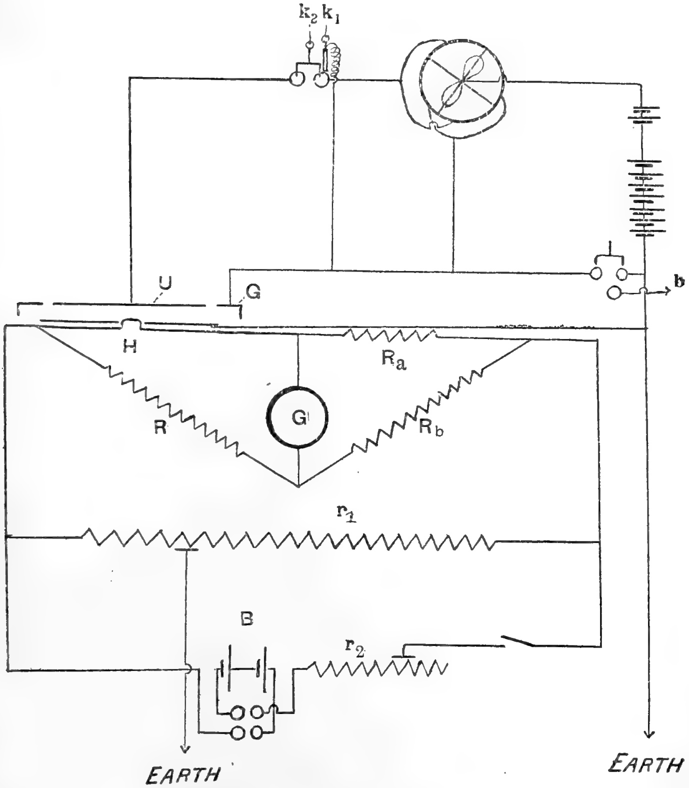
The current, therefore, is always finite and vanishes when $t=\infty$. Nevertheless the potential is infinite when t is infinite. This approach to an infinite value of the potential is not observed in practice. This is probably due to the fact that the current falls off with the time so rapidly that it soon becomes comparable with the small leaks inherent in the apparatus, and with the discharging current carried by ions of the opposite sign. For these reasons a limit is soon found to the potential to which the upper plate can be charged in this way.

The two formulæ (11) and (12), which give the current as a function of the potential-difference and the potential-difference as a function of the time respectively, are not independent of one another, since the former can be obtained from the latter by differentiation with respect to the time. To test the theory, therefore, it is only necessary to examine the truth of one of the two formulæ. This has been done for the formula $\log_\epsilon \frac{i}{i_0} = -\frac{ve}{\mathrm{R}\theta}\mathrm{V}$ in a manner which will now be described.

Experimental Arrangements.

The general arrangements of the apparatus used to investigate the kinetic energy of the negative ions from hot platinum is shown diagrammatically in fig. 1. The central portion of a narrow platinum strip H was bent upwards as shown through a square hole at the centre of the lower of two circular plates, so as to be flush with the upper surface of the latter. The upper plate U was somewhat smaller than the lower, and was surrounded by a guard-ring G. Both plates were perpendicular to the common axis passing through their centres. The upper plate was connected to one pair of the quadrants of a Dolazalek electrometer by means of the key k_1k_2. The plug k_2 was connected with the guard-ring and with the second pair of quadrants. By means of the key b it could be connected either with the earth or any

Fig. 1.



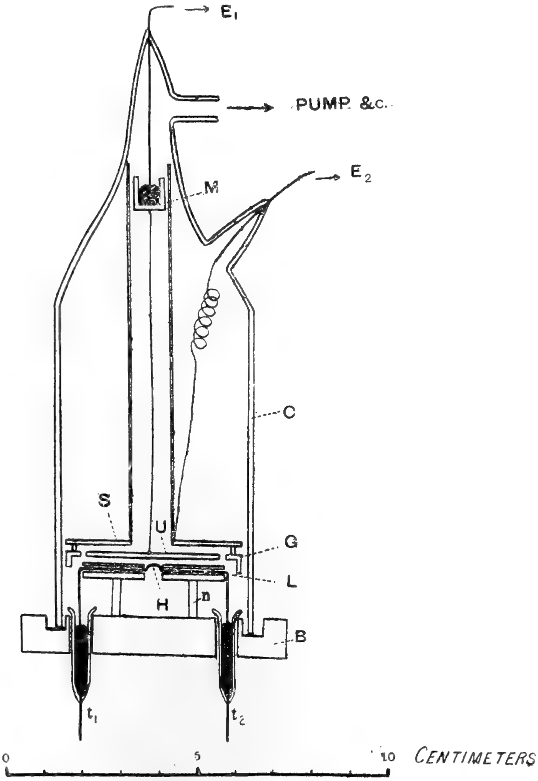
desired potential. In this way the rate of charging of the upper plate could be determined both with the two plates initially at the same potential and with any desired difference of potential between them. The charging quadrants could also be connected to a subdivided standard condenser not shown in the diagram.

The platinum strip was heated by a current furnished by the battery B and regulated by two sliding rheostats in parallel (shown as one in the diagram) at r_2. One of these had a much higher resistance than the other, and served as a fine adjustment. The temperature was determined from the resistance, which was measured by the Wheatstone's bridge arrangement, of which H, R_a, R_b, and R formed the four arms. This is the method previously used by Richardson. The essential conditions that R and R_b should both be large compared with R_a and H, and that R_a should carry the current without heating, were satisfied.

It is important that the middle point of the exposed portion of the hot strip should be at zero potential. If a fine wire was welded to the middle portion of H and soldered to the lower plate it was found that this gave rise to local variations in the heating, and also that any slight displacement of the strip during the experiments put it out of adjustment. These difficulties were overcome by shunting the whole Wheatstone's bridge circuit with a high resistance r_1, any point of which could be connected to earth. By trial a point in r_1 was found so that when it was connected to earth the initial rate of leak to the upper plate was unchanged on reversing the main heating current. The condition for this is evidently that the centre of the hot strip should be at zero potential. By simply reversing the main current from time to time this adjustment could be tested and a readjustment made, if it were required during the course of the experiments. The lower plate was permanently connected to earth.

A section through the platinum strip, showing the plates and arrangement of apparatus in their immediate neighbourhood, is shown in fig. 2. The detailed construction of the plates will be described later. The lower plate consisted of two sections screwed together. The platinum strip was held between them and insulated from them by strips of mica. The thickness of the platinum strip was ·0018 cm. Its other dimensions were ·2 × ·5 cm. Its ends were welded to heavier platinum leads which dipped into glass mercury-cups sealed into the heavy brass base-plate B. These served to introduce the heating current. The resistance of the portion of the platinum strip which emitted the ions was between ·04 and ·006 ohm. That of the leads about ·1 ohm. The heating current was usually in the neighbourhood of 2 amperes. The lower plate L was supported by a brass ring soldered to the brass plate B. The upper plate and guard-ring were rigidly connected together and insulated from each other by ebonite pieces. These are not shown in fig. 2.

Fig. 2.



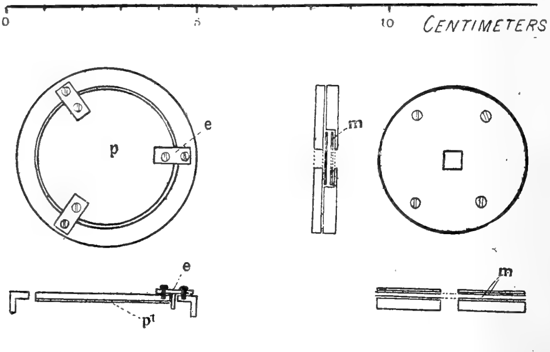
Additional ebonite supports, also not shown, enabled it to rest on the lower plate, and also kept it insulated from the latter. These supports also ensured that the plates were always at a constant distance apart and parallel to each other. Connexion with the electrometer was made by means of a stout wire soldered to the top of the upper plate, which supported a mercury-cup M insulated from the shield S by ebonite. The wire connecting it to the electrometer system dipped into this mercury-cup.

The whole of this portion of the apparatus was enclosed by a glass tube C, so that any desired degree of evacuation could be obtained. The bottom of this tube was ground flat and rested in a groove in the base-plate, to which it was joined with sealing-wax done over with soft wax. All sealing-wax joints were made air-tight in this way. The platinum wires E_1 and E_2 were of course fused into the glass. An outlet tube connected with the mercury-pump, McLeod gauge, drying-apparatus, and tap for letting in gases. The drying agent used was phosphorus pentoxide redistilled in oxygen. In order to make certain that effects were not being caused by charges accumulating on the glass the upper plate and the wire leading from it were shielded by the flanged brass tube S. This was connected to the guard-ring and also to earth by means of the extensible wire E_2. It will be seen that the system was very thoroughly protected from any effects which might arise from charging up of insulation.

The particular design of apparatus was adopted so that it might very readily be taken apart and a new platinum strip substituted whenever that became desirable. It was admirable from that point of view.

The detailed construction of the two plates is shown in fig. 3. The three ebonite pieces which served to insulate the upper plate from the guard-ring and the lower plate, and also to support both on the lower plate, are denoted by *e*. The plan of the lower plate shows the square hole where the hot strip came up flush with the surface. The two sections show the way in which the platinum strip was supported. The mica insulating strips are denoted by *m*. A sheet of

Fig. 3.



UPPER PLATE AND GUARD RING

LOWER PLATE

thin platinum foil was soldered to the lower side of the upper plate so as to avoid any effects which might conceivably be due to anything of the nature of contact electromotive force.

The diameter of the upper plate used in the experiments was 3·6 cms. and the distance between the two plates was two millimetres. In discussing the results the formulæ for infinite planes will be used. Strictly speaking we ought to apply formula (8), substituting the values of $F(u_0)$ and $F'(W)$ in (9). When this is done an integral is obtained which cannot be evaluated in finite terms. It is, however, easy to show from expression (8) that the fractional error introduced by neglecting the finiteness of the radius ρ_0 of the upper plate will be comparable with a quantity lying between $\epsilon^{-k\frac{\rho_0^2 Ve}{2x_0^2}}$ and $\frac{x_0^2}{x_0^2+\rho_0^2}\epsilon^{-2kVe\frac{\rho_0^2}{x_0^2}}$, depending on the value of V. A preliminary calculation showed that with the dimensions of the apparatus chosen this error would always be smaller than the expected error of observation. This conclusion was subsequently confirmed by experiments in which the current to the upper plate, to the guard-ring, and to the two together were measured and compared. Under all conditions the current to the guard-ring was small compared with that to the plate, the ratio of the two being smaller than the probable observational error. Since the guard-ring was constituted so as to intercept all the ions from the lower plate which were not received by the upper plate, it is clear that practically all the ions from the metal strip which were not returned to the lower plate by the field reached the upper plate.

The fiducial points used in calibrating the temperature-resistance curve were the temperature of the room, the melting-point of potassium sulphate (1066° C.) and the melting-point of platinum (1820° C.) The temperature varied perceptibly along the strip owing chiefly to the conduction of heat from the ends. In standardizing it, therefore, the potassium sulphate was placed on the hottest portion, as this, owing to the tremendous rapidity with which the emission of ions increases with the temperature, would be the region which gave rise to the greater proportion of the total. In determining the resistance at the melting-point of platinum, that at which the strip melted was observed. This would obviously give the temperature of the hottest portion. When the three temperatures were plotted against resistance they were found to lie as nearly as possible on a straight line.

This is not in agreement with the known variation of the resistance of platinum with temperature. Presumably the discrepancy arises from a change in the relative distribution of the heat along the strip as the temperature changes. The experimental temperatures were obtained from the measured resistances by reference to a chart constructed in the above way. We believe that this method of getting the temperature is trustworthy though not very accurate.

The electrometer and everything connected with it were insulated on blocks of paraffin or ebonite, so that the rate of leak to or from the upper plate could be measured when it was charged to any desired potential. Potentials as high as 400 volts were used in some of the experiments.

Results of the Experiments.

In the earlier experiments trouble was experienced on account of the occurrence of positive ionization as well as negative. With a new wire, as is well known, the positive ionization is large compared with the negative, but decays away with time, so that after long continued heating the positive ionization becomes small compared with the negative. The latter was found to remain practically constant under comparable conditions throughout the experiments. In order to get rid of the positive ionization it was found necessary to heat the platinum strip from ten to thirty hours before taking readings. In these experiments it was never found possible to get rid of the positive ionization completely ; a considerable leak was always obtained if the upper plate was charged to a high negative potential. We think that most of this positive ionization was caused by gas evolved from the apparatus when the metal strip was heated. Fortunately the positive leak was small when the negative potential applied to the upper plate was small. In the experiments it was found that the negative ionization emitted by the strip was never able to charge the upper plate to a potential greater than one volt. If, therefore, the positive leak when the upper plate was charged to a potential of -2 volts was inappreciable compared with the negative leaks against the potential which were measured, it was taken that the positive leak had been sufficiently got rid of. Great care was taken to ensure that this condition was always fulfilled in practice.

One of the authors (Mr. F. C. Brown) observed that the positive leak could be got rid of more quickly by charging the upper plate to a high negative potential, for example 200 volts. This procedure was, however, found to entirely alter the nature of the subsequent discharge of the negative ionization, the emitted ions being capable of going against a much higher potential than formerly. A detailed investigation of this interesting effect has been carried out by Mr, Brown, and will shortly be published, so that it is not necessary to say much about it here. It is evident that after such treatment the hot metal is in a peculiar state. In order to ensure that the metal was in a normal state we were careful to always keep the potential of the upper plate in the neighbourhood of zero so as to make sure that the hot metal strip was never placed in a strong electrostatic field. Incidentally it may be mentioned that it was found that the abnormal state induced in this way could be got rid of by heating the strip for a short time to a very high temperature. This property was made use of in some of the experiments which follow.

The pressure of the gas (air) in the different experiments varied considerably from ·001 to as much as ·06 mm. So far as the authors were able to judge, the actual value of the pressure had no effect on the phenomena investigated, provided it was as low as the above limits indicate.

The chief experimental problem in hand was the determination of the current to the upper plate, when this was allowed to charge up, as a function of the potential-difference between the two plates. This relation when obtained enables the applicability of the formulæ (10) and (11) to be tested. The platinum strip and the lower plate were always maintained at zero potential. The potential of the upper plate at any instant was determined by the reading of the electrometer to which it was connected. The electrometer was arranged to give 115 divisions deflexion for a volt, as this degree of sensitiveness was found to be most convenient for these experiments. The deflexions could be estimated to one-tenth of a division. In measuring the currents a suitable capacity was connected to the quadrants of the electrometer. The readings of the latter, which was nearly dead beat, were recorded at definite intervals of time, and the current was obtained from the formula $i=c\frac{\Delta V}{\Delta t}$, where c is the capacity of the electrometer and its connexions, including the condenser, Δt is the interval of time between two readings, and ΔV is the corresponding increment of potential. Strictly, of course, this formula is only true for infinitesimal intervals, but by inserting a sufficiently large capacity in the system it was found in practice that the rate of increase of potential with the intervals used did not diminish very much during any one interval. The error thus introduced was also averaged out to some extent by taking the current thus obtained to correspond to the potential at the middle of the interval. In some of the experiments a different method of reducing the observations was made use of. The observations of potential and time were used to plot a curve connecting these two variables. The values of $\frac{dV}{dt}$ were then obtained from this curve by geometrical differentiation. This method was not found to give results which were either more consistent or more accurate than those given by the other, so that as it was much more laborious it was discarded.

The maximum potential of the upper plate against which a measurable current would go was always about ·6 of a volt. With potentials of this magnitude the current was small, and the rate of change of voltage was only measurable when either a very small capacity or no capacity at all was added to that of the electrometer. Generally speaking it was found that the insertion of two capacities which changed the total capacity in a ratio of about 50 to 1 enabled the currents to be measured conveniently throughout the whole range. Two series of readings were usually taken with the heating current in opposite directions. By taking the mean of two deflexions corresponding to any given potential any error arising from the central point of the hot strip not being connected to earth was eliminated.

As the potential-difference between the two plates was always small, the fall of potential along the hot strip itself is of considerable importance. It was not possible to determine what this amounted to, but it was estimated to be between ·08 and ·012 volt, and was probably nearer the lower than the higher of these two limits. Assuming that the middle of the strip was at zero potential the greatest potential at any point of the hot metal would lie between the limits $\pm$·04 volt and $\pm$·006 volt. It is difficult to be quite certain how the results would be affected by the existence of this external field along the strip.

A large number of series of observations were taken in the manner indicated with slightly varied conditions. The numbers recorded in one of them are shown in the accompanying table. It will be noticed that with the same mean potential-difference (·11 volt) between the plates the currents measured were independent of the capacity used. The actual determinations were $21{\cdot}5 \times 10^{-12}$ ampere with ·001 microfarad and 22×10^{-12} ampere with ·1 microfarad. The temperature in this experiment was 1283° C.

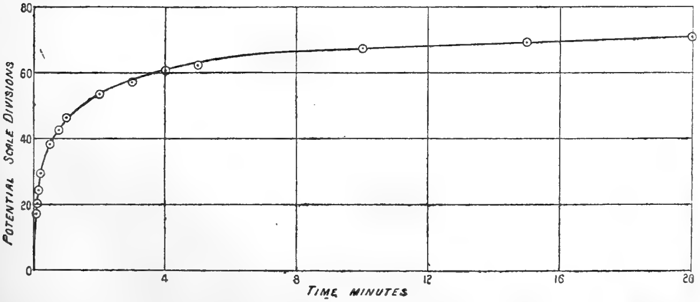
Negative Ionization.

Capacity, microfarads.	Pressure, mm.	Time.	Electrometer Readings, mm.			Increment of potential, scale divisions.	Interval of time, seconds.	Current, amperes $\times 10^{12}$.	Mean potential, volts.
			Heating current						
			direct	reversed	mean				
0·001	0·015	10 sec.	26	24	25	25	10	21·5	0·11
		20 sec.	34	32	33	8	10	6·9	·25
		30 sec.	40	38	39	6	10	5·1	·31
		1 min.	51	50	50·5	11·5	30	3·0	·39
		1·5 min.	58	56	57	6·5	30	1·9	·47
		2 min.	62·5	61	61·7	4·7	30	1·36	·53
		2·5 min.	66·0	64·5	65·2	3·5	30	1·00	·55
		3 min.	69	67·5	68·2	3·0	30	·84	·58
		4 min.	72·8	...	...	3·8	60	·54	·62
0·10	0·015	30 sec.	1·8	1·2	1·5	1·5	30	42·8	·014
		2 min.	4·0	5·2	4·6	3·1	90	33·0	·035
		3 min.	6 3	7·8	7·05	2·4	60	35·0	·055
		1 min.	2·6	2·6	2·6	2·6	60	37·3	·018
		5 min.	9·9	11·9	10·9	8·3	240	27·0	·08
		7 min.	13·0	15·0	14·0	3·1	120	22·0	·11
		10 min.	17·1	19·7	18·4	4·4	180	18·0	·14
		13 min.	20·2	...	...	3·1	180	14·0	·16
		17 min.	24·0	...	...	3·8	240	13·5	·19
		20 min.	26·3	...	...	2·3	180	10·7	·22

Resistance 7570, temperature 1556 absolute scale. Gas constant $4{\cdot}1\times10^3$.

A series of observations similar to those in the table have been plotted in fig. 4, so as to exhibit the potential to which

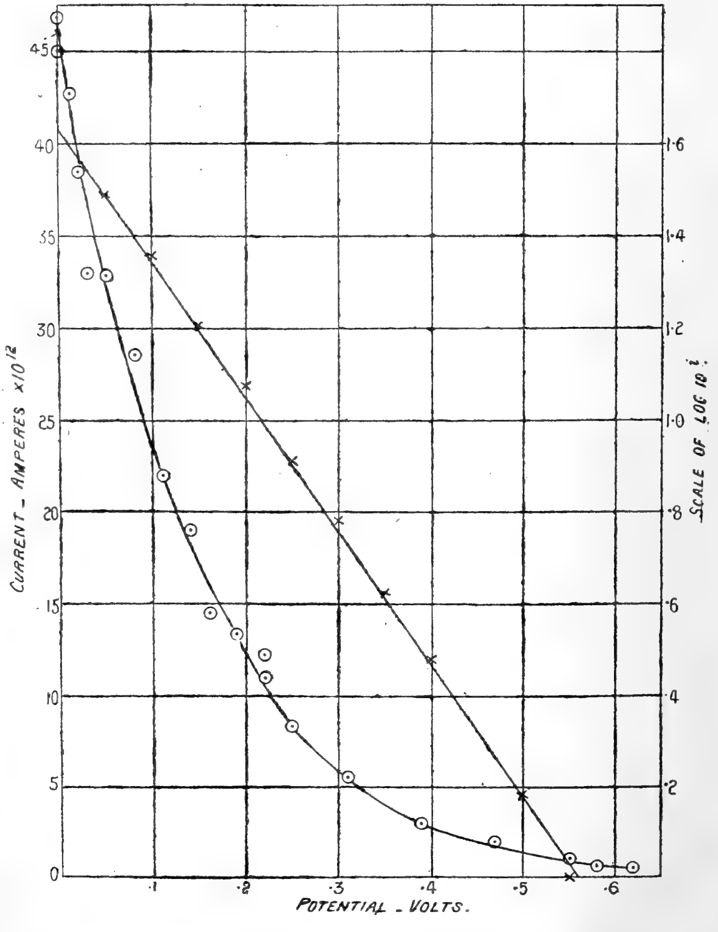
Fig. 4.



the upper plate charges as a function of the time. The general form of this curve is in agreement with the equation (12) which was deduced theoretically.

Fig. 5 exhibits the current to the upper plate as a function of the potential-difference tending to stop it. The points with circles round them denote the values of the current recorded in the preceding table at the potentials given by the abscissæ. These points are seen to be distributed fairly evenly about the smooth curve shown. In order to test the theoretical formulæ (10) and (11) a series of points on the

Fig. 5.



smooth curve were taken, and the logarithms of the corresponding values of the current were obtained. These are plotted against the potential-difference in the figure. The scale of the logarithmic curve is shown on the right-hand side of the diagram.

If we use logarithms to the base 10 formula (11) becomes

$$\log i_0 - \log_{10} i = {\cdot}432 \frac{\nu e}{R\theta} V.$$

As i_0, ν, e, θ, and R are constant in any one experiment, the curve obtained by plotting $\log_{10} i$ against V should be a straight line. The accuracy with which the linear relation was fulfilled is shown by the diagram. From the slope of this line the value of the coefficient $-\frac{\nu e}{R\theta}$ could be deduced. Substituting the known value of νe, the quantity of electricity required to liberate half a cubic centimetre of hydrogen at 0° C. and 760 mms. by electrolysis, and the value of θ, the absolute temperature, found experimentally, a value of R the gas constant could be determined by these experiments and compared with the well-known value of this constant. This particular experiment gave for R the value $4{\cdot}1 \times 10^3$ C.G.S. units compared with the standard value $3{\cdot}7 \times 10^5$. The agreement is fairly good when all the difficulties of the investigation are taken into account.

A large number of experiments were made with platinum under varied conditions, and this linear relation was always verified provided the general method of treatment of the platinum which has been described was adhered to. In most of the experiments the surrounding gas was air at a low pressure; but the effect of replacing the air by hydrogen at a similar pressure was examined. In another set of experiments the platinum was covered with calcium oxide by heating a drop of calcium nitrate solution placed on it. In both these cases it was noticed that for some time after the change in the conditions had been made the above law connecting the current with the potential-difference was obeyed just as with platinum alone surrounded by air. It was also noticed that on first heating the strip after letting in hydrogen or after coating it with lime, the value of the current at any given temperature was practically unchanged from that which had obtained for pure platinum at the same temperature in air. The subsequent increase in the emission of ions, whether caused by hydrogen or by lime, appeared to take some time to establish itself, and as soon as a marked increase in the initial absolute value of the current occurred, it was found that the law was no longer obeyed. Thus the character of the phenomena appears to change when the metal is heated for a long time either in a hydrogen vacuum or when coated with lime. The results which we obtained after heating for some time in hydrogen were too irregular to draw very definite conclusions from; but in the case of the lime-covered strip more consistency was observed. The main feature of the change consisted in a reduction of the curvature of the curve connecting the current and the potential. This reduction was greater the higher the temperature of the lime-coated strip, and also therefore the greater the absolute value of the current. At higher temperatures the current appeared within the limits of experimental error to be a linear function of the potential instead of an exponential function, In one experiment the current was $3{\cdot}4\times10^{-8}$ amp. for $V=0$ and diminished as a linear function of the potential-difference to the value zero for $V=1{\cdot}22$ volts. Usually the current reached zero for a somewhat smaller voltage than this. The general effect of both hydrogen and lime on the hot platinum appears to be to change the law of distribution of energy among the emitted electrons entirely, and also to change the average value of the kinetic energy to some extent. In every case the average value of the kinetic energy was found to be greater than what it would have been for pure platinum at the same temperature in air. This change is, comparatively speaking, not very great. The greatest increase recorded in our experiments amounted to about twice the value for platinum alone.

It has been pointed out that the normal behaviour of the strip was also deranged if the hot metal was subjected to the action of a strong electric field at any time. In this case both the law of distribution of energy and the average value of the latter appear to be entirely changed. This peculiar state of the metal can be got rid of very rapidly by heating it for a short time to a high temperature. After this treatment the current against the potential again obeys the formula $\log_\epsilon i_0-\log_\epsilon i=\frac{\nu e}{R\theta}V$ with the same value of the coefficient $\frac{\nu e}{R}$ as in the normal case.

The value of R calculated from eight different series of experiments which have been selected as illustrating all the different conditions under which the linear relation between $\log i$ and V was found to be satisfied are given in the accompanying table. It will be observed that other conditions besides the previous treatment of the hot metal were varied during the experiments. The pressure of the gas varied from ·006 to ·06 mm., the temperature from 1473 to 1840 ablute, and the maximum current from 3×10^{-12} to $4{\cdot}7\times10^{-12}$ ampere. The last series in the table was obtained after the hot metal had been put into the peculiar state already described by charging the upper plate with a high negative potential, and this peculiar state had afterwards been destroyed by strongly heating the strip. The last observation but one refers to similar conditions, except that the peculiar state was induced by charging the upper plate negatively. It is possible that some change took place in the strip which made the recorded temperatures too high in these two experiments.

The values of R calculated from the different experiments are shown in the last column of the table. These range from $2{\cdot}9\times10^3$ to $4{\cdot}2\times10^3$ with a mean value of $3{\cdot}5\times10^3$. The disagreement of these numbers among each other is probably greater than could arise from errors in the measurements of any of the physical quantities involved, such as the temperature for example. When we consider the number of things which appear to affect this phenomenon in a way which is not yet understood, the agreement is probably as satisfactory as could be expected. The agreement of these numbers with the theoretical value $R=3{\cdot}7\times10^3$ is very striking, and seems scarcely likely to be a chance coincidence.

Date.	Treatment of Platinum before Observations.	Pressure, mm.	Absolute Temperature.	Maximum Current, amperes.	R.
Jan. 29.	16 hours' heating	·015	1556	$4{\cdot}7\times10^{-11}$	$4{\cdot}1\times10^3$
Jan. 31.	....	·008 ·009	1473	$1{\cdot}2\times10^{-11}$	$4{\cdot}2\times10^3$
b. 5.	Just after lime was placed on platinum	·006 ·06	1503	3×10^{-11}	$3{\cdot}5\times10^3$
Feb. 10.	Just after hydrogen was let into vacuum	·04	1553	4×10^{-11}	$3{\cdot}6\times10^3$
Mar. 8.	About 35 hours' heating	·015	1660	$1{\cdot}4\times10^{-11}$	$2{\cdot}9\times10^3$
Mar. 9.	About 30 hours' heating	·01	1560	3×10^{-12}	$3{\cdot}1\times10^3$
Mar. 13.	Highly charged with negative electricity and strongly heated subsequently	·02	1840	4×10^{-11}	$3{\cdot}2\times10^3$
Mar. 14.	Highly charged with positive electricity and strongly heated subsequently	....	1813	1×10^{-11}	$3{\cdot}4\times10^3$

In order to test the theory further the obvious thing to try was whether the coefficient $\frac{ve}{R\theta}$ deduced from the log i, V diagram really was universally proportional to the absolute temperature. A glance at the preceding table will show that in the case of platinum this is a difficult if not impossible task. The disagreement between the different determinations of R shows a greater ratio of variation than the fractional change in the absolute temperature over the whole range of temperature during which the effect could conveniently be measured. For this reason it seemed likely that it would prove impossible to disentangle any change in the coefficient due to θ being changed from changes due to unknown causes. We have therefore not attempted to test this part of the theory by experiments on platinum itself.

The negative ionization from the liquid alloy of sodium and potassium suggested itself as a more likely way of attacking this question. With this substance the current can conveniently be measured at temperatures as low as 500° absolute; so that if the theory were obeyed by this substance the value of $\frac{\nu e}{\mathrm{R}\theta}$ ought to be about three times as great as in the experiments on platinum. In making experiments with this substance we have had considerable experimental difficulties to contend with, and so far have only been able to obtain results of a qualitative character. So far as our experiments go, they indicate that the nature of the negative ionization from the substance is not at all what was expected. Instead of the current falling off more rapidly with the potential than with hot platinum, it falls off less rapidly, indicating that the emitted electrons have a much greater quantity of kinetic energy than those emitted from platinum at a much higher temperature. The experiments that we have been able to make with the alloy so far are not sufficiently accurate to decide whether the formula $\log i - \log i_0 = k\mathrm{V}$ is obeyed with a different value of k or not. We hope to be able to resume this part of the investigation in the autumn.

Discussion of Results.

In presenting the results of this investigation the method has been adopted of making certain hypotheses as to the distribution of energy among the emitted electrons. From these hypotheses formulæ have been deduced which were then compared with the experimental observations. This method is justifiable on the ground that these theoretical considerations first suggested the investigation, and also because in the case of platinum the phenomena are in accordance with the theory. We have seen, however, that a number of cases have arisen where the law of distribution of energy among the particles does not coincide with Maxwell's law, so that to analyse these cases it is important to have a more general method of deducing the mode of distribution of the energy than that which has been made use of. This may always be done in the following way:—First of all construct the curve giving the current-densities as ordinates in terms of the opposing potentials as abscissæ. Our interpretation of this curve is that the current C_V corresponding to any potential V is equal to e the charge on an ion multiplied by the number of ions shot off in unit time for which $\frac{1}{2}mu^2$ is greater than eV. Calling this number $N_{(V)}$ we have then $C_V = eN_{(V)}$. But if the number of ions emitted per second for which the normal component of the energy lies between eV and $e(V+dV)$, (*i. e.* between $\frac{1}{2}mu^2$ and $\frac{1}{2}mu^2+mu\,du$) is denoted by $eN'_{(eV)}dV$ we shall have

$$N_{(V)} = e\int_{eV}^{\infty} N'_{(eV)}dV.$$

So that

$$N'_{(eV)} = \frac{d}{d(eV)}N(V) = -\frac{1}{e^2}\cdot\frac{dC_V}{dV}.$$

To obtain the number which have velocity components perpendicular to the emitting surface lying between u and $u+du$ we have simply to replace eV by its kinetic equivalent $\frac{1}{2}mu^2$. We thus get

$$muN'(\tfrac{1}{2}mu^2)du = -\frac{1}{e}\frac{dC_V}{dV}dV.$$

The number of particles whose normal velocity or energy lies between given limits can thus always be calculated from the tangent to the CV curve.

If we apply this method to the experimental numbers obtained for platinum in what we have called the normal condition, the function giving the number having energy between assigned limits is that required by Maxwell's law. This is sufficiently obvious, since otherwise the equations obtained previously would not have been satisfied. In the case where the electrons were emitted from platinum covered with lime the CV curve lost its exponential character and became a straight line at high temperatures. In this case $\frac{dC_V}{dV}$ is constant, so that the number of particles whose energy lies between x and $x+dx$ is proportional to dx and independent of x, or, in other words, the number of particles having an amount of $\frac{1}{2}mu^2$ lying within a given range is independent of the amount itself. This is only true within certain limits; in the case referred to the number of particles which had an amount of energy greater than that which corresponds to 1·22 volts was too small to be detected.

The measurements that we have made in the cases in which the distribution of energy is abnormal are too meagre as yet to enable much to be said positively as to the causes which make the distribution of the energy differ from the Maxwell type. There are, however, certain obvious causes which might change the distribution of energy. If a double layer formed outside the metal, and the direction of the electric force in the double layer was such that it tended to drive the ions away from the metal, the distribution of energy would be altered. Admitting that the free electrons inside the metal have the distribution of velocity given by Maxwell's law, those which escaped into the double layer would also have this distribution provided they were enabled to get out by virtue of their kinetic energy overcoming the surface forces. All the ions which reached the double layer would escape into the region outside, but the value of $\frac{1}{2}mu^2$ for each of them would be increased by the work done in passing through the layer. Thus, in this simple case, the distribution of energy among the emitted particles would be that given by Maxwell's law + a constant. If the electrons escaping were deflected by collisions with atoms inside the double layer itself this simple law of distribution would be altered and would become very complex, but in any case we should expect that any variation from the normal would result in an increase in the average energy of the particles. This explanation is supported by the facts, so far as this particular conclusion is concerned; for in all the cases of deviation from the type which we have examined the mean kinetic energy appeared to be greater than that required by Maxwell's law.

The most reasonable way of interpreting the results which have been obtained so far appears to us to be to suppose that generally speaking the distribution of velocity among the free electrons inside the metal is that given by Maxwell's law for a molecule of gas at the same temperature as that of the metal. That when the electrons which escape simply have to do a certain amount of work against surface forces this law also holds for the distribution of energy among the electrons which have escaped. It seems probable, however, that there are a large number of cases of the escape of electrons from hot metals when the mechanism is not so simple as this. There may for instance be a double layer like the one already alluded to; there is some evidence that the very large change produced by absorbed hydrogen on the leak from hot platinum may be due to an effect of this kind. It is possible also that the expulsion of these electrons in some cases is due to a more indirect process. It might for instance be an effect of the radiant energy of the metal analogous to the photoelectric effect. In this case the kinetic energy would probably be much greater than the thermal value. We hope that further research will throw light on this point.

It seems to us an important point to have established that in one case at any rate, that of platinum heated in air at low pressure, the distribution of the square of the velocity component normal to the surface among the electrons emitted is identical with Maxwell's law of distribution of the same quantity for a gas at the temperature of the metal. It has been suggested to us that experiments of this kind do not necessarily enable us to deduce the law of distribution of velocity among the emitted particles, for the reason that formulæ similar to those on which our conclusion is based might be deduced by a purely hydrodynamical kind of treatment assuming that the particles exerted a pressure which was related to the temperature according to the law $pv=\mathrm{R}\theta$. Since this kind of treatment supposes the matter concerned to behave as though it were continuous it would follow that the experiments would not warrant any conclusion as to the distribution of velocity among the particles. It appears to us, however, that this is an unfair view of the question to take. It is now well established that the electric currents under investigation are carried by charged particles whose charge and mass are known. Admitting for the moment our interpretation of the experiments, it follows that at 1650° absolute the mean value of u, the component of the velocity, perpendicular to the plate, of the ions emitted is about $1{\cdot}5\times10^7$ cm. per sec. The distance between the plates being 2 millims., the average time occupied by the ions in crossing under zero field would be $1{\cdot}3\times10^{-8}$ sec. The maximum current in any of the experiments was $4{\cdot}7\times10^{-11}$ ampere, which corresponds to an emission of $3{\cdot}6\times10^8$ ions per sec. The number of ions present at any instant between the two plates would therefore be comparable with 5. The average distance between them would be so great that their mutual forces would be entirely negligible. On these grounds it appears to us that the only reasonable view to take is that the current is carried by discrete charged particles whose motion after they have left the plate is determined solely by the magnitude of the electric field and their initial velocity. Unless we are prepared to deny the atomic theory of electricity there appears to be no escape from the conclusion that the distribution of velocity among the emitted particles is that which has been deduced from these experiments.

This method does not enable us to determine by experiment the distribution of velocity among the electrons in a closed space including a piece of hot metal when the final state of statistical equilibrium has been reached. All that we are able to do is to examine the distribution of velocity among the particles emitted from the hot metal at any instant, and to show that in the case of platinum at least the results are consistent with what would be required if in the state of statistical equilibrium the distribution of velocity among the electrons outside the metal were determined by Maxwell's law. This leads to a strong presumption that the distribution of velocity among the external electrons in the steady state would be given by Maxwell's law, with the mean translational kinetic energy identical with that of the molecules of a gas at the temperature of the metal. This involves the further conclusion that the distribution of velocity among the free electrons inside the metal is also determined by Maxwell's law. For if the free electrons inside the metal are free in the sense of the kinetic theory of gases, the only difference between those inside and those outside the metal will be due to the difference of their potential energy. There is a well-known theorem in the kinetic theory of gases which proves that when two regions of the same gas at the same temperature are compared, the regions being such that the mean potential energy of the molecules is different in the two regions, the mean translational kinetic energy is the same in both, and is distributed according to the same law. The only effect of the difference of potential energy is to make the concentration of the molecules different in the two regions. Applying this theorem to the case of the electrons inside and outside a piece of hot metal, it follows that the mean translational energy and the way in which it is distributed among the electrons will be the same both inside and outside the metal. The conclusion that the average translational kinetic energy and the law of distribution of velocity of the electrons inside a metal are identical with those among the molecules of a gas at the same temperature as that of the metal is of great importance in the electron theory of metallic conduction and thermal radiation.

Princeton, N. J., June 5, 1908.

XXXI. *On the Radioactivity of Potassium and other Alkali Metals. By* Prof. J. C. McLennan *and* Mr. W. T. Kennedy*.

I. *Introduction.*

IN the course of some experiments made by them on the radioactivity of a series of salts which had hitherto been considered inactive, Messrs. Campbell and Wood (Proc. Camb. Phil. Soc. vol. xiv. pt. 1, p. 15, 1907) found that potassium salts exhibited a radioactivity greater than that of any other substance previously examined which did not contain any of the so-called radioactive elements.

In seeking for the source of this activity these experimenters found it impossible to separate out any active impurity from the salts examined, and they were led by the results of their investigation, which included measurements on the activities of a limited number of compounds of potassium, to conclude that the activity originated with the potassium itself and was an atomic property of that metal.

In a later paper (Proc. Camb. Phil. Soc. vol. xiv. pt. 2, 1907) Campbell described some additional experiments dealing with the character of the radiation emitted by the potassium salts, and in concluding expressed the opinion that the radiation consisted of β rays possessing an average velocity less than that of the β rays of uranium.

In a recent note by one of us ('Nature,' May 14th, and Phys. Zeit. Aug. 1st) an account is given of some experiments which involved a minute examination of the radioactivity of a large number of potassium and other salts. In this note it was stated that while the results of this examination confirmed the discovery made by Campbell and Wood, that potassium salts generally possess an exceptionally high activity, and emit a radiation possessing considerable penetrating power, they did not support the conclusion that the activity of these salts was connected with a normal atomic property of potassium and that it was always directly proportional to the amount of that metal present in the salt.

The salts used in this examination were those ordinarily sold as chemically pure, and in drawing the conclusion just referred to it was assumed that the salts were, as they purported to be, of a high grade of purity. It has been found, however, since the publication of this note that the assumption was by

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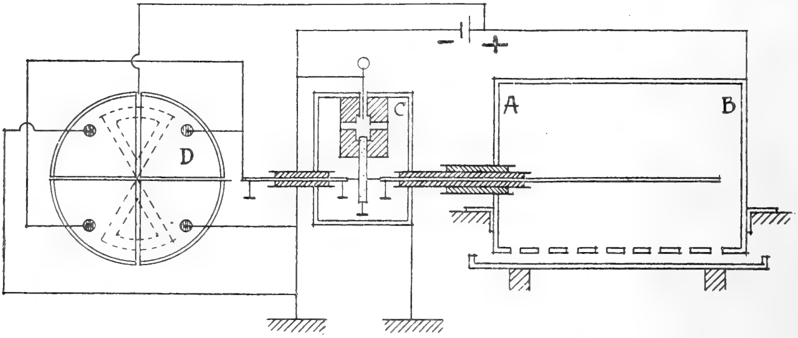
* Communicated by the Authors.

no means warrantable; and from the results of additional measurements it has been found necessary to modify the conclusions mentioned in the earlier notices.

In measuring and comparing the activities of the different salts, these were each spread out in turn in uniform layers on a shallow tray which was placed on the bottom of the ionizing chamber shown in fig. 1, which was 40 cm. long, 26 cm. wide, and 28 cms. deep. The saturation currents through the air in the chamber were measured with a sensitive quadrant electrometer, and were taken as measures of the activities of the different salts.

Fig. 1.



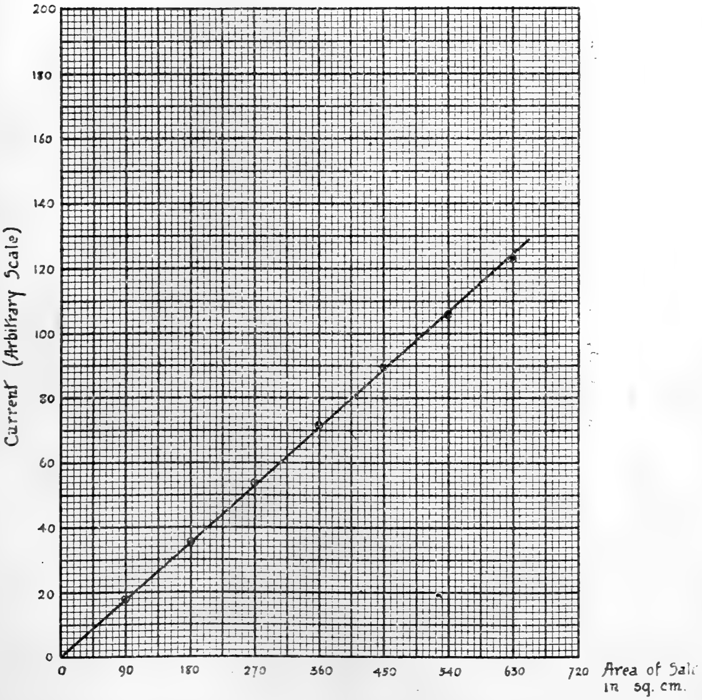
II. *Relation of Activity to Area of Salt exposed.*

Before proceeding with the examination of the different salts some preliminary measurements were made on the activity of potassium sulphate when different areas of a layer of this salt were exposed to the air in the chamber. A layer of the salt some 6 mm. in thickness was placed in the tray mentioned above, which was 35 cms. long and 18 cms. wide, and then covered with a thick plate of metal divided into sections 18 cms. long, and 5 cms. wide. These sections were, one after another, removed from the tray, so that larger and larger areas of the salt were left exposed to the air in the chamber. The saturation current corresponding to each area was measured, and the values which are given in Table I. and plotted in fig. 2, show that the saturation currents were directly proportional to the areas of the salt exposed. From this result it was evident that the substance which constituted the source of the radiation was uniformly distributed throughout the mass of the salt.

TABLE I.

Area of salt exposed in sq. cm.	Saturation current. Arbitrary Scale.
5×18	17·87
10×18	35·5
15×18	53·8
20×18	71·5
25×18	89·75
30×18	106
35×18	123

Fig. 2.



III. *Relation between Thickness of Salt Layer and Activity.*

Some additional measurements were made to ascertain the relation of the activity of a number of the salts to the thickness of the layer of salt exposed. In making these measurements the salts were ground to a fine powder and then sifted as uniformly as possible on the bottom of a shallow tray which had a surface area of 228 sq. cms. This tray was then placed in the ionizing chamber, and the saturation currents measured for each layer as before.

The results obtained with potassium sulphate are recorded in Table II., and a curve representing them is shown in fig. 3. From these it will be seen that the saturation currents steadily increased with the thickness of the layer of salt exposed until a thickness of 2·5 cm. was reached, when the current assumed a steady value and remained the same for greater thicknesses.

Additional observations were made with the halogen salts of potassium, and still others with two samples of potassium cyanide, one with a sample of potassium hydroxide, and one with a second specimen of chloride of potassium. The results of these measurements are given in Tables III. and IV., and curves representing them in figs. 4 and 5. From all the results recorded it will be seen that layers of the different salts between 2 and 3 mms. were amply sufficient to give the maximum saturation currents.

TABLE II.

Activity of Potassium Sulphate.

Thickness of salt layer (mm.).	Activity of salt. Saturation current (Arbitrary scale).
0·188	32
0·43	61
0·625	86
1·09	112
1·56	128
2·03	134
2·50	142
3·75	142
5·00	142

Fig. 3.

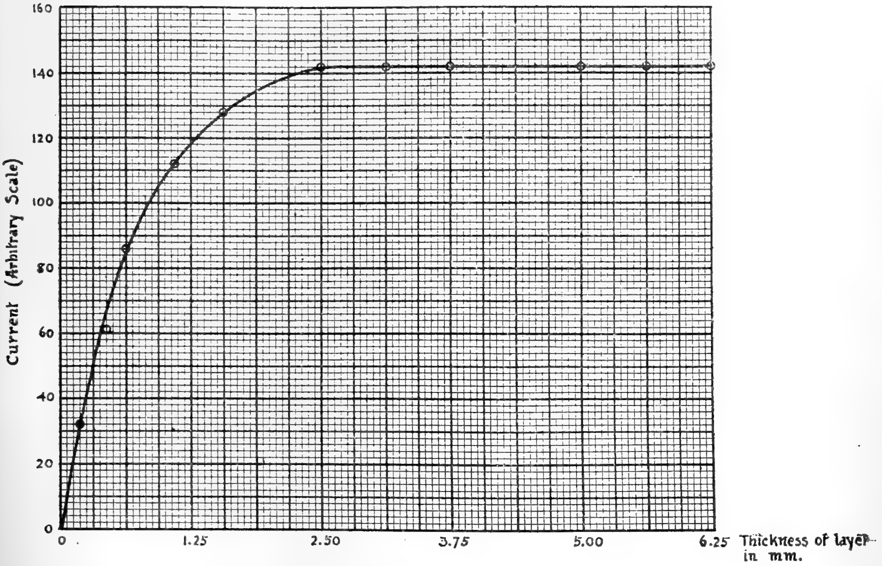


TABLE III.

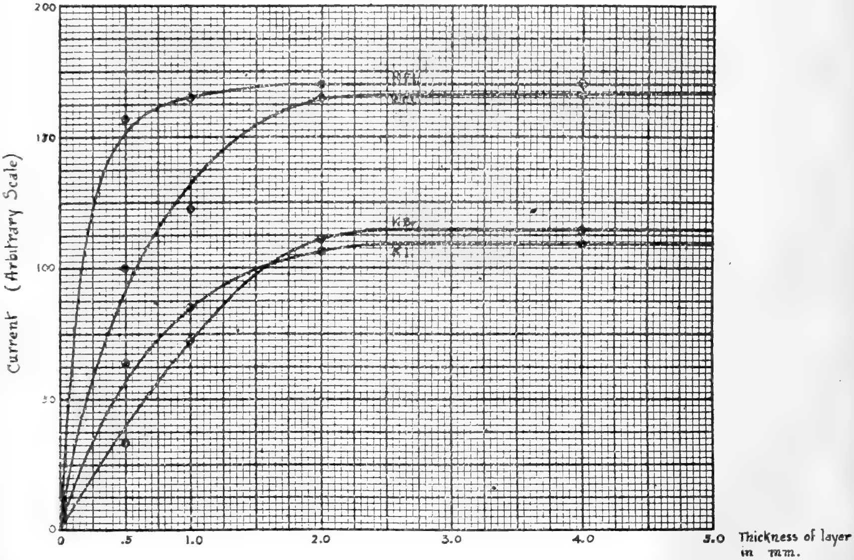
Activity of Potassium Salts of Halogen Group.

Thickness of salt layer (mm.).	Activity of salt. Saturation current (Arbitrary scale).			
	Potassium Fluoride.	Potassium Chloride.	Potassium Bromide.	Potassium Iodide.
·5	157	100	33·5	64
1·0	165	122·5	72·5	85
2·0	170	165	110·5	106
4·0	170	166·2	114·4	109

TABLE IV.

Thickness of salt layer (mm.).	Activity of salt, Saturation current (Arbitrary scale).		
	Potassium Chloride.	Potassium Hydroxide.	Potassium Cyanide (Kahlbaum).
·5	82·5	58	65
1·0	110	96·3	100
2·0	150	132·5	160
4·0	152·5	160	167·5

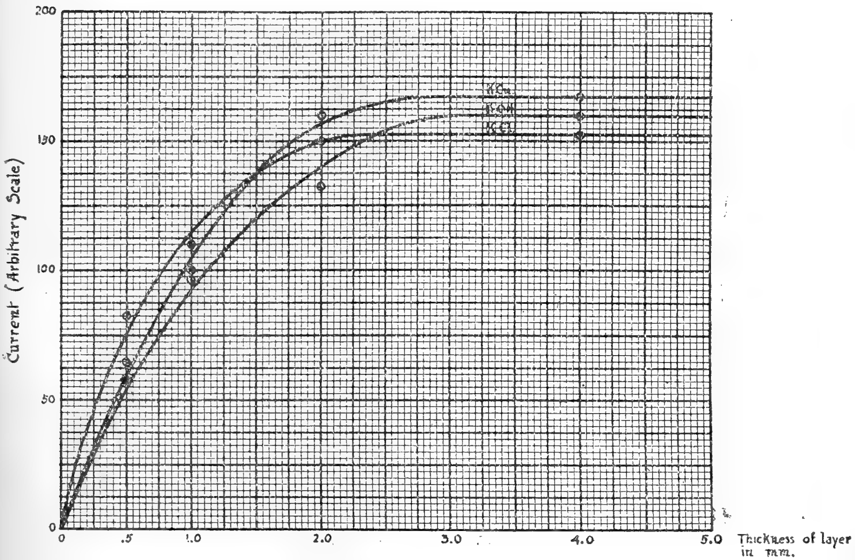
Fig. 4.



IV. *Activities of different Potassium and other Salts.*

After ascertaining that the activity of a selected salt was directly proportional to the area exposed, and that layers having a thickness of approximately 2·5 to 3 mm. furnished a measure of the maximum activity of the salt, a series of measurements was made on the activities of a large number of potassium salts as well as on a number of others of the different alkali metals.

Fig. 5.



The results of the examination of these different salts are given in Table V. (p. 384), and in all cases they represent the activities of layers of sufficient thickness to give the maximum saturation currents.

From this table it will be seen:—

First. That samples of a selected salt obtained from different sources exhibited widely differing degrees of activity. Two of the chlorides, as Nos. 3 and 4 show, differed by more than 40 per cent. in their activities, and two of the hydroxides, Nos. 7 and 8, by nearly an equal amount. In the case of the cyanide of potassium the variation in activity was especially marked. As can be seen from Nos. 10 and 12, two samples of this salt exhibited activities which were approximately only 5 per cent. and 20 per cent. respectively of that shown by a number of other specimens of the same composition.

In addition to the results recorded in Table V. it may be stated that on one occasion a sample of potassium cyanide obtained from Kahlbaum was compared with one of potassium sulphate and one of potassium chloride obtained from Mercks,

TABLE V.

Table of Activities.

No.	Salt.	Source of salt.	Percentage of metal in salt. =K.	Activity of salt Saturation current, (Arbitrary scale =A.	$\frac{A}{K}10^2$.	No.
1...	$KF(H_2O)_2$	Mercks	41·5	207	499	1
2...	KCl	Mercks	52	152	292	2
3...	KCl	Kahlbaum	52	208	400	3
4...	KCl	Commercial	52	150	288	4
5...	KBr	Mallinckrodt	33	105	320	5
6...	KI	Mallinckrodt	24	110	466	6
7...	KOH	Mercks	70	223	319	7
8...	KOH	Kahlbaum	70	160	228	8
9...	KOH	Mercks	70	200	285	9
10...	KCN	Eim. & Am.	60	41	68	10
11...	KCN	Kahlbaum	60	183	305	11
12...	KCN	Mercks	60	8	15	12
13...	KCN	Commercial	60	191	318	13
14...	KCN	Commercial	60	208	346	14
15...	KCN	Commercial	60	185	308	15
16...	KNO_3	Commercial	38·6	85	218	16
17...	KNO_2	Mercks	46	125	272	17
18...	$KClO_3$	Kahlbaum	32	128	400	18
19...	$KMnO_4$	Commercial	25	80	320	19
20...	$KMnO_4$	Commercial	25	78	312	20
21...	$K_2C_2O_4$	Commercial	47	126	268	21
22...	$K_2C_2O_4$	Commercial	47	93	198	22
23...	$K_2SO_3(H_2O)_2$	Mercks	40·2	20	50	23
24...	K_2SO_4	Kahlbaum	45	141	313	24
25...	$K_2CO_3(H_2O)_2$	Kahlbaum	45	141	313	25
26...	$K_2C_2O_7$	Commercial	36·4	128	387	26
27...	K_3PO_4	Mercks	55	166	300	27
28...	$K_4Fe(CN)_6(H_2O)_3$	Kahlbaum	37	174	470	28
29...	$K_6Fe_2C_{12}N_{12}$	Kahlbaum	36	163	459	29
30...	K (metal)	Mercks	100	195	195	30
31...	Na (metal)	Commercial	100	0	0	31
32...	NaCl (evapor.)	Commercial	39	0	0	32
33...	NaCl (rock) (1)	Commercial	39	66	169	33
	NaCl (rock) (2)	Commercial	39	0	0	
	NaCl (rock) (3)	Commercial	39	0	0	
34...	Na_2CO_3	Commercial	43	0	0	34
35...	$LiCl(H_2O)_2$	Mercks	9	0	0	35
36...	$Li_3C_6O_7$	Mercks	23·3	0	0	36
37...	Li_2CO_3	Commercial	19	0	0	37
38...	$Rb_2Al_2(SO_4)_4(H_2O)_{24}$	Commercial	16·3	4	2·5	38
39...	$CsCl$	Commercial	80	5	6	39
40...	NH_4Cl	Commercial	33	14	40	40
41...	NH_4Br	Commercial	18·4	0	0	41
42...	$(NH_4)_2CO_3$	Commercial	37·5	0	0	42
43...	NH_4NO_3	Kahlbaum	22	0	0	43

and all three salts were found to possess to within one per cent. the same activity. On another occasion, a sample of potassium cyanide obtained from Kahlbaum was compared with a specimen of the same salt manufactured by Mercks, and was found to display an activity more than four times as intense as that of the latter.

In this connexion the extremely low value found for the activity of the sample of potassium sulphite tested also merits emphasis. Potassium metal itself, it will be seen, exhibited a marked activity, but the value assigned to it, however, is not to be taken as comparable with the values recorded for the different salts of this metal, inasmuch as it was not possible to prepare layers of the metal for examination as regular and uniform as those of the salts.

From a consideration of all the results given in Table V. it would appear:—

First. That the values of $\frac{A}{K} \times 10^2$ found for the different potassium salts exhibited extremely wide variations, and that if the purity of the salts was assumed, these were such as to practically preclude the view that the activity of the salts was due to a normal atomic property of potassium.

Second. That while one sample of sodium chloride in the form of rock-salt showed an activity comparable with that exhibited by a number of potassium salts, several other samples of rock-salt were found to be quite inactive. Metallic sodium, too, and also a specimen of sodium carbonate, when examined, did not exhibit the slightest trace of radioactivity, and consequently it would appear that the activity observed in the single instance of sodium chloride mentioned was due to the presence in this salt of a trace of an active impurity. The low values obtained by Elster and Geitel in their measurements on the conductivity of air in a salt mine would also support this view.

Third. That with the exception of ammonium chloride which emitted a feeble activity, none of the lithium and ammonium salts showed the slightest trace of radioactivity, and that a sample of rubidium alum exhibited an activity which was extremely small, and a specimen of cæsium chloride one which was only just measurable.

V. *Activities of Different Samples of Potassium Cyanide.*

From suggestions received by the writers from a number of sources it seemed desirable to make a closer examination of the activities of different specimens of potassium cyanide; and with the object of doing this five different samples were obtained from one manufacturer, one from a second, and also one from a third manufacturer.

The activities of these salts were examined in the manner indicated above, and the salts themselves have since been analysed by Professor A. B. Macallum, who has very kindly determined the potassium content of each of them for us, using the platinum method.

The results of this examination are recorded in Table VI., the relative activities being given in Column I. of this table. In making the analyses, equal weights of the different salts were taken and the potassium present in each sample of the salt determined as a percentage of the total weight. These percentages are recorded in Column II. of Table VI.

TABLE VI.

Activities of different samples of Potassium Cyanide.

Source of Salt.	COLUMN I.	COLUMN II.
	Relative Activities of Salts.	Percentage by weight of Potassium present in Salts.
Manufacturer "A" Sample No. 1.	8·85	52·15
Manufacturer "B" Sample No. 1.	1·40	9·44
Manufacturer "C" Sample No. 1.	·15	2·84
" ., No. 2.	·10	2·76
" " No. 3.	·60	9·57
" ,, No. 4.	·00 (slight)	2·36
" " No. 5.	1·47	7·64

In arriving at these results the different salts were placed in bottles and sealed immediately after their activities were ascertained. They were also kept sealed until the analyses were made. This precaution was taken in order to prevent the absorption of moisture from the air, as otherwise, since the salts are hygroscopic, values for the percentage contents of potassium in the salts would have been obtained which would not have been applicable in a discussion of their relative activities determined some time previously.

From the results set forth in Table VI. it will be seen that exceedingly wide variations were found in the potassium content of the different specimens. It will be seen, too, that those salts which possessed the greater potassium content also exhibited the higher activities, and that in the case of the more active the radioactivities were approximately proportional to the potassium contents of the salts. The results obtained with potassium cyanide in this series of measurements, therefore, rather support the view taken by Campbell that the activities of potassium salts are directly proportional to the amount of potassium present in them.

In the light of these results it would appear advisable, too, before drawing definite conclusions from the numbers given in Table V., to make a chemical analysis of each of the salts and to accurately determine its potassium content.

VI. *Absorption Experiments.*

In order to obtain an estimate of the penetrating power of the radiations emitted by the potassium salt, quantities of the sulphate, the chloride, and the cyanide were spread in turn in uniform layers on a tray and placed beneath and close to the bottom of the ionizing chamber AB, fig. 1. In these measurements the bottom of the chamber consisted of a finely meshed gauze, which permitted the rays to pass into the chamber with as little absorption as possible. The tray containing the salt was then gradually lowered so as to increase the air-column traversed by the rays before they entered the chamber, and the ionization currents were measured with the salt at different distances. The values of the currents obtained with three of the salts mentioned are shown in Table VII. These values have been reduced for purposes of comparison to a common maximum intensity, and the reduced

Table VII.

Absorption Experiments.

Distance (cm.).	Potassium.		
	Sulphate (Current arbitrary scale).	Chloride (Current arbitrary scale).	Cyanide (Current arbitrary scale).
2·1	178	235	240
4·7	158	200	205
9·1	118	166	178
16·6	81	94	125
24·4	59	65·4	96
31·9	39	44	64
39·1	28·5		33

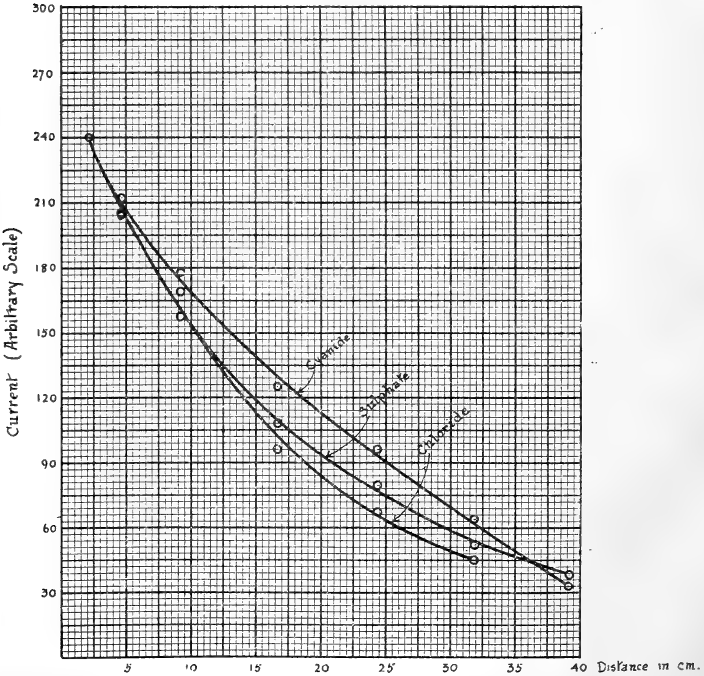
readings are given in Table VIII., curves representing them being shown in fig. 6. From these it will be seen, just as

TABLE VIII.

Absorption Experiments (Reduced values).

Distance (cm.).	Potassium.		
	Sulphate.	Chloride.	Cyanide.
2·1	240	240	240
4·7	212	204	205
9·1	158	169	178
16·6	108	96	125
24·4	79·7	67	96
31·9	52	45	64
39·1	38	...	33

Fig. 6.



Campbell and Wood have pointed out, that the rays emitted by potassium salts possess considerable penetrating power.

The saturation currents were not reduced to half value until the columns of air traversed amounted to between 12 and 15 cms., and even with the salts at a distance of 40 cms. from the chamber the ionizing currents were still approximately 15 per cent. of their highest values.

From the form of the curves it is evident that the radiations from the different potassium salts were not identical in their composition. The absorption curves for the sulphate and the chloride were very similar, but that for the cyanide was markedly different, and indicated by its shape that the rays from this salt, besides being heterogeneous in character, contained a predominating proportion of the more penetrating types.

It is of interest to note, too, that the absorption curves in fig. 6 show no irregularities in their initial portions, such as one would have expected if the radiations had consisted, amongst others, of a type possessing the characteristics of the α radiations from the known radioactive elements.

These results, it will be seen, are in accordance with Campbell and Wood's observations, and confirm the conclusions reached by them that the radioactivity exhibited by the potassium salts possesses the characteristics of either a β or an easily absorbed γ radiation, rather than those of an α type.

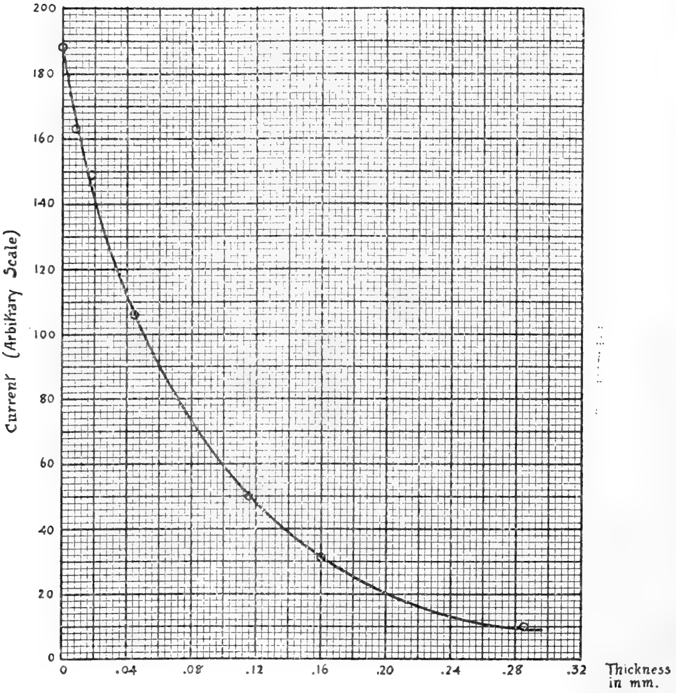
In a second series of measurements on the absorption of the potassium rays, the tray was filled with a quantity of potassium sulphate and then placed in the ionizing chamber, resting on the bottom. The salt was covered successively with an increasing number of sheets of tinfoil, and the saturation current measured for each set of the absorbing sheets. The foil used was 0·0089 mm. in thickness. The values of the currents corresponding to the different thicknesses of tinfoil are given in Table IX., and the manner in

Table IX.

Thickness of tinfoil. (cm.)	Saturation current (Arbitrary scale).
0·00000	188
·00089	163
·00178	149
·00446	106
·01157	50
·01607	31
·02839	10

which the value of the currents decreased is indicated by the curve in fig. 7. In arriving at the numbers recorded in Table IX. corrections were made from a preliminary set of observations for the activity of the tinfoil sheets which were found to emit an extremely feeble though measurable radiation. From the values given in Table IX. it will be seen that it was necessary to cover the salt with foil representing a total thickness of 0·6 mm. before the radiation from the salt was reduced to one-half its original intensity.

Fig. 7.



The mean values of the absorption constant λ for the different thicknesses were deduced from the formula

$$I = I_0 e^{-\lambda d},$$

where I_0 was the ionization current obtained with the unscreened salt, and I the current when *d* centimetres was the thickness of the tinfoil traversed. The deduced values of λ are given in Table X., and as will be seen these show a gradual decrease as the number of sheets of tinfoil used for a screen was increased.

TABLE X.

Absorption by Tinfoil.

Thickness of tinfoil (cm.).	$\frac{I}{I_0}$.	λ.
0·00089	·867	160
·00178	·793	130
·00446	·563	124
·01157	·265	115
·01607	·165	112
·02839	·053	104

The values obtained by Rutherford* for the constant λ when studying the absorption of the β rays from uranium with screens of tinfoil was 96, and later the value found by Crowther† for the same constant under similar circumstances was 69·3. A comparison of these values and those given in Table IX. makes it evident that while the rays emitted by the potassium salts were very heterogeneous in character, they did not contain any types possessing greater penetrating power than the β rays emitted by uranium salts. This result, too, is in keeping with what Campbell and Wood found in their investigations on the absorption of these potassium rays.

VII. *Activity of Potassium Salts and Secondary Radiations.*

A set of measurements was made with the object of ascertaining whether the radiation emitted by the potassium salts, which from its characteristics evidently consisted of β rays, was due to some property inherent in the salts, or whether it was due to a secondary radiation, of exceptionally high intensity, excited in the salt by the penetrating radiation which is known to exist at the surface of the earth.

A cylinder of lead some 60 cms. high and 25 cms. in diameter was prepared, and the natural conductivity of the air in this cylinder determined. A layer of potassium sulphate was then placed in a tray on the bottom of the cylinder, and when the conductivity of the air was again measured it was found to be approximately twice as high as it was before the salt was introduced.

From this it was evident that the radiation from the salt

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* Rutherford, 'Radioactivity,' 2nd edition, p. 137.

† Phil. Mag. Oct. 1906, p. 379.

contributed to the conductivity practically as much as the combined action of the earth's penetrating radiation and that emitted by the walls of the cylinder. If then the activity of the salt consisted solely of a secondary radiation one should expect, with a penetrating radiation gradually increasing in intensity, to obtain proportionately greater effects when the salt was in the cylinder than when it was removed from it.

In order to realize these conditions, a few milligrams of radium bromide sealed in a glass tube were enclosed in a heavy block of lead, and this was placed at a number of different distances from the cylinder and the conductivity of the air in the chamber ascertained, with the radium in each position. The observations were made first with the salt in the cylinder and then repeated for each position of the radium after the salt had been removed.

The results of these measurements are given in Table XI.,

TABLE XI.

Position of radium bromide.	Saturation current. (Arbitrary scale) Salt in cylinder.	Saturation current. (Arbitrary scale) Salt not in cylinder.
First	6053	6272
Second	2568	2641
Third.....	907	945
Fourth	271	273
Fifth	209	227

and from the numbers given in the table it will be seen that although the ionization currents were increased over thirty-fold, the ionization, and consequently the secondary radiation produced by the gamma rays from the radium, was invariably less when the salt was in the cylinder than before the salt was introduced.

Inasmuch as the ordinary or spontaneous ionization in the cylinder was found to be increased approximately twofold by the introduction of the salt, it is clear, in the light of the numbers given above, that this increase in the conductivity was due to a primary activity possessed by the salt, and not due to a secondary activity imparted to it by the influence of external radiations.

VIII. *Miscellaneous Experiments.*

With a view to ascertaining whether the activity of potassium salts arose from the presence in the salts of traces of any of the active elements, radium, thorium, or actinium, an attempt was made to drive off any emanation which they might contain by raising the salts to moderate temperatures. Although a number of the salts was treated in this way, with none of them, however, was the slightest indication obtained of a loss of activity such as should accompany the expulsion of radioactive gases.

Although these experiments made it probable that the activity was not due to the presence of traces of the elements radium, thorium, and actinium, or of their immediate products, in the salts, it was still possible that the activity might be due to the presence in minute quantities of uranium or of one of the active products of slow decay of radium. With the object of testing this surmise a sample of potassium sulphate which had been found to exhibit a comparatively high activity was heated to a little over 1000° C., and maintained at that temperature for a considerable time.

After the salt had been subjected to this treatment it was again examined, but was found to possess exactly the same activity as before being heated.

Similar attempts were made to reduce the activities of samples of potassium chloride and potassium cyanide, but in none of these tests was any reduction of activity obtained as a result of the heating.

To test still further the possibility of driving off by volatilization any active impurities which might be present, a quantity of active potassium sulphate, contained in a graphite crucible, which on examination showed no sign of activity, was placed in a coke furnace, first melted and then heated as highly as possible for a time. During this heating the sulphate became partially converted into the sulphides of potassium. After cooling, the mixture, which was ground to a fine powder and tested for radioactivity in the manner indicated above, was found to possess the same activity as before the treatment.

As the melting-point of potassium sulphate is approximately 1060° C., and inasmuch as the temperature of the salt during this experiment was raised very much beyond this point, it is clear that a temperature was reached considerably above the points of volatilization of the radium products of slow decay, and it follows therefore, from the absence of any loss of activity from the heating, that none of these active products were present in the salt, and that the source of its activity must be sought for elsewhere.

The only remaining known active product whose presence in the salt could account for its activity appeared to be uranium X, and although it was not clear how such a product could become mixed with the salts of potassium, attempts were made to separate it out by recrystallization, by precipitation with ammonium carbonate, and also by treating solutions of the salts with ether after the manner of Meyer and Schweidler*. By none of these processes, however, was it found possible to effect to a measurable degree the separation of any active product.

Attempts were also made with some of the salts to separate out by electrolysis active impurities which might be present, but it was again found impossible to bring about any separation of the active constituents in this way.

XI. *Summary of Results.*

1. It has been shown that the activity of uniform layers of active potassium salts was directly proportional to the area of the salt exposed.
2. With uniform layers of a number of potassium salts the activity was found to increase with the thickness of the layer, and maximum activities were obtained with all the salts examined with layers of the salts from 2 to 3 mm. in thickness.
3. Wide variations were found in the activities of different potassium salts, and of potassium salts of the same composition obtained from different sources, and ordinarily sold as chemically pure. In particular, different samples of potassium cyanide were found to vary widely in their potassium content, but the activities of the different samples were found to be approximately proportional to the amount of potassium present.
4. The rays from the potassium salts, which were found to be heterogeneous and to possess considerable penetrating power, exhibited characteristics similar to those of the β radiation emitted by uranium X. The penetrating power of the latter, however, is somewhat greater than that possessed by the potassium rays.
5. Experiments have been described which go to show that the activity of potassium salts is not due to the excitation of a secondary radiation in the salts by the

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* Meyer and Schweidler, *Wien. Ber.* 113, July 1904.

action of penetrating rays coming from external sources.

6. By various tests it was found impossible to trace the activity of potassium salts to the existence in them of minute quantities of any of the known radioactive elements or their active products.
7. Of all the elements in the alkali group, potassium alone has been found to exhibit marked radioactivity. Both sodium and all of its salts were found to be quite inactive, and although a sample of rubidium alum exhibited an activity which was extremely small, and a specimen of cæsium chloride one which was only just measurable, sufficient evidence has not been adduced to support exclusively the view that the activities observed were due to a physical property of the metallic constituents of these salts.

In conclusion, we wish to express our very great indebtedness to Prof. Lang and to Prof. Lash Miller, as well as to other members of the staff in the Department of Chemistry, for their kindness in placing at our disposal a number of the specimens of the salts examined.

Physical Laboratory, University of Toronto,
August 5, 1908.

XXXII. *Note on an Improvement in the Method of Determining Visibility Curves.* *By* C. S. Wright, *B.A.*, 1851 *Exhibition Scholar*, 1908, *University of Toronto* *.

One of the chief objects of Michelson in designing the interferometer which bears his name, was to analyse a source of light and determine if possible the distribution of intensity in that source. This is arrived at by estimating the visibility of the fringes formed by the interference of the two beams of light in the interferometer for various differences in path of the two rays.

The method of observation consists simply in moving back one interferometer plate till the difference in path Δ between the two interfering beams is such as to give a visibility of one half the maximum—the latter being obtained for $\Delta=0$. The half-width of the spectral line used as the source of illumination is then given by $\frac{0\cdot22\,\lambda^2}{\Delta}$.

While determining the visibility curves for the spectral lines of some of the elements, it occurred to the writer that

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* Communicated by Prof. J. C. McLennan.

if some standard could be used giving fringes of a known visibility and in the same position as those due to the interferometer, the method of determining the half-width would reduce to a very simple photometric determination.

As the standard a mica plate was found very convenient, which was placed in the path of the light entering the interferometer, and inclined at such an angle as to give straight-line fringes perpendicular to those given by the interferometer and in approximately the same focal plane. A simple adjustment of the angle of the mica plate was all that was necessary to alter the width of the mica fringes or the angle of intersection of the two sets, so as to make them similar in every respect.

It was found in practice that when the fringes formed a system of squares the points of equal intensity could be determined with considerable exactitude.

For absolute measurements of the half-width of the spectral line this standard would require to give fringes of a visibility one half the maximum. But if comparative measurements only were required, such as the change in width of the spectral line brought about by different conditions of temperature, pressure, &c., operating on the same, this method would find a very practical application. It should therefore be of special service in following such modifications in the constitution of radiating atoms as are brought into evidence by changes in their spectral lines.

Physical Laboratory, University of Toronto,
May 1, 1908.

XXXIII. *Researches upon Osmosis and Osmotic Pressure.* *By* L. VEGARD, *Cand. real.* (*Research Student at the Cavendish Laboratory, Cambridge*).

[Plate IX.]

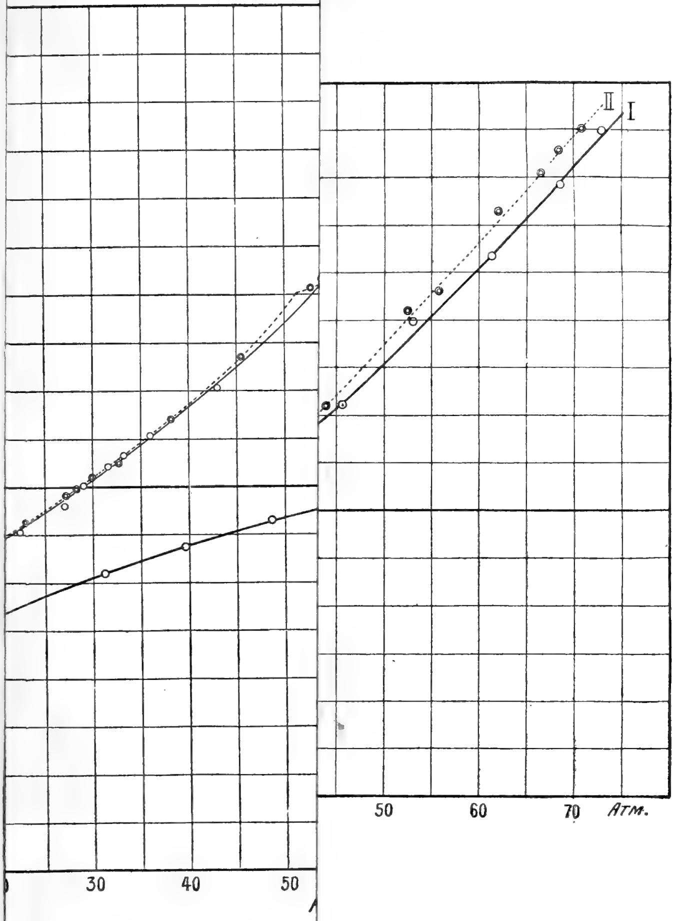
[Continued from p. 271.]

§ 4.

Measurements of Osmotic Properties of Cane-Sugar Solutions.

11. THE mode of operation in the experiments was as follows :—

Before each trial the osmometer was cleaned with distilled water and dried by filter-paper. The cell was filled with distilled water and put on the tap by the rubber tubing, and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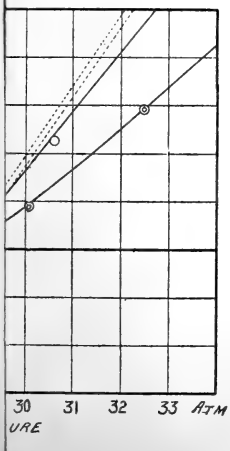
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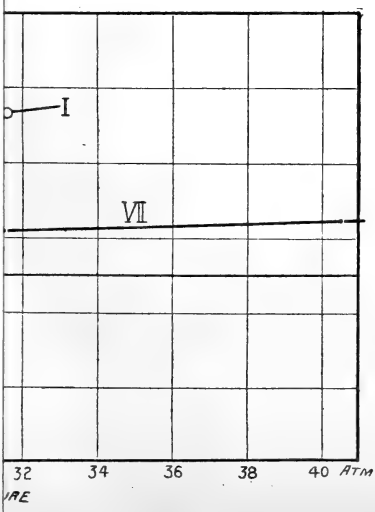
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Fig. 7.

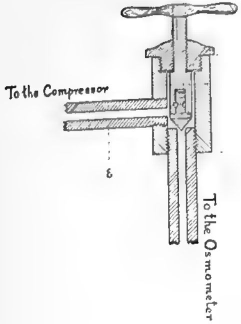


Fig. 8.

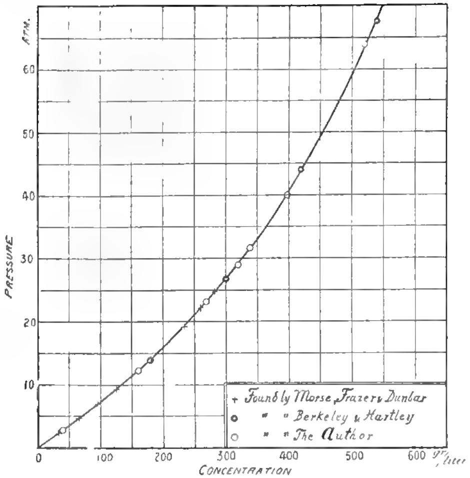


Fig. 11.

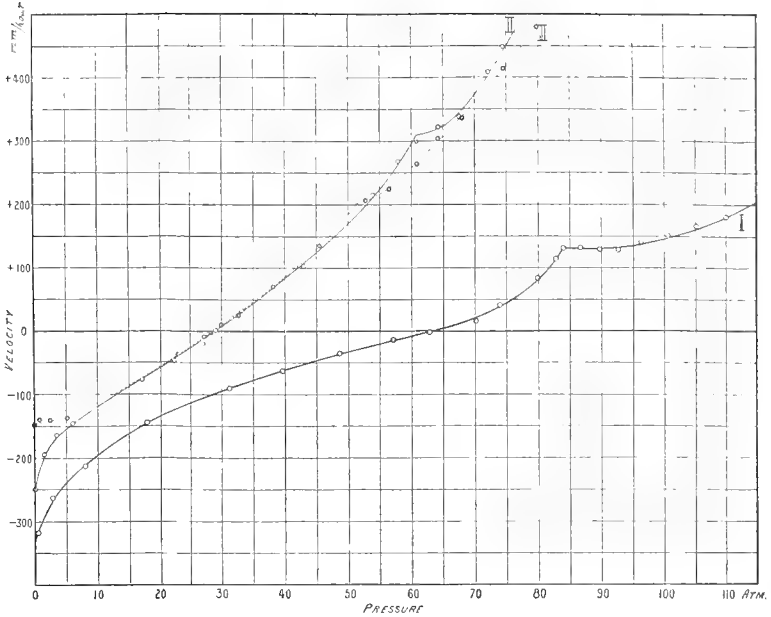


Fig. 12.

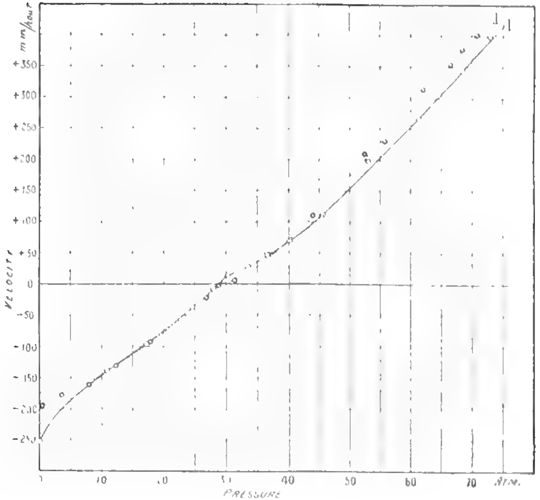


Fig. 9.

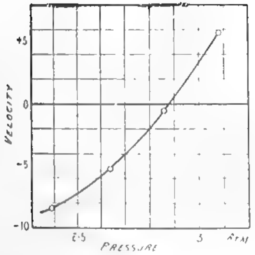


Fig. 10.

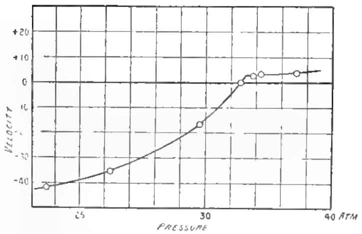


Fig. 13.

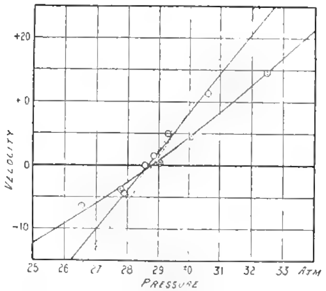


Fig. 14.

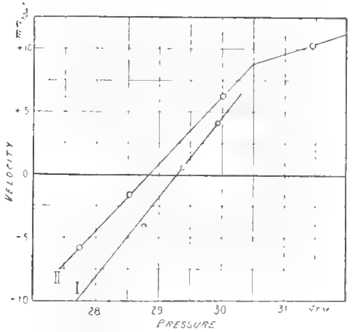
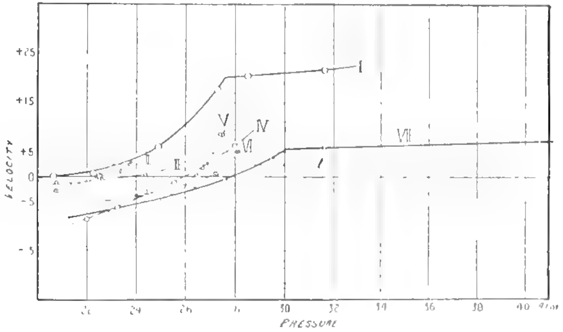


Fig. 15.



care was taken that water filled the capillary, and the rubber tubing on the top of it was filled with distilled water.

Then the vessel A containing the solution is screwed on to the disk B.

As to the putting up of the cell, I have found it best first to put the rubber tubing on the cell and bend the upper end of it back on the cell. The fixing of the cell then only takes a few seconds, and the whole apparatus can be put up in about 10 minutes.

In the measurements it was necessary to keep a nearly constant temperature. This was obtained by putting the osmometer into a stone jar, and this again into a larger one. The two vessels were either filled with water that had nearly the mean temperature of the room or filled with ice- or snow-water.

A similar arrangement was used for the manometer, only that the vessels were glass cylinders so as to be able to read the mercury level without taking the manometer out of the thermostat, and here I always let the water take the temperature of the room.

Before taking down the apparatus it was well dried. The solution was tested in the way described. When the cup A is taken down, the rest of the osmometer is washed out with water and everything except the membrane itself is dried. This is necessary in order to be sure that no sugar should come into the cell when it was taken down. The cell is emptied by a pipette and the water analysed.

The measurements are made in two different ways. In the first method, the capillary that leads to the compressor was closed by sealing-wax and the pressure was effected by the osmotic action itself.

In the second method, the pressure was raised by means of the compressor to the height desired.

Measurements by the First Method.

12. The apparatus being put up was left to itself at constant temperature, and the mercury column examined until maximum of pressure. Then the rubber tubing on the top of the capillary is taken off and the water-level examined for some hours.

EXPERIMENT 1.

Apparatus put up Oct. 27, 1907.
Resistance of the membrane 290,000 ohms at 3° C.
Concentration of original solution: 170·6 gr./l. at 16° C.

Observations 1*a*.

Date.	t_o.	t_m.	a.
h m			
Oct. 28, 8 0 P.M.	12·6	......	51·58 cm.
,, 29,	12·8	......	21·12 ,,
,, 30, 2 30 ,,	12·60	13·12	10·40 ,,
,, 30, 5 45 ,,	12·65	13·04	10·39 ,,
,, 31, 5 40 ,,	12·10	12·18	10·13 ,,
Nov. 1, 5 15 ,,	11·55	11·50	10·048 ,,
,, 2, 3 25 ,,	10·16	10·38	10·076 ,,
,, 3, 5 10 ,,	9·25	9·80	10·000 ,,

The temperature was lowered to 0° and another equilibrium examined.

Observations 1*b*.

Date.	t_o.	t_m.	a.
h m			
Nov. 4, 3 30 P.M.	0·0	9·80	12·75 cm.
,, 6, 4 55 ,,	,,	9·96	10·377 ,,
,, 7, 3 0 ,,	,,	9·90	10·303 ,,
,, 8, 9 30 A.M.	,,	9·77	10·278 ,,
,, 8, 2 15 P.M.	,,	9·84	10·268 ,,
,, 9, 10 30 A.M.	,,	9·94	10·226 ,,

t_o=temp. in osmometer. t_m=temp. in manometer.
a=reading of manometer.

The solution from the osmometer was tested with Fehling's solution, but no measurable inversion was found. The solution kept clear after heating for some time to 100°, but after some hours a very faint precipitate was observed on the bottom of the glass. The same experiment carried out with a fresh solution of cane-sugar gave the same result, so it should not be due to inversion, but even if it were it was too small to be measured.

The testing of the solution with polarized light gave the following result:—

Tube.	a_0.	a.
Short......	22° 39′	21° 41′
Long	34° 7′	32° 45′

The water in the cell being insufficient for filling the tube had to be diluted.

6·5 cm.^{3} water from the cell + 15 cm.^{3} water gave an angle of polarization of 10′.

As 1 mm.^{3} corresponds to 5 mm. in the capillary we get

$l_\pi = 2{\cdot}5$ mm. per hour ; and
$g_t = 2{\cdot}0$ gr./l. = conc. of water in exp. 1*a*.
$g_3 = 3{\cdot}8$ „ = „ „ 1*b*.

We have no observations for the velocity of osmotic flow for this experiment; but, as will be seen later, we have observations for the same cell for other concentrations. From these we get

q.	$\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}$.
3·95 atm.	21
32·83 „	16

If we take the mean value we get

$$\Delta\pi = 0{\cdot}13 \text{ atm.}$$

EXPERIMENT 2.

Apparatus put up Nov. 11.
Resistance of the membrane 400,000 ohms at 1°·6 C.
G = 302·8 gr./l. at 11°·8 C.

Date.	t_0.	t_m.	a.
h m			
Nov. 21, 8 15 P.M.	10·05	10·55	8·3 cm.
„ 22, 11 10 A.M.	9·75	10·20	6·25 „
„ 22, 6 45 P.M.	9·82	10·20	6·107 „
„ 23, 2 15 „	9·88	10·39	5·667 „
„ 23, 6 30 „	9·90	10·37	5·657 „
„ 24, 10 50 A.M.	9·45	9·70	5·660 „
„ 24, 6 0 P.M.	9·25	9·50	5·645 „

The considerable time required for the osmosis to reach the maximum pressure is due to the fact that in putting up the apparatus some air was left in the osmometer, and the space occupied by the air had first to be filled before the pressure could increase considerably. When first attention is directed to this point it is, however, easy to prevent any air-bubbles being left in the osmometer.

Unfortunately I had forgotten to fill the rubber tubing on the top of the capillary with water, with the result that the water in the cell diminished, and on taking down the cell only about one drop of water was left on the bottom of the cell. Notwithstanding this the apparatus had kept a constant pressure for nearly three days. And, as will be seen, this pressure must be almost as near to the ideal equilibrium pressure as it is possible by these experiments to get it.

This trial may serve as a proof for the good qualities of the membrane. For the least leak of solution would have been sufficient to give the small quantity of water soaked by the inside of the cell a remarkable concentration. And, as a matter of fact, the analysis of the water that had been allowed for some time to soak the inside of the cell gave no detectable rotation.

The osmotic flow had caused a considerable change in the concentration of the solution. The result of analysis is as follows :—

$$a_0 = 40° 15'$$
$$a = 35° 47'.$$

Testing with Fehling's solution gave no inversion.

Experiment 3.

Apparatus put up Nov. 29, 10 P.M.
Resistance of the membrane 290,000 at 0°·9 C.
G=403·48 gr./l. at 11°·2 C.

Observations.

Date.	t_o.	t_m.	a.
h m			
Dec. 1, 11 0 A.M.	6·88	7·15	4·10 cm.
„ 1, 6 0 P.M.	6·92	7·30	3·658 „
„ 1, 11 0 „	6·93	7·31	3·525 „
„ 2, 11 0 „	6·82	7·14	3·400 „
„ 2, 2 30 „	6·87	7·27	3·370 „
„ 2, 5 0 „	6·96	7·39	3·352 „
„ 3, 10 0 A.M.	7·10	7·49	3·355 „

$$a_0 = 53° 25'$$
$$a = 52° 31'.$$

The water in the cell gave no detectable rotation.

The results of these measurements are given in the following table :—

Exp.	a_m.	v.	T_m.	$-r$.	q.	π_0'.	C_{15}.	t_0.
1*a* ...	10·041	1·618	283·6	0·0060	13·68	12·48	161·7	10·3
1*b* ...	10·247	1·653	282·9	0·0060	13·36	12·15	159·9	0
2......	5·645	0·8958	282·5	0·0097	24·55	23·17	268·9	9·25
3......	3·367	0·5261	280·4	0·0149	41·26	39·85	396·2	7·0

a_m=manometer reading corresponding to apparent equilibrium.
C_{15}=concentration corresponding to 15° C.
T_m=absolute temperature of the air in the manometer.

Experiments by the Second Method.

13. In these experiments the pressure, by means of the compressor, was given a certain value and the corresponding velocity λ' was observed. The reversion pressure was determined by measuring velocities on both sides of the equilibrium point. As a liquid for the compressor I used the same solution as used in the osmometer.

On account of the osmotic flow or other causes the pressure will not keep quite constant, and as it is impossible to get the cell arrangement quite stable the change of pressure will call forth a small variation of the water-level in the capillary.

In order to find the velocity corresponding to a constant pressure we can employ two different methods:—

(1) By means of the compressor we can on an average keep a constant pressure, which can be done by keeping the mercury column on an average upon a certain mark. We can always here arrange matters so that the position of the water-level at the beginning and end is read by the same pressure. This method wants no corrections, and it is especially to be recommended for measurements far from the equilibrium point.

(2) Near to the reversion point it will be better to use another method, as the variation here is generally very small. The positions of the mercury column and water-level are observed at the beginning and end of a certain time.

Assume that the readings of mercury column are a_1 and $a_1+\Delta a_1$ mm.

Assume that the readings of water-level are b_1 and b_2 mm.

Then we have that the pressure corresponding to a reading

$$a_1+\frac{\Delta a_1}{2} \text{ corresponds to a velocity } \frac{b_2-b_1+\epsilon\Delta a_1}{\tau}.$$

τ is the time and ϵ is the change of water-level for the change of 1 mm. of the mercury column, and this quantity is easily found by observing the change of the water-level for a certain change of the mercury column.

Experiment 4.

Apparatus put up Dec. 17.
Resistance of the membrane 360,000 ohms at 2°·5 C.
G=340 gr./l. at 8°·7 C.

Date.	Time.	t_o.	t_m.	Mean Reading.	π.	λ'.
	h m h m					
Dec. 17	4 40 to 7 5 P.M.	4·35	4·45	5·427 c.m.	23·63	−42·0 mm./hour.
,, 18	3 20 — 6 10 ,	4·27	4·50	4·921 ,,	26·25	−35·6 ,,
,, ,,	6 40 — 7 55 ,,	4·33	4·50	4·380 ,,	29·78	−16·8 ,
,, ,,	8 0 — 9 35 ,,	4·45	4·67	4·108 ,,	31·90	+ 2·8 ,,
,, ,,	9 48 — 11 40 ,,	4·57	4·90	4·071 ,,	32·18	+ 3·5 ,
,, 19	10 25 A.M. 3 0 ,,	4·40	4·60	4·558 ,,	28·54	−25·7 ,,
,, ,,	6 0 — 7 50 ,,	4·35	4·43	4·166 ,,	31·40	0·0 ,,
,, ,,	8 10 — 8 50 ,,	4·36	4·40	3·905 ,,	33·60	+ 3·6 ,,

$$\alpha_0 = 45^\circ\ 9'. \quad \alpha = 45^\circ\ 10'.$$

The analysis of water from the cell gave the following result :

5 cm.^{3} water from the cell +15 cm.^{3} water gave an angle of polarization of 4′. This gives

$$g = 1{\cdot}8 \text{ gr./l.}$$

$$\Delta\pi = 0{\cdot}17 \text{ atm.}$$

$$\underline{C_{15} = 337{\cdot}5 \text{ gr./l.}} \quad \underline{\pi_0' = 31{\cdot}57 \text{ atm.}}$$

Experiment 5.

Apparatus put up Jan. 6, 1908.
G=40·00 gr./l. at 12° C.

Observations.

Date.	Time.	t_o.	t_m.	Mean Reading.	π.	λ'.
	h m h m					
Jan. 8	11 45 A.M.—2 10 P.M.	0	10·4	39·89	2·39	−8·4 mm./hour.
,, ,,	2 20 P.M.—4 48 ,,	0	10·3	36·77	2·64	−5·2 ,,
,, ,,	6 0 ,, —8 0 ,,	0	12·3	34·79	2·86	−0·5 ,,
,, 9	12 5 ,, —2 15 ,,	0	8·8	32·50	3·08	+5·8 ,,

The analysis of solution gave no change in the concentration, and the water in the cell gave no rotation. Then we get:

$$\underline{\pi_0'=2{\cdot}88 \text{ atm.}} \quad \underline{\dot{C}_{15}=40{\cdot}0 \text{ gr./l.}}$$

14. The following measurements were carried out at the Cavendish Laboratory. The osmometer is as a whole the same as before. A new manometer had to be used, and in order to increase the accuracy for measuring high pressures the end of the manometer had a smaller diameter than the rest. In the end of the tube was a little column of mercury, so the enclosed air now could be measured between two mercury columns in a calibrated tube. The calibration was done in the same manner as earlier described.

Further, the glass tubes connecting the osmometer with the compressor and the manometer were replaced by two steel tubes. The tube to the compressor could be closed by means of screw-tap shown in Pl. IX. fig. 7. This was done to secure a safe tightening for very high pressures. The compressor being made of brass seemed to a very small extent to yield at high pressures, and thus give rise to a small leak between the pieces E and D (fig. 2, Pl. VIII.). When the passage between the osmometer and the compressor was open, the passage to the screw (α) could be closed by the inner cylinder pressing against a leather ring; thus the movement of the screw was restricted to about half a revolution. The conical tap (γ) that can turn in the cylinder (β) is made of very hard steel pressing against the softer metal of the steel tube. This screw-tap, made at the Cavendish Laboratory, has worked quite perfectly.

Besides a determination of the equilibrium pressures, these experiments have been especially directed to a closer investigation of the velocity curve λ' and at the same time some experiments have been made to determine the effect of temperature upon the pressure π_0'. The cell is the same as used in the experiments at Christiania.

Experiment I.

Velocities corresponding to a solution containing 520 gr. in the litre at 15° C. The apparatus was put up on the 5th of March. The observations were made March 6 and 7. The temperature in the osmometer was 11°·5 C. The velocity of osmotic flow was examined for different values of π, observing the change of water-level in a certain time. With somewhat large velocities the time for each pressure was about 10–15 minutes. Near the reversion-point the time used was longer—sometimes more than one hour.

The results are given in the following table. The observations will be given in the order in which they are observed.

Fig. 11. Curve I.			
March 5.		March 6.	
π.	λ'.	π.	λ'.
atm.	mm./hours.	atm.	mm./hours.
0·50	−318	73 89	+ 40
2·68	−263	79·91	+ 84
5·19	−234	82·69	+112
8·14	−213	83·95	+130
17·79	−144	86·58	+130
21·69	−114	89·80	+128
31·30	− 90	92·6	+127
39·72	− 63	96·4	+140
48·60	− 35·2	100·7	+149
57·18	− 14·2	105·2	+165
62·88	− 2·2	110·1	+172
70·28	+ 15·4	78·4	+ 72

The apparatus was taken down on March 7. The testing of solution gave no detectable change in rotation. It must be remembered that the apparatus during the nights had been placed under the reversion pressure. The water in the cell gave as the mean of a number of observations the polarization angle −1′, which means that no change can be detected. As the reversion pressure we get

$$\pi_0' = 63{\cdot}8 \text{ atm.}$$

Experiment II.

The solution contained 320 gr. cane-sugar in the litre at 14°·2. Resistance of the membrane 275,000 ohms at 1°·5.

The apparatus was put up in the morning on March 18. During the day velocities were measured corresponding to values of π from 0 to 75 atm.

The following day was devoted to the determination of the temperature effect. At first the turning point was determined at the temperature 11°·3 by measuring as accurately as possible the rate of flow near this point. Then the temperature was lowered to 0° by putting the apparatus into a vessel filled with ice crushed into small pieces and some water. To make sure that the osmometer had assumed this temperature, it was left to itself for about $1\frac{1}{2}$ hours before the observations began.

The next day the velocities were measured in the same manner as on the first day for values of π going from about 80 atm. to 0.

During the nights the osmometer was placed under a pressure near to the equilibrium pressure.

The results are given in the following table and graphically represented by Pl. IX. fig. 11 (curves II. and III.) and fig. 13.

March 18. t_0=11°·4 C. Fig. 11, Curve II.		March 19. t_0=11°·3 C. Fig. 13, Curve I.		March 20. t_0=11°·6 C. Fig. 13, Curve III.	
π.	λ'.	π.	λ'	π.	λ'.
atm.	mm./hour.	atm.	mm./hour.	atm.	mm./hour.
0·05	−250	27·89	− 4·5	22·79	− 37·2
1·54	−194	30·63	+11·4	27·10	− 9·2
3·43	−163	29·27	+ 5·0	28·40	− 1·2
6·16	−146	28·53	+ 0·0	29·88	+ 10·4
11·22	−125	28·83	+ 1·5	32·77	+ 24·0
17·01	− 76·2			38·15	+ 70·0
22·40	− 47·7			28·70	− 0·6
26·95	− 20·4	t=0° C. Fig. 13, Curve II.		45·53	+135
29·09	+ 1·5			52·68	+208
31·60	+ 21·7			56·47	+224
33·23	+ 32·2			60·86	+265
36·00	+ 51·6	27·78	− 3·7	64·22	+303
41·33	+ 70·9	29·02	+ 0·1	68·01	+335
42·87	+103	30·40	+ 4·3	74·52	+413
50·95	+170	32·52	+14·5	79·66	+480
53·86	+216	36·18	+30·7	5·10	−136
57·89	+268	26·52	− 6·3	2·51	−140
60·88	+298			0·85	−141
64·24	+323			0·00	−148
68·11	+336				
72·26	+409				
74·53	+448				

There was no detectable change in the angle of rotation. The water in the cell was analysed very carefully. The mean of a number of readings gave an angle of 0′·1.

Experiment III.

This experiment is a repetition of the preceding experiment. The same method and the same concentration were used. The resistance of the cell, however, is greater, being now 360,000 ohms at 1°·2. The analysis after the experiment gave neither leak nor change in concentration.

The results are given in the following table :—

March 30. t_0=12°·3 C. Fig. 12, Curve I.		March 31. t_0=11°·8 C. Fig. 14, Curve I.		April 1. t_0=13°·5. Fig. 12, Curve II.	
π.	λ'.	π.	λ'.	π.	λ.
atm.	mm./hour.	atm.	mm./hour.	atm.	mm./hour.
0·00	253	28·77	−3·9	52·44	+210
10·86	−139	29·94	+4·2	70·80	+400
17·28	− 79	29·38	+0·6	68·50	+377
24·62	− 39	27·91	−8·1	66·40	+354
27·93	− 8·0			61·50	+315
30·30	+ 11·2			55·80	+230
33·57	+ 25·1	t=0.		43·80	+107
36·52	+ 45	Fig. 14, Curve II.		31·56	+ 3·6
40·10	+ 69			28·80	− 5·0
45·60	+110			26·89	− 23·5
53·10	+198	28·52	− 1·5	22·35	− 72·0
61·40	+268	30·02	+ 6·3	17·88	− 92
68·60	+341	31·46	+10·3	12·43	−131
72·80	+380	27·75	− 5·7	7·98	−160
				3·60	−177
				0·55	−198

EXPERIMENT IV.

We shall further describe one experiment that, as far as the determination of the equilibrium pressure is concerned, must be regarded as unsuccessful, but still it will be of interest for the study of the properties of the membrane. It is also necessary to give the result for the sake of completeness, as then all the measurements of osmotic pressure done are given in the paper.

This was the first experiment done at Cambridge, and it seems as if the transport of the cell has caused some diminution of its good qualities. The electric resistance had gone down to 20,000 ohms at 2° C. ; but, as we have seen, it soon recovered.

The solution contained 320 gr. in the litre at 15° C. The apparatus was put up on Feb. 22, and the velocities near the reversion-point examined during the following days. The apparatus was allowed to stand under the reversion-pressure during the nights. As it was my intention to look for a temperature effect the temperature in some of the measurements was lowered to 0°.

The observations, however, gave much lower equilibrium pressure than anticipated, and at the same time the observations showed a considerable variation in the apparent equilibrium point. The equilibrium pressure had increased with time.

The apparatus was taken down on March 3. The solution was somewhat clouded, so the determination of the polarization angle was somewhat less accurate. But the change in rotation was less than 10′.

The increase in pressure cannot be explained by inversion, but the cell must have the power to some extent to work itself up.

The analysis of water gave a comparatively great leak.

6·3 cm.^{3} water from the cell +18 cm.^{3} distilled water gave a rotation angle of +13′. The same tube gave for the solution used an angle of 42° 3′. This corresponds to an average velocity of 2·5 mm./hour.

The results of the measurements are given in the tables below and graphically represented by fig. 15 (Pl. IX.).

Feb. 22.
$t_0=14°·0$.
Curve I.

π.	λ′.
atm.	mm./hour.
31·60	+21·5
28·55	+20·3
27·29	+17·6
24·90	+ 6·0
22·28	+ 0·5
20·65	0·0

Feb. 24.
$t_0=12°·4$.
Curve II.

π.	λ′.
23·84	+2·7
22·50	−0·1
23·35	+0·9
21·42	−3·3

Feb. 25.
$t_0=0°$.
Curve III.

π.	λ′.
atm.	mm./hour.
20·78	−1·3
21·32	−1·5
22·65	−0·25
24·42	+0·12

Feb. 26.
$t_0=12°·5$.
Curve IV.

π.	λ′.
28·02	+6·2
22·00	−7·5
23·26	−6·3
24·39	−2·65
25·57	−1·4

Feb. 27.
$t_0=12°·75$.
Curve V.

π.	λ′.
atm.	mm./hour.
27·53	+8·3
25·92	−1·9
26·15	−0·7
26·45	+0·4
26·75	+3·3
27·06	+6·9
27·40	+8·3

Feb. 28.
$t_0=0$.
Curve VI.

π.	λ′.
atm.	mm./hour.
24·00	−3·7
25·31	−1·4
27·25	+0·5
28·12	+4·8

March 2.
$t_0=0$.
Curve VII.

π.	λ′.
40·61	+6·8
29·55	+3·5
31·51	+6·6
27·67	−0·5
26·38	−2·2
22·91	−7·3

§ 5. *Results.*

15. The equilibrium pressures π_0' for cane-sugar are given n the following table:—

Experiment.	π_0'.	C_{15}.	t_0.
	atm.	gr./litre.	centigrade.
5.	2·88	40·0	0·0
1 *b*..........	12·15	159·9	0·0
2.	23·17	268·9	9·25
II.	28·80	319·9	0·0
III.	28·85	320·0	0·0
4.	31·57	337·5	4·4
3.	39·85	396·2	7·0
I.	63·80	520·0	11·5
1 *b*..........	12·48	161·7	10·3
II.	28·67	319·9	11·3
III.	29·29	320·0	11·8

In the table the pressures are given at the temperature at which the measurements were made. This is done simply because we have no experimental determination of the temperature effect for the greatest concentrations. Further, we shall see that the temperature effect upon the pressure π_0' is smaller than the effect upon π_0.

The curve fig. 8 represents the relation between π_0' and C. The points given are directly taken from the first part of the table. On the figure are also marked some of the points determined by Berkeley and Hartley and Moore and Frazer. As to the points determined by the latter, I have taken those determined at the lowest temperature as giving comparatively the highest pressure. We see that the determinations are in very good agreement. The pressure π_0' appears to be very nearly a single-valued function of the concentration.

All of these measurements correspond to a very small leak, often so small as not to be detectable by the method used. And as we have strong reason to believe that π_0' is continuous with regard to the leaks the values found should then very nearly give the osmotic pressure π_0. The study of the leak would require a more accurate testing of the water in the cell. Only in experiment 1 is there a somewhat considerable leak, but still the pressure π_0' gives a value corresponding to a very small leak. This is easily explained from the theory, for it would only mean that the leak in this case is very nearly a solution leak that has very little power to influence the osmotic activity.

The Velocity Curves.

16. The dependence of the velocities λ' upon the pressure π is graphically represented by a series of curves, figs. 9, 10, 11, 12, 13, 14 (Pl. IX.).

We see that in all cases the observed velocities determine a well-defined curve.

In figs. 9, 10, 13, and 14 it is only velocities near to the reversion point that are measured.

Figs. 11 and 12, however, corresponding to the experiments I., II., III., give the curves from $\pi=0$ to a pressure far beyond the equilibrium pressure, and we shall first consider these more complete curves.

17. *Curve corresponding to experiment* I. (fig. 11, curve I.). —When we start from the point $\pi=0$ the velocities diminish rapidly and $\frac{d\lambda'}{d\pi}$ decreases, then we have an inflexion point $\frac{d\lambda'}{d\pi}$ having a minimum value. The inflexion point lies in this case very near to the reversion point. After passing these points the quantity $\frac{d\lambda'}{d\pi}$ begins to increase and continues to do so until we reach a certain point corresponding to the pressure $\pi=83{\cdot}9$ atm. and a velocity $\lambda'=130$ mm./hour.

Here we have a sudden fall in the value of $\frac{d\lambda'}{d\pi}$. The turning of the curve is so sharply defined, that we must regard it as a point of discontinuity in the function $\frac{d\lambda'}{d\pi}$. Before this point $\frac{d\lambda'}{d\pi}$ has the value 19·5 expressed in our units; on the other side of the point $\frac{d\lambda'}{d\pi}$ is nearly equal to zero. This point we shall call the *characteristic point* of the velocity curve. From this point the curve goes nearly horizontal, the velocities being nearly constant.

The measured velocities even show some decrease; but this is not greater than can be ascribed to faults in the observations. First at a pressure of about 95 atm. we shall notice a remarkable increase of the velocity, and by increasing pressure the curve bends upwards.

18. *Curves corresponding to a concentration* 320 gr./l.

Experiment II. represented by fig. 11, curves II. & III.
" III. " fig. 12.

The temperature is about the same for all four curves.

The two curves fig. 11 (II.) and fig. 12 (I.) correspond to the state of the systems just after the apparatus had been put up, and the observations commenced at the lowest pressure. It is the same mode of operation as used in experiment I. The course of the curves is also quite similar. We have an inflexion point in the interval $0<\pi<\pi'$, and on the other side of the reversion point we have a point of discontinuity in the function $\frac{d\lambda'}{d\pi}$ with a fall in the value by increasing pressure. After passing this point the curves bend upwards, and now much more rapidly than in the first case.

The position of the characteristic point for the two curves is, however, very different. For the curves fig. 11 it has the coordinates $\pi=61$, $\lambda'=312$. Or we get it first for a pressure more than twice the equilibrium pressure. For the curve fig. 12 the characteristic point lies close up to the reversion point, the coordinates being $\pi=30{\cdot}3$, $\lambda'=13{\cdot}5$.

We also notice that in the interval $0<\pi<\pi'$ the absolute value of the velocities is greater in experiment III.

The two other curves, drawn as dotted lines, were observed after the apparatus had been placed under pressure for about two days. We see that in both cases the curves have undergone a considerable change.

The change can be characterized thus:—

(1) The characteristic point has moved towards the reversion point.

(2) The velocities near the pressure $\pi=0$ have considerably diminished.

By this motion of the characteristic point towards the reversion point the latter is in both cases very little affected. In experiment III. we have a small increase in the reversion pressure during the first twenty-four hours, but it keeps later nearly constant.

Let us imagine that we place one of the two plates upon the other so that the π axis and zero points coincide. Then we should find that all the curves have a considerably different course, mainly due to the different position of the characteristic point. *In spite of this variation in the velocity curves we see that all of them very nearly cut the* π *axis in the same point.* This is the more remarkable as the curves show great differences quite up to the point of intersection. At all events the variations in the reversion point are very small in comparison to the variations of the curves close up to this point.

Curves observed in the Neighbourhood of the Reversion Point.

19. *The velocity curves for the experiments* 4 *and* 5. (Figs. 9 and 10.)

The curve fig. 9 shows a very well-defined characteristic point that lies close up to the reversion point.

In the experiment 5 no characteristic point is observed. From the bend of the curve we have reason to believe that it is not far off, as the sudden bending upwards is very characteristic of the approach to the point of discontinuity.

EXPERIMENT IV. (fig. 15).

The experiment is represented by a series of curves in the neighbourhood of the equilibrium point, and we notice a great variation from day to day. Each curve corresponds to a constant temperature and to observations taken in succession on the same day. The curves are marked with numbers in the same order as they were observed.

Only in the first and last curve the observations are extended so far as to give the characteristic point, which in this case is very well marked. It appears that also this time we have a motion of the characteristic point towards the reversion point; but in this case *the motion of the curve is also extended to the reversion point*, the change in the reversion point is of the same order as the change in the curve itself.

On the figure is also drawn the curve (l) representing the average velocity of leak.

If the leak had not altered during the experiment this line would cut the different curves in points corresponding to the pressure (π_0'). The curve VII. last observed would then give a pressure (π_0') of 28·8 atm., or about the same pressure as found at the same temperature in experiment III., where the membrane was very perfect and no leak was to be observed. At the beginning, however, the leak would have a great influence upon π_0'. This would mean that if the leak during the working up of the membrane had kept constant, it must have been changed from one which had a great power of influencing the pressure π_0' into a solution leak. Such a transformation, however, is very improbable, and we are led to the assumption that the increase in the pressure π_0' must be accompanied by a decrease in the leak.

Conclusions to be derived from the Study of the Velocity Curves.

20. The osmosis is in every case characterized by the osmotic velocity, This property forms the sum of effects of

a more or less complicated process going on in the membrane and its nearest surroundings; and it is the principal measurable property by which the osmosis is able to manifest itself. From the definition of the osmotic velocity (§ 3, equation 2 *a*) we see that when the leak is small the apparent velocity curve (λ') will give the characteristic feature of the λ curve.

As stated in equation 2 *b*, § 3, the velocity depends on the three quantities π, C, and T, and further upon a number of quantities characteristic of the membrane. If the quantities that are able to influence the osmotic velocity were defined quantities that could be given certain values, the function λ could be found by experiment by finding the influence of each property separately.

On account of the nature of the problem we are only able to master the quantities π, C, and T, while the others escape for the most part our control. To some extent, however, they can be altered by using more or less "perfect" membranes. And even if these quantities dependent on the membrane and mechanism of osmotic flow cannot be given the values desired, they will, as we have seen from the experiments, not keep constant. They will vary from one experiment to another, and even in one and the same experiment the velocity curve shows great changes; and the study of these variations must necessarily be of importance for the study of the osmosis by the system under consideration.

And upon the whole, if we wish to make clear the mechanism of osmosis, in other words to find the function ψ (§ 3 eq. 2 *b*), the study of the velocity must form a necessary part of this research. The possible explanation must first of all account for the properties of the velocity curves, and especially the study of the characteristic point and its motions must be of special importance, as giving a good test for the possible explanation.

The mode of proceeding for these studies will naturally be the following:—

(1) The velocity curve for each system must be determined for different concentrations and temperatures.

(2) The variations of the velocity curve due to the variations in the properties of the membrane must be examined for a number of concentrations and temperatures.

And we see that from this point of view it will be of great importance also to study the properties of the imperfect membranes as generally giving rise to the greatest variation.

As long as we have the same cell the changes in the velocity curves corresponding to the same temperature and concentration must be ascribed to a difference in the properties of the membrane. But if we have to use different cells, the question may arise how to find the change due to the membrane. It will in general be difficult to find the absolute value of the change of velocity due to the change of the membrane; but still we are able from the form of the curves to determine whether such changes have occurred.

Suppose we have at the same temperature and concentration measured the velocity curves for cells 1 and 2. Let the velocities corresponding to a pressure π be λ_1 and λ_2; then if we had membranes with constant qualities all over the surface, and if the two membranes had the same qualities, we should have

$$\frac{\lambda_1}{\lambda_2} \text{ independent of } \pi.$$

If then the quantity $\frac{\lambda_1}{\lambda_2}$ varies with π, this variation must be due to a difference in the properties of the membrane. Such a variation of the curves that always will make $\frac{\lambda_1}{\lambda_2}$ a function of the pressure we shall have *when the characteristic point corresponds to different pressures.*

In the experiments here made the same cell has been used, and then we can simply say:—The motion and different position of the characteristic point correspond to a variation in the properties of the membrane. The absolute distance between the characteristic points gives no measure of the change. It seems *a priori* probable that a certain distance corresponds to a greater change when the characteristic point is near to the reversion point than when it is far off. This is also confirmed by experiments. In experiment II. the characteristic point is very far from the reversion point, and we see that a comparatively great motion of the characteristic point has caused a very small variation in the reversion point.

In experiment III. the characteristic point is near to the reversion point, and now a comparatively small motion calls forth a remarkable change in the reversion point. Also in experiment IV., where the change of the reversion point is very great, the reversion point is near to the characteristic point.

The importance of investigations made after this method will be evident from the measurements already given. From the study of the velocity curves we come to the following conclusion for the system considered:—

(1) *The lowering of the reversion point is accompanied by an increase of the leak.*

(2) *As long as we have a comparatively great osmotic leak a motion in the characteristic point is accompanied by a motion in the reversion point of the same order. But when the leak diminishes the motion of the reversion point compared with the motion of the characteristic point will diminish, and with a very small leak (exp.* II., III.) *the reversion point will keep almost invariable for the considerable changes of the velocity curve.*

Then we see that by diminishing the leak we approach a point independent of the variable properties of the membrane. And as we have seen in § 3, this will give a strong support for the continuity of π_0' up to the point of perfect semipermeability.

The question whether the pressures measurable by our membranes will be able to give an approximate value of the osmotic pressure was the main point in a discussion in 'Nature' * during the year 1906, called forth by a paper of Professor Kahlenberg †. At the general discussion upon osmotic pressure that took place in a meeting of the Faraday Society last year, Professor Kahlenberg sums up his opinion by the following statement ‡:—

"All experimental evidence we have goes to demonstrate (1) that there is no such thing as a semipermeable membrane in the strict sense of the word, and (2) the more nearly a membrane is semipermeable in character in practice, the greater is the selective action; in other words, it is the pronounced selective action of the membrane which makes it approximately semipermeable. It is clear, therefore, that such a membrane as thermodynamic reasoning postulates can never be realized in practice, nor can we hope by experiment to produce even approximately such a membrane; for as we experimentally approximate toward fulfilling the first requirement, semipermeability, we do this at the sacrifice of the second requirement, passivity."

As to the first statement it is probably true; and it is the more so as a statement that only expresses that a certain process in nature does not follow a mathematical ideality will

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* Earl of Berkeley, 'Nature,' 1906, vol. lxxiv. p. 7; Earl of Berkeley & E. G. J. Hartley, vol. lxxiv. pp. 54, 245; W. E. D. Whetham, vol. lxxiv. pp. 54, 102, 295; Professor Henry Armstrong, vol. lxxiv. p. 79; Professor L. Kahlenberg, vol. lxxiv. pp. 19, 222; Norman R. Campbell, vol. lxxiv. p. 79.

† Professor L. Kahlenberg, Journ. of Ph. Chem. vol. x. pp. 144–209.

‡ Transactions of the Faraday Society, vol. iii. part 1, 1907.

generally be true. At all events, we shall never be able to prove that such a statement is false.

The second statement is identical with the denial of continuity of π_0' up to the point of no leak, or when the leak approaches zero the reversion pressure should approach the value

$$\mathrm{Lim}_{l=0}(\pi_0') = \pi_0 + a,$$

where a is a finite quantity so large as to make π_0' essentially different from π_0, and the cause of the quantity a he finds in the so-called selective action of the membrane.

It seems that such a point of discontinuity is such an unfrequent occurrence in nature, that it cannot be accepted without a positive proof. And as a matter of fact, we shall in most theoretical reasoning on physics be compelled to assume continuity up to the point of ideality. So, for instance, the proof of the second law of thermodynamics rests upon the assumption that the properties of cycles that can be actually carried out converge toward the properties derived from an ideal reversible cycle.

The same statement, however, is only built upon the fact that the pressures measured by imperfect membranes generally depend to a great extent upon the membrane used. But this fact gives no support for the view put forth by Professor Kahlenberg ; for, as we have seen in § 3, even if we assume continuity up to the point of no osmotic leak, we came to the conclusion *that the existence of a leak that is able to influence the osmotic activity would make the pressure* π_0' *a function of the properties of the membrane.*

We should have a positive support for the view of Kahlenberg if we were able to show that the measured equilibrium pressure would come out *greater* than the thermodynamic osmotic pressure.

In the case of ferrocyanide and cane-sugar, on the contrary, we have, as we have seen, a positive support for the assumption of continuity.

As seen from § 3, the correction for osmotic leaks would require an acquaintance with the mechanism of osmotic flow that we do not possess. But for the system considered we have

$$\pi_0 > \pi_0' > \pi'.$$

By experiment we only get a lower limit for the pressure π_0'. The best way of coming to a value near to π_0 would be to determine π_0' in each case as accurately as possible, and then the highest pressure would give the value nearest to the ideal pressure. And by the method described the pressure π_0' can be determined very exactly for pressures from 0 to over 100 atm. ; and the exactness will in general increase when the leak diminishes, as a smaller osmotic leak generally corresponds to a greater value of $\frac{d\lambda'}{d\pi}$.

In general, however, we shall not get a better value by taking the mean of several observations corresponding to different leaks. Only in the case where we had a series of values whose differences were less than the error in the determination of π_0' would it be natural to take the mean value.

The Temperature Effect.

21. The influence of temperature upon the reversion pressure has been examined in three experiments, I., II., III., which are described earlier. The pressure π_0' will generally depend upon the qualities of the membrane. If then the membrane and consequently π_0' undergo a change which is not a temperature effect, the experiment must be arranged so as to give a determination of this change. This can be obtained in the following manner.

The temperature is to be changed in one and the same experiment without taking down the cell and changing the solution. The time between the measurements by the two temperatures ought to be as short as possible. Further, the reversion pressure must be examined after going back to the original temperature. This mode of proceeding has only been entirely followed in the last two experiments.

In this manner we can reduce the temperature coefficient to a constant membrane, or we get the temperature effect π_0' as it actually exists at a certain moment.

It will be a special question to decide how far the determined temperature coefficient will give any value for the effect of temperature upon Osmotic Pressure.

By the temperature coefficient of π_0' we shall understand the quantity $\left(\frac{d\pi_0'}{dT'}\right)_C$, meaning the change in π_0' per degree when the concentration is kept constant.

When working between two temperatures we can only find the average temperature coefficient α_0'. Assume that by changing the temperature from 0 to t the pressure π_0' increases by a quantity $\Delta\pi_0'$, then

$$\alpha_0' = \frac{1}{t}\frac{\Delta\pi_0'}{\pi_0'} + \frac{d\pi_0'}{dC}\frac{C}{\pi_0'}\beta.$$

β is the average temperature coefficient of the solution between 0 and t. $\frac{d\pi_0'}{dC}$ can be found from the curve fig. 8. For small pressures we can put $\frac{d\pi}{dC}\frac{C}{\pi}=1$.

The observations corresponding to the experiments II. and III. are given in the curves figs. 13, 14. The curves marked I. correspond to the highest temperature. As we see the velocities measured determine very well-defined curves, so that the error in the determination of $\Delta\pi'$ will not exceed 0·02 atmosphere. The curves drawn as dotted lines correspond to the determination on the neighbouring days.

The determination gives the following result :—

Exp.	C.	t.	a_0'.
I.	161	10·3	0·00296
II.	320	11·3	0·0000
III.	320	11·8	0·0017

We see from II. and III. which correspond to the same concentration that the temperature coefficients for π_0' even for very good cells is a very variable quantity. Let us consider these two experiments more closely.

There can be no doubt that the membrane in experiment III. was more perfectly semipermeable than in experiment II. This is evident from the following facts :—

(1) The maximum electric resistance is greater in experiment III.

(2) The reversion pressure corresponding to the highest temperature is greater in experiment III.

(3) The velocities corresponding to $\pi<\pi_0'$ are greater in experiment III.

This indicates that the temperature coefficient will come out greater for a more perfect membrane. If this rule holds quite up to perfect semipermeability, we should get for the system considered :

$$\left(\frac{d\pi_0}{dT}\right)_C > \left(\frac{d\pi_0'}{dT}\right)_C. \quad \ldots\ldots \quad (8)$$

Further, we see from the curves that in both cases the quantity $\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}$ will be increased by increase of temperature.

In the case of small leaks we have the osmotic pressure determined by equation 6 *a*, § 3. By differentiating with regard to T and by putting

$$\left(\frac{\partial\psi}{\partial\pi}\right)_0=\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}=\delta,$$

we get

$$\frac{d\pi_0}{d\mathrm{T}}=\frac{d\pi_0'}{d\mathrm{T}}+\frac{1}{\delta}\left(\frac{d\Sigma}{d\mathrm{T}}-\frac{\Sigma}{\delta}\frac{d\delta}{d\mathrm{T}}\right). \quad . \quad . \quad . \quad (9)$$

Remembering that Σ, δ, and $\frac{d\delta}{d\mathrm{T}}$ are positive quantities, we get from (8) and (9) that $\frac{d\Sigma}{d\mathrm{T}}$ is positive. That is to say, that the quantities $\frac{\partial\psi}{\partial l_r}\,l_r$ increase with the temperature. The temperature will most likely to some extent affect both quantities, but at all events we must assume an increase in the leak. This follows from the behaviour of the membrane for electric currents. Firstly, we have seen that the membrane becomes weaker by increasing temperature; and secondly, we have seen that even if the membrane keep a constant mechanical structure, it *shows a great temperature effect* which is best explained by assuming that the permeability of the membrane for the ions is increased by temperature. And the increase of permeability for the ions must correspond to an increase in the leak of solute.

As long as we cannot determine the quantities Σ and $\frac{d\Sigma}{d\mathrm{T}}$, we cannot in general derive the temperature effect upon osmotic pressure from the measured quantity. Then we only get the relation (8). Just as by the determination of the absolute value of osmotic pressure, we find by direct measurement only a lower limit for the quantity $\left(\frac{d\pi}{d\mathrm{T}}\right)_{\mathrm{C}}$, and consequently the way of proceeding in the measurements will be similar. We shall have for a certain concentration to determine α_0' as exactly as possible in each case; then the highest value would give the value nearest to the temperature coefficient of the Osmotic Pressure.

By the method described the determination of α_0' can be done very accurately. The accuracy will mainly depend upon the exactness with which the velocity can be measured and upon the quantity $\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}$.

In general, we shall have the greatest accuracy for the most perfect membranes, and this is due to two circumstances: for the first the value of $\left(\frac{d\lambda'}{d\pi}\right)_{\pi'}$ will be greater for a better membrane, and for the second the reversion point will keep more constant.

From the measurements here done we have for the temperature coefficients between 0 and 11·5:

$$\text{For } C=161 \quad \left(\frac{d\pi_0}{dT}\right)_C > 0{\cdot}00296,$$

$$,, \quad C=320 \quad \left(\frac{d\pi}{dT}\right)_C > 0{\cdot}0017.$$

Thus the temperature effect upon π_0' is made up of two parts, (1) the temperature effect upon the permeability of the membrane, (2) the temperature effect upon osmotic pressure; and these two effects counteract each other.

I wish to thank Prof. O. E. Schiotz of Christiania for suggesting this work to me and for the interest he has taken in it. I should also like to thank Prof. J. J. Thomson for allowing me the privilege of continuing the work in the Cavendish Laboratory.

XXXIV. *On the Principle of Relativity. By* EDWIN BIDWELL WILSON, *Ph.D., Professor in Mathematics at the Massachusetts Institute of Technology* [*].

IN the present formative state of the theory of atomic electricity, when, in addition to the idealized mathematical electron which is the simple and frequently sufficient "point of beknottedness" in the æther, we have the Abraham electron spherical and rigid, the Lorentz-FitzGerald electron deformable under rectilinear motion into an oblate spheroid with constant equatorial diameter, and the Bucherer-Langevin electron deformable under rectilinear motion into an oblate spheroid of constant volume, it is necessary to pursue several methods of attacking the problems that arise in connexion with the theory; and of these methods the principle of relativity is among the most interesting and powerful, whether considered in its mathematical, physical, or philosophical import.

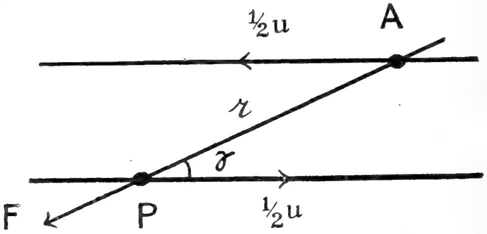
[*] **Communicated by the Author.**

This principle has been discussed by Lorentz *, by Poincaré † with reference to the theory of groups, by Einstein ‡, and recently in this Magazine by Cunningham §, and by Bucherer ‖, who introduces a new principle of relativity. It is not my desire at this time to go into the mathematics of a question which has been discussed at such length, but merely to point out a few general observations suggested, especially with reference to Bucherer's formula (1), and then to show the application of those remarks to any such theory of relativity.

With a slightly modified notation, Bucherer's formula for the force **F** exerted by one electron upon another is

$$\mathbf{F} = \frac{\mathbf{r}_1 q^2 (v^2 - u^2)}{r^2 (1 - \beta^2 \sin^2 \gamma)^{\frac{3}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where q is the charge of the electron, v is the velocity of light, u is the total relative velocity of the two electrons, r is the distance between them, β is the ratio u/v, and γ is the angle between the direction of motion and the line joining the electrons. In the figure the velocity u is divided into two equal parts, one-half being attributed to each of the electrons which are assumed to be moving (instantaneously) in parallel lines ¶. The electron at A is what Bucherer calls the active electron ; that at P, the passive one. The role of P and A could be interchanged, and a force equal and opposite to **F** would then act on A from P. In this theory, action and reaction are equal and opposite.



It will be taken for granted that Kaufmann and, for that matter, innumerable other experimenters have observed and

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* "Electromagnetic Phenomena in a system moving with any velocity smaller than that of Light," Proceedings of the Amsterdam Academy, 1904.

† "Sur la dynamique de l'électron," *Rendiconti del Circolo Matematico di Palermo,* vol. xxi.

‡ *Annalen der Physik,* vol. xvii.

§ October 1907.

‖ April 1907.

¶ Of course, on any strict conception of relativity such an apportionment would be impossible; but relative to the floor and walls of the laboratory, it is not only possible but highly convenient.

measured swiftly-moving β rays—that is to say, electrons moving with velocities well up to within a few per cent. of the velocity of light, or at any rate much in excess of half that velocity. Suppose, now, that two sources of β rays were set functioning in such a manner as to discharge the rays directly towards each other along a right line. The distance between the sources is quite immaterial so long as the β particles may be considered as subject solely to their mutual action without disturbance from other influences. With this arrangement, $\gamma=0$. If, for simplicity, it be imagined that only one β particle leaves each source, the two particles will move toward each other along the line joining them, and the force becomes merely

$$\mathbf{F} = -\frac{q^2(v^2-u^2)}{r^2}.$$

If the rays are not too swift, that is, if their velocity relative to the experimenter is under half that of light, the total relative velocity is less than v and the force $\mathbf{F}$ is negative—a repulsion, as is usual with negative charges. If, however, each particle has the velocity $\frac{1}{2}v$, their relative velocity is equal to v and the force $\mathbf{F}$ vanishes at all distances. Inasmuch as the electron, on any theory, is generally supposed to travel with a uniform velocity unless interfered with, it would appear that in this case a collision were imminent. If, on the other hand, the rays were distinctly swift, their relative velocity would considerably exceed that of light and, indeed, might approach $2v$. In this case the force would actually be attractive and an impact would appear even more sure.

If, then, the formula (1) has been correctly interpreted, one of two consequences would appear to follow. Either *two β particles cannot be discharged directly toward each other with an arbitrary initial distance between them and each with a velocity greater than half that of light*; or *two particles so discharged would attract instead of repel.*

In practice, it would be impossible to discharge merely two particles, and we should have to consider the action of pencils of β rays. It does not seem, however, as if the main conclusions could be qualitatively upset, especially if the force on an electron is to be evaluated by summation over the individual particles acting. In this case of pencils of rays, there would be another interesting inference from (1). Consider, for example, two particles moving in opposite directions along parallel lines. Let the initial velocity of each particle be greater than $\frac{1}{2}v$, and for convenience it may be assumed that $\frac{1}{2}u=0{\cdot}578\,v$. Then the force $\mathbf{F}$ in (1) will again be attractive when the particles are at great distances relative to the perpendicular distance between their paths. But here the denominator of **F** has the form

$$r^2[1-(1{\cdot}155\sin\gamma)^2]^{\frac{3}{2}};$$

and hence, when the position of the particles is such that γ is nearly 60°, the attractive force becomes enormous. In fact, when $\gamma=60°$ and $\sin\gamma=0{\cdot}866$, the force is infinite; and when $\gamma>60°$, the force is neither attractive nor repulsive, but imaginary.

Without going into the question of the inertia of the particles, it would be impossible to state what would be their final configuration if they were started in such a position that $\gamma<60°$; however, unless the inertia became infinite, an impact at an angle of less than 60° appears highly probable. It is conceivable that the inertia of both of the particles would be infinite when their relative velocity u was greater than v; in which case the impossibility of discharging the particles in the manner proposed would follow. Bucherer, however, directly asserts (p. 419) that the masses are the same as those derived from the Maxwellian theory. What, therefore, the result of an attempt to start the particles with a velocity $\frac{1}{2}u>0{\cdot}578v$ might be in the region for which $\gamma>60°$ and the force is imaginary, is difficult to conceive.

The foregoing observations are not intended specifically as an objection to Bucherer's theory. It is quite possible, and even probable, that I have outraged his formula and mistaken his point of view, as he asserts in the current (March) number of this Magazine was the case with Cunningham. I should not, however, merely on that account abandon my position; for it seems to me as though, now that very swift β rays are a common subject of experiment, the question of relativity has an aspect somewhat different from that which it had previously. Either we can or we cannot obtain, with the swift β rays, velocities which, measured relatively, are greater than that of light. If we cannot, then some principle of relativity, analogous to Bucherer's new principle by which electrodynamics is based wholly on the relative motion of the electric and magnetic masses and the forces between systems are evaluated by summation of formulas like (1) extended over the masses constituting the systems, may stand; but if we can, then it appears that, unless this extreme form of the principle of relativity is abandoned, at any rate relative to swift β rays, there must ensue a veritable tangle of results fully as discordant as those which the principle hopes to avoid.

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XXXV. *On the Principle of Relativity and the Electromagnetic Mass of the Electron. A Reply to* Dr. A. H. Bucherer. *By* E. Cunningham, *Lecturer in Applied Mathematics, University College, London* [*].

IN the March number of this Magazine (p. 316), Dr. A. H. Bucherer objects to the statement made by me in a paper published also in this Magazine (Oct. 1907) that his Principle of Relativity [†] was identical with the Lorentz-Einstein principle. Without at all wishing to depreciate the ingenious method which Dr. Bucherer has adopted to avoid the difficulties which cluster round this part of electromagnetic theory, I should like to consider his objections and to go more fully into the question as to whether the statement which I made was correct.

The following paragraph is quoted from my paper:—"It is required, among other things, to explain how a light-wave travelling outwards in all directions with velocity c relative to an observer A, may at the same time be travelling outwards in all directions with the same velocity relative to an observer B moving relative to A with velocity v." May I explain that I did not wish to assert that it was required by any known fact of observation, but that I took it to be involved in the statement of the principle. I may have read into it more than was intended, but if the Maxwell equations are assumed to hold when referred, as occasion requires, to various frames of reference moving relatively to one another, the deduction cannot be escaped that the velocity of propagation of a spherical wave will be found to be exactly the same, whatever the frame of reference. Thus what was proved in my former paper was that *if I have not read too much into Dr. Bucherer's principle in supposing that he assumes the Maxwell equations to hold, whatever particular point is considered to be at rest*, then that principle cannot be applied without taking into consideration a possible difference between the space and time measures of two observer's moving relatively to one another, and that in fact this transformation between the space and time measures must be that associated with the names of Lorentz and Einstein.

Passing to another point raised by Dr. Bucherer, I feel myself on firmer ground, inasmuch as I am free from the fear that I may still be misconstruing his principle. He asks

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[*] Communicated by the Author.

[†] Phil. Mag. April 1907.

me to carefully compare it with that of Lorentz. May I say that I should scarcely have ventured to approach the subject in this Magazine if I had not already done so, and that on exactly the point to which my attention is again called, viz., the expression given for the forces on a moving electron. An inspection of these instead of showing the impossibity of obtaining them by the Lorentz-Einstein transformation, shows that they may actually be derived from the ordinary Maxwellian expressions by means of that process. It may perhaps be worth while carrying out the calculation.

Consider first two electrons, A, B moving relatively to each other, the notation being that of Dr. Bucherer's paper. Taking the axis of x in the direction of the velocity of B relative to A, let the coordinates of B relative to A at a certain instant be x', y', z' to an observer moving with A. Then taking A to be at rest in the æther, the electric intensity at B due to it has components $\frac{qv^2}{r'^3}(x', y', z')$. Now apply the Lorentz-Einstein transformation. Then at the same instant to an observer moving with B the electric intensity is $\frac{qv^2}{r'^3}(x', \beta y', \beta z')$. But the coordinates of B relative to A to an observer moving with B will be $x=\frac{x'}{\beta}$, y, z; so that the intensity may be expressed as

$$\frac{\beta qv^2}{r'^3}(x, y, z) \quad \text{where} \quad \beta=\left(1-\frac{u^2}{v^2}\right)^{-1/2}.$$

If γ is the angle between the line AB and the direction of u as seen by the observer moving with B, $\sin\gamma=\frac{\sqrt{y^2+z^2}}{r}$ and $r'^2=\beta^2 r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)$.

Thus finally the intensity to an observer moving with B is

$$\frac{qv^2(x, y, z)}{\beta^2 r^3\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}},$$

or in Dr. Bucherer's notation

$$\frac{\mathbf{r}_1 qv^2 s}{r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}},$$

and therefore the force upon the electron B supposed at rest in the æther is

$$\frac{\mathrm{r}_1 q^2 v^2 s}{r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}.$$

Similarly, suppose B to be a unit magnetic pole instead of an electron of charge q. We require now to know the magnetic intensity at B to an observer moving with it. Starting from the electrostatic force due to A as before, the Lorentz-Einstein expression for the magnetic intensity referred to axes moving with B is

$$\frac{\beta q u}{r'^3}(0,\ z',\ -y')$$

$$=\frac{qu}{\beta^2 r^3\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{/2}}(0,\ z,\ -y);$$

or in Dr. Bucherer's notation

$$\frac{qs}{r^3\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}\mathrm{V}u\mathrm{r}_1,$$

which is his expression (3). Similarly expressions (2) and (4) may be derived.

Having shown that these expressions may be obtained by means of the Lorentz transformation, there is hardly need to go further and obtain the expressions for the force acting on an electron moving in a uniform magnetic or electric field, since these are obtained by Dr. Bucherer by integration of the simpler expressions. But as a further verification of the equivalence of the two principles the work will be carried out for the case of the electric field, which gives the more complicated result.

Let the field be of intensity E_0, and let an electron of charge q move with velocity u at an angle α with the direction of E_0 as seen by an observer at rest with the field. Then to an observer moving with the electron, the direction of the normal to the condenser plates will be slewed round to an angle α' with the direction of u where $\tan\alpha'=\tan\alpha\sqrt{1-\frac{u^2}{v^2}}$ so that

$$\cos\alpha'=\frac{\cos\alpha}{\sqrt{1-\frac{u^2}{v^2}\sin^2\alpha}} \quad\text{and}\quad \sin\alpha'=\frac{\sin\alpha\sqrt{1-\frac{u^2}{v^2}}}{\sqrt{1-\frac{u^2}{v^2}\sin^2\alpha}}.$$

Now referred to the original frame of reference the electric field was made up of $E_0 \cos\alpha$ parallel to u and $E_0 \sin\alpha$ perpendicular to u. Hence, according to the Lorentz-Einstein transformation, referred to axes moving with the electron it is made up of $E_0 \cos\alpha$ parallel to u and $\beta E_0 \sin\alpha$ perpendicular to u.

Thus the total component in the direction of the normal to the condenser plates is

$$E_0(\cos\alpha\cos\alpha' + \beta\sin\alpha\sin\alpha')$$

$$= \frac{E_0}{\sqrt{1-\frac{u^2}{v^2}\sin^2\alpha}} = \frac{E_0\sqrt{1-\frac{u^2}{v^2}\cos^2\alpha'}}{\sqrt{1-\frac{u^2}{v^2}}}.$$

The component parallel to the plate is similarly

$$E_0(\cos\alpha\sin\alpha' - \beta\sin\alpha\cos\alpha')$$

$$= \frac{E_0\sin\alpha\cos\alpha}{\sqrt{1-\frac{u^2}{v^2}\sin^2\alpha}}\left(\frac{1}{\beta}-\beta\right)$$

$$= -\frac{E_0\sin\alpha\cos\alpha\frac{u^2}{v^2}}{\sqrt{1-\frac{u^2}{v^2}}\sqrt{1-\frac{u^2}{v^2}\sin^2\alpha}}$$

$$= -\frac{E_0\frac{u^2}{v^2}\sin\alpha'\cos\alpha'}{\sqrt{1-\frac{u^2}{v^2}}\sqrt{1-\frac{u^2}{v^2}\cos^2\alpha'}}$$

The two components can be replaced by two in the directions of u and of the normal to the plate respectively of magnitudes

$$-\frac{E_0\frac{u^2}{v^2}\cos\alpha'}{\sqrt{1-\frac{u^2}{v^2}}\sqrt{1-\frac{u^2}{v^2}\cos^2\alpha'}}$$

and

$$\frac{E_0}{\sqrt{1-\frac{u^2}{v^2}}\sqrt{1-\frac{u^2}{v^2}\cos^2\alpha'}}.$$

Now the ratio of the areas of a given portion of the plate as seen by an observer at rest relative to them and to the electron respectively, is $\sec\alpha : \sec\alpha'$, so that if σ is the true density of the electricity on the plate, the apparent density to an observer moving with the electron is

$$\sigma' = \frac{\sigma\cos\alpha'}{\cos\alpha} = \frac{\sigma\sqrt{1-\frac{u^2}{v^2}\cos^2\alpha'}}{\sqrt{1-\frac{u^2}{v^2}}},$$

and $\quad E_0 = 4\pi\sigma v^2.$

Hence the electric intensity obtained above is made up of two components

$$-\frac{4\pi\sigma' v^2\cdot\frac{u^2}{v^2}\cos\alpha'}{\left(1-\frac{u^2}{v^2}\cos^2\alpha'\right)} \quad \text{and} \quad \frac{4\pi\sigma' v^2}{\left(1-\frac{u^2}{v^2}\cos^2\alpha'\right)}$$

in the directions of u and the normal to the plate respectively to an observer moving with the electron; and this agrees exactly with expression (8) for the force on the electron.

With regard to the evaluation of the mass of the electron, I must admit that I did not fully understand Dr. Bucherer's process, but I cannot rid myself of the feeling that he has somehow supposed the electron to be moving and at rest simultaneously in its different aspects as *active* and *passive* respectively.

In this connexion there is another difficulty that appears, if the transformation of space and time measures between the two observers be neglected, which may most simply be illustrated by considering the case of two electrons which at a certain instant have the same velocity u through the æther. Then, since the relative velocity is zero, the force acting on either will according to Dr. Bucherer's principle be the electrostatic force $\frac{q^2}{r^2}$ in the direction of the line joining the electrons. But the longitudinal and transverse masses being different, the acceleration of the electron will not in general be in the direction of the force, so that instead of the relative motion of the electrons due to their mutual action being in the line joining them, this line will begin to rotate; in fact, it will tend to set itself at right angles to the direction of motion, a conclusion scarcely consonant with a principle of relativity.

If we revert to the ordinary theory as applied to the same illustration, the field due to one electron in the neighbourhood of the other consists of an electric intensity

$$\frac{q\left(1-\frac{u^2}{v^2}\right)}{r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}$$

in the direction of r, and a magnetic intensity

$$\frac{qu\sin\theta\left(1-\frac{u^2}{v^2}\right)}{vr^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}$$

at right angles to r and to u.

Combining these, the mechanical force on the second electron is made up of a component

$$\frac{q^2\cos\theta\left(1-\frac{u^2}{v^2}\right)}{r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}$$

in the direction of motion, and a component

$$\frac{q^2\sin\theta\left(1-\frac{u^2}{v^2}\right)^2}{r^2\left(1-\frac{u^2}{v^2}\sin^2\gamma\right)^{3/2}}$$

perpendicular to this direction.

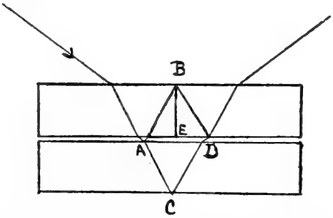
Thus, the only theory which would give an acceleration in the direction of r is one in which the ratio of the transverse to the longitudinal mass is $\left(1-\frac{u^2}{v^2}\right)$ as in the Lorentz theory. Taking the Abraham values of the masses the line joining the electrons will rotate as before.

XXXVI. *On Interference Fringes obtained with Glass Wedges, and their Application to the Examination of Plate Glass.*

By S. R. Milner, *D.Sc.*[*]

If two pieces of ordinary plate-glass of approximately the same thickness are placed one on the top of the other, and the air-film between them is observed by sodium light, the system of Newton's fringes, formed by the interference of the light reflected from the two surfaces of the air-film, is of course seen. Occasionally, by very close inspection, another system of fringes may be seen which is formed by the interference of the rays such as ABD, ACD (fig. 1), which have been further reflected from the non-adjacent faces of the plates so as to meet again at the interface; but these fringes, when observed in the ordinary way, are so very faint in comparison with the light reflected direct from the interface that they can only very exceptionally be distinguished. They will, however, become clearly visible if we cut off all the light reflected from the film except that by which they themselves are formed. At perpendicular incidence this would appear to be impossible, but when the incident light is inclined to the plates it can be done in a very simple way indeed, by merely interposing an obstacle having a sharp edge in the path of the incident light. If this be done, on looking at the plates by the reflected light a series of successive shadow images of the obstacle will be seen formed by reflexion at the various surfaces: the first I_1 by reflexion at A (fig. 2—the refraction in the glass is for simplicity omitted in the figure), the second I_2 by direct reflexion from the film BC, and the third I_3 by the rays which have undergone either two reflexions at, or two transmissions through, the film. Where the first and second of these images overlap, but not the third, *i. e.*. in the region FG of the film, the rays which give rise to the fringe system under consideration are the only ones which reach the eye, and in this space the fringes become clearly marked and undiluted

Fig. 1.



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[*] Communicated by the Author.

with any other light. In the same space by looking in the direction EF the transmitted system can also be seen just within the first shadow of the obstacle. Unlike the Newton's rings, the transmitted system is quite as bright as the reflected one, and is perhaps the more convenient for observation. The region FG is followed by second (GH) and third &c., corresponding spaces in which the fringes can also be seen, due to still further reflexions of the light from the non-adjacent glass faces, but the fringes are usually distorted and rapidly become fainter unless the incidence is very oblique.

Fig. 2.

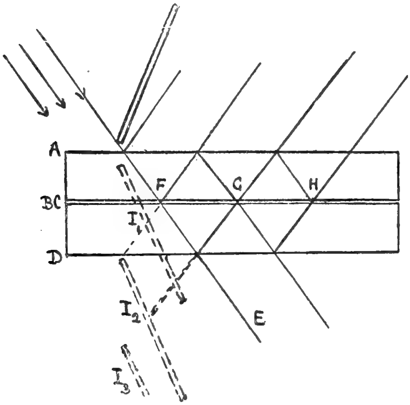


Fig. 3.

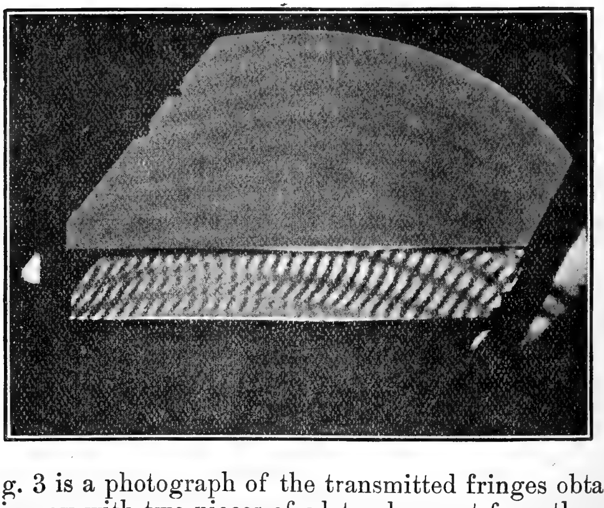


Fig. 3 is a photograph of the transmitted fringes obtained in this way with two pieces of plate-glass, cut from the same sheet and laid one on the other at random. The obstacle was simply a blackened card held in front of the plates, which were inclined at 45° to the light from a sodium burner and photographed direct in the camera. The upper part of the plates, being illuminated by the directly transmitted light, shows the Newton's rings only, and the fringes under consideration are those in the first shadow space, which forms a broad band parallel to the edge of the card, and of about the same thickness as that of one of the pieces of glass. These fringes are quite as marked as the Newton's rings, although of course the total intensity of the light is less in the shadow space (the upper part of the glass was shaded with a card during 9/10 of the exposure to render the intensities of the two parts more equal in the photograph).

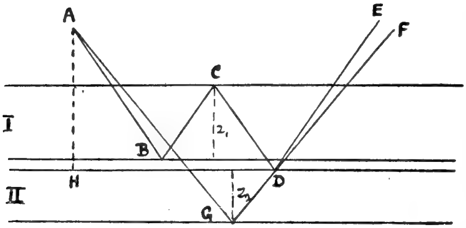
I noticed these fringes first when examining some pieces of plate-glass by Newton's rings for planeness of surface, and was struck with the extremely simple means they give of determining at the same time the variations in thickness of the plates. In testing a piece of glass for uniformity of thickness, when it is plane parallel to within a few wave-lengths all over its surface the circular system of fringes discovered by Haidinger can be used, but these fringes disappear whenever the wedge angle is at all appreciable. I have seldom been able to see them on ordinary plate-glass, which, although it may have an excellent surface, is almost invariably wedge-shaped and often with a considerable angle. In spite of this, for many purposes ordinary plate-glass will serve very well; for example, in the numerous cases where a beam of light has to pass through two pieces of glass in succession, slightly wedge-shaped glass will be quite satisfactory so long as the two pieces are suitably arranged so that their wedge angles annul each other's effect. For such purposes the interference-fringes discussed in this paper form a very simple method of testing glass. There is no necessity to have a standard glass of uniform thickness. If two pieces of plate-glass are cut from the same sheet each can be tested absolutely by means of the other. The way in which this may be done will be rendered more clear by considering some of the properties of these fringes, which are very characteristic, and different from those of Newton's rings.

1. As will be seen from fig. 1, the fringes represent the loci of points at which the thickness of plate i. is a constant amount greater or less than that of plate ii. Since each of the two interfering rays passes through the air-film the positions of the fringes are independent of the thickness of the air-film. Thus, on pressing the two plates together or separating them the fringes remain apparently fixed to the

glass, while the Newton's rings move rapidly across the field. This statement requires a little modification, as will be seen later, in consequence of multiple reflexions, but the movement of the fringes due to this cause is limited to half a fringe width.

2. *Determination of Central Fringe.*—The position of the central fringe of the system, *i. e.* that which corresponds to equal paths in the two plates, is independent of the angle of incidence of the light, but this is not the case with any other fringe. Consider the interference of any two rays, ABCDE and AGDF (fig. 4), one in each plate, each of which passes through the point D and falls on the pupil of the eye at EF.

Fig. 4.



Let r and $r+dr$ be the angles which they make with the normals to the plates (HAB and HAG in the figure, in reality the angles of refraction in the glass) and z_1 and z_2 the thicknesses of the plates at the points C and G. If the waves start in the same phase from the point A, the relative retardation δ at the point D will be

$$\delta = \frac{2z_1 + \mathrm{AH}}{\cos r} - \frac{2z_2 + \mathrm{AH}}{\cos(r+dr)}$$

$$= \frac{2(z_1 - z_2)}{\cos r} - \frac{2z_2 + \mathrm{AH}}{\cos^2 r} \sin r \, dr.$$

But by the geometry of the figure

$$\mathrm{HD} = (2z_1 + \mathrm{AH}) \tan r = (2z_2 + \mathrm{AH}) \tan(r+dr),$$

and on expansion this equation gives

$$\frac{(2z_2 + \mathrm{AH})}{\cos^2 r} \sin r \, dr = \frac{2(z_1 - z_2)}{\cos r} \sin^2 r \, dr,$$

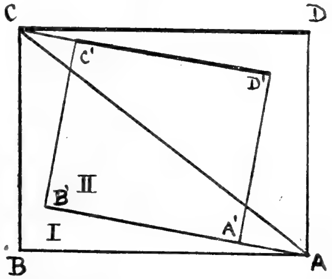
and consequently

$$\delta = 2(z_1 - z_2)\cos r. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since δ is independent of the position of the starting-point of the two rays, it follows that the fringes will be seen by focussing the eye on the air-film, whatever be the position or size of the source of light. The fringes thus appear fixed to the glass when looked at in a definite direction, but if the eye is moved towards the normal to the plates so as to make the angle of refraction less, equation (1) shows that the same retardation will be produced by a smaller difference in thickness of the plates, *i. e.* the fringe under observation will move towards the central one of the system. By this means the position on the plates of the central fringe can be readily located.

3. *Effect of Rotation of one Plate.*—Over a reasonably small area each piece of plate-glass may be looked on as forming a wedge of very small angle. Since the fringes represent the loci of points of constant difference in thickness, the direction of the fringes and the fringe width are purely questions of the geometry of two superposed wedges, and the effects of rotating one wedge on the other may be easily followed by making use of fig. 5. This is a plan of the two wedges superposed; portions only of the wedges are drawn, of which the thin ends AB, A′B′, and the thick ends CD, C′D′ (marked by a thick line), have exactly equal thicknesses. Produce these ends until they intersect at A and C. Then the line AC is a line of equal thickness in the two plates, and represents the central fringe of the system, and the other fringes are lines parallel to this. When the wedges are so placed that their contour-lines are parallel to each other, the thin ends of each wedge being coincident, the fringes will be parallel to the contour-lines and very broad. As one wedge is turned round on the other, the fringes in general narrow and also turn round, with a different angular velocity from that of the wedge, but they again become parallel to the contour-lines when the wedge has been turned round through two right angles, *i. e.* when the wedges are again parallel to each other, but the thin end A′B′ of i. is coincident with the thick end CD of ii. The

Fig. 5.



width of the fringes is now a minimum, and it may be so small that they cannot be seen except with a microscope*.

4. *Effect of Displacement of one Plate on the other.*—This will in general alter the length of the optical path of one of the interfering beams, and produce a rapid motion of the fringes across the field. There are, however, two special directions of motion in which this will not be the case. If the plate i. is moved along a contour-line of ii., the fringes will remain apparently fixed to plate i.; if it is moved along one of its own contour-lines, the fringes will remain apparently fixed to plate ii.

5. *Examination of Plate-glass Sheet.*—By making use of the properties of the fringes enumerated in the above paragraphs, one can run over a large sheet of plate-glass, and either determine its best portion as regards uniformity in thickness, or plot out its contour-lines and measure the angle of its wedge, with great ease. Having chosen a small square of glass of approximately the same thickness as the sheet (this is most simply done by cutting off a small piece from the plate itself), we place it anywhere on the sheet, and let the light from a sodium burner fall on the two at an angle of about 45°. On holding a card in the incident light and examining the shadow the fringes can often be seen at once. They may, however, be too fine to see, in which case they will usually come prominently into view if we slowly rotate the small piece on the surface of the other, and by further rotation they may be broadened as desired (v. § 3). If we then fix the attention on a particular fringe and move the small piece by trial always in such a direction that the fringe remains apparently fixed to it, a contour-line of the large sheet will be traced out.

When a contour-line has been obtained it is easy to measure the angle of the wedge formed by the sheet at any point. Move the small piece at right angles to the contour-line and count the number of fringes which pass by a fixed

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* While the fringes in their positions of maximum and minimum fringe width are always parallel to the contour-lines, their intermediate positions as one wedge is rotated vary considerably with the angles of the wedges. All possible cases are comprised in the following formula which follows simply from the geometry of the two wedges. Let a_1 a_2 be the angles of the wedges i. and ii., θ the angle BAB′ between their contour-lines, ϕ the angle BAC which the fringes make with a contour-line of wedge i., ζ the fringe width, then

$$\frac{2\cos r}{\lambda}\zeta\sin\theta=\frac{1}{a_1}\sin(\phi-\theta)=\frac{1}{a_2}\sin\varphi,$$

r being the angle of refraction, and λ the wave-length of the light in the glass.

point on the piece for a given displacement. The alteration in thickness of the sheet is $\lambda/2\cos r$ for each fringe that passes the point.

The Fringes in White Light.—In general the central fringe of the system is not in the field of view, but its position may easily be found by applying the observation of § 2. The coloured fringes exhibit in an interesting way the effect of multiple reflexions in the film. The multiple reflexions which occur in Newton's rings may be looked on as giving separate systems of fringes which are all superposed on each other, the observed colours being the resultant effect of them all. In the wedge fringes similar multiple reflexions at the air-film occur, but unlike the Newton's rings, the individual systems may be completely separated from each other. Without analysing the effects in detail, we can see that a ray which has been reflected from the non-adjacent face of plate i. can interfere with any ray which has passed through plate ii., and has also been reflected any even number of times at the air-film, and *vice versa*. Hence, if p_1 and p_2 are the optical paths through plates i. and ii. in any place, and f that of the air-film, interference-systems will be produced the centres of which are at such places that

$$p_1+2nf=p_2+2mf,$$

n and m being any whole numbers. The system $n=m$ has its centre at the point of the wedges where $p_1=p_2$, the systems $n=m\pm1$ at the points where $p_1=p_2\mp2f$, and so on. When the film is very thin the systems are all superposed on each other, giving a complex set of coloured fringes, but on slightly separating* the plates this splits up into the different systems, one of which remains fixed, while the others move off to right and left with different velocities until they are quite separated.

The system of fringes which remains stationary can be kept in the field of view even if the plates are separated by several centimetres, so long as they are kept parallel to each other, and are in fact the fringes which are used in the well-

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* More simply by tilting one plate on the other perpendicular to the plane of incidence. By then tilting *in* the plane of incidence, each of the previously formed systems again splits up into two, which move off the field in opposite directions. The effect is very beautiful in practice, as many as a dozen sets of coloured fringes often being in the field at the same time. The second separation is due to each of the previous systems being really the superposed effect of two systems, one on each surface of the air-film. The simplest form of each system is illustrated in fig. 1 and fig. 4 respectively. The interfering rays which form them pass through the air-film in different places (*e. g.* at A and D, fig. 1, and conversely, at D and B, fig. 4), and consequently if the film is not plane parallel, their centres appear at different places on the plates.

known Jamin refractometer. It is perhaps worthy of note how comparatively simple it is to obtain the fringes and practically construct a refractometer out of ordinary plate-glass. All that is necessary is to cut two pieces from the same sheet so as to include the same contour-line. They then necessarily show the fringes with white light, and the width of the fringes can be made as great as desired by rotating one piece on the other.

Multiple Reflexion in Sodium Light.—The various systems due to multiple reflexion of course exist with sodium light, but in consequence of the large number of fringes then visible the systems always overlap, and it is the resultant effect only which is seen. This accounts for the curious behaviour of the fringes which is observed when one plate is slightly tilted on the other. Each fringe, instead of keeping quite fixed to the glass as the tilting occurs, appears to vibrate rapidly from side to side through half a fringe width. It suddenly disappears, reappears half a fringe width away, disappears, and reappears in its original position again. This is exactly the effect that the superposition of individual systems of fringes moving in opposite directions across the field would produce.

The same effect shows itself in another way in the photograph of the fringes (fig. 3). The fringes have disappeared in certain regions of the shadowed space which bear a close relation to those where, under ordinary conditions of illumination, Newton's rings would be seen, and on each side of these regions the fringes are displaced through half a fringe width. This behaviour of the fringes introduces an occasional uncertainty of half a fringe width in testing a piece of glass in the way described above. The uncertainty need not arise with a little care; but even if it does, for the purposes for which plate-glass would be used the resulting error is usually of little importance.

XXXVII. *A Pressure-integral as Kinetic Potential.*

By R. HARGREAVES*.

PRESSURE is usually introduced into the equations of hydrodynamics in the character of a normal stress. To that meaning corresponds the use of *surface-integrals* of the components of pressure, to determine the force exerted by the liquid on solids immersed in it. But where there is no vorticity, an integral

$$p+\rho\frac{\partial\phi}{\partial t}+\frac{\rho}{2}\left(\overline{\frac{\partial\phi}{\partial x}}\Big|^2+\overline{\frac{\partial\phi}{\partial y}}\Big|^2+\overline{\frac{\partial\phi}{\partial z}}\Big|^2\right)=f(t)\quad . \quad . \quad (1)$$

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* Communicated by the Author.

exists, in which each term is of the order energy per unit volume. It is reasonable to expect that a *volume-integral of this equation through the whole liquid* will have significance; and the object proposed here is to determine this significance and to interpret the pressure-integral.

Now in the hydrodynamical equations $\rho\frac{\mathrm{D}u}{\mathrm{D}t}=-\frac{\partial p}{\partial x}, \ldots$ the right-hand members have the form taken by Lagrange's expressions for force, when it is recognized that p is a function of (xyz). The volume-integral $\int p d\tau$ will, however, depend on the coordinates defining the positions of the solids, on their time-rates, and on the constants of circulation. It is permissible, therefore, to conjecture that the pressure-integral is a kinetic potential giving the whole dynamical effect of the liquid motion. Accordingly, the volume-integral of (1) is an equation defining the kinetic potential in terms of energy and quantities of like order.

In § 1 we examine this integral for a problem * propounded and solved by Lord Kelvin, that of the motion of solids in infinite incompressible liquid, when the solids have apertures which permit circulation. The above interpretation presents the solution in direct connexion with the fundamental equation (1). Section 2 contains a proposition in general dynamics relating to the nugatory character of a term of the form $\frac{df}{dt}$ appearing in the expression for kinetic potential. In § 3 the method of § 1 is applied to the case of gases, where intrinsic energy has to be taken into account.

§ 1. In the first place we may ignore the arbitrary function $f(t)$ in (1), because the integral of this term taken through the whole liquid does not depend on the coordinates or velocities of the moving solids; we have, therefore,

$$\int\left(p+\rho\frac{\partial\phi}{\partial t}+\frac{\rho}{2}\Sigma u^2\right)d\tau=0. \quad . \quad . \quad . \quad . \quad (2)$$

Now consider $\frac{d}{dt}\int\rho\phi\, d\tau$ the whole rate of change of the integral. The change embraces two parts, one in which the integrand is differentiated, this part being $\int\rho\frac{\partial\phi}{\partial t}d\tau$; and another in which the limits are concerned. Near the surface of a solid $d\tau$ may be written as $d\nu\, d\mathrm{S}$, where $d\nu$ is an element

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* Phil. Mag. May 1873.

of the normal drawn outwards to the liquid, and dS is an element of surface; thus near the surface the integral is $\int dS \int_\nu \rho\phi\, d\nu$. Since $\frac{d\nu}{dt} = v_\nu$ the normal component of velocity of the solid, the second part of the rate of change is $-\int \rho v_\nu \phi\, dS$, ϕ having a surface value. If ϕ is many-valued we have to consider also the surfaces of barriers moving with the solids. For a barrier σ we get an integral $-\int \rho v_\nu \phi\, d\sigma$ on one face of the barrier, and on completing the circuit so as to come to the other face we have $\phi + \kappa$ for ϕ, κ being a constant of circulation, and $-v_\nu$ for v_ν, the sum for the two faces giving $\int \rho v_\nu \kappa\, d\sigma$. Thus with circulation admitted the whole value of the rate of change is

$$\frac{d}{dt}\int \rho\phi\, d\tau = \int \rho \frac{\partial \phi}{\partial t}\, d\tau - \int \rho v_\nu \phi\, dS + \int \rho v_\nu \kappa\, d\sigma, \quad . \quad (3)$$

where of course a summation for several surfaces and barriers may take the place of the one written. Again we have

$$\int \rho \Sigma u^2\, d\tau = \int \rho \Sigma u \frac{\partial \phi}{\partial x}\, d\tau = -\int \rho\phi \frac{\partial \phi}{\partial \nu}\, dS + \int \rho \frac{\partial \phi}{\partial \nu} \kappa\, d\sigma$$

$$= -\int \rho v_\nu \phi\, dS + \int \rho \frac{\partial \phi}{\partial \nu} \kappa\, d\sigma,$$

since $\frac{\partial \phi}{\partial \nu} = v_\nu$ at a surface S. This in conjunction with (3), yields

$$\frac{d}{dt}\int \rho\phi\, d\tau = \int \rho \frac{D\phi}{Dt}\, d\tau + \int \rho\left(v_\nu - \frac{\partial \phi}{\partial \nu}\right)\kappa\, d\sigma. \quad . \quad (4)$$

Adding this to (2) written in the form

$$\int \left(p + \rho \frac{D\phi}{Dt}\right) d\tau = \int \tfrac{1}{2}\rho \Sigma u^2\, d\tau,$$

we obtain

$$\int p\, d\tau + \frac{d}{dt}\int \rho\phi\, d\tau = \int \frac{\rho}{2} \Sigma u^2\, d\tau - \int \rho\left(\frac{\partial \phi}{\partial \nu} - v_\nu\right)\kappa\, d\sigma. \quad (5)$$

The potential ϕ may be written as $\psi + \omega$, where ψ is a linear function of the velocities of the solids, and ω of the constants of circulation, with coefficients depending in each case on the coordinates of the solid as well as on $(x\, y\, z)$. In virtue of Kelvin's extension of Green's theorem, there is no term in energy involving ψ and ω jointly, and if we use

$$K \equiv \int \frac{\rho}{2}\frac{\partial \omega}{\partial \nu}\kappa\, d\sigma, \quad T \equiv -\int \frac{\rho\psi}{2}\frac{\partial \psi}{\partial \nu}\, dS$$

for the energies belonging to cyclic and acyclic motions respectively, (5) is

$$\int p\, d\tau + \frac{d}{dt}\int \rho\phi\, d\tau = T - K + \int \rho\left(v_\nu - \frac{\partial \psi}{\partial \nu}\right)\kappa\, d\sigma,$$

or with

$$\left.\begin{aligned} &\int p\, d\tau \equiv P, \; I \equiv \int \rho\left(v_\nu - \frac{\partial \psi}{\partial \nu}\right)\kappa\, d\sigma \\ &P + \frac{d}{dt}\int \rho\phi\, d\tau = T - K + I \equiv L\, ; \end{aligned}\right\}, \quad . \quad (6)$$

where T is a quadratic in velocities, K in the constants of circulation, and I is a bilinear function of these quantities. As L is Kelvin's kinetic potential the question before us now is, what is the effect of the term $\frac{d}{dt}\int \rho\phi\, d\tau$ on the dynamical position.

§ 2. If L is a function of coordinates θ and the time-rates $\dot\theta\, \ddot\theta \ldots \overset{(n)}{\theta}$, its time-rate or whole rate of increment can be expressed as a sum of terms $\dot\theta\, \Theta_0$, together with the time-rate of a function derivable from L. It is sufficient to write a single variable. In

$$\frac{dL}{dt} = \frac{\partial L}{\partial \theta}\dot\theta + \frac{\partial L}{\partial \dot\theta}\ddot\theta + \frac{\partial L}{\partial \ddot\theta}\dddot\theta + \ldots + \frac{\partial L}{\partial \overset{(n)}{\theta}}\overset{(n+1)}{\theta},$$

the first term has the required form, and subsequent terms are

$$\ddot\theta\frac{\partial L}{\partial \dot\theta} = \frac{d}{dt}\left(\dot\theta\frac{\partial L}{\partial \dot\theta}\right) - \dot\theta\frac{d}{dt}\frac{\partial L}{\partial \dot\theta},$$

$$\dddot\theta\frac{\partial L}{\partial \ddot\theta} = \frac{d}{dt}\left[\ddot\theta\frac{\partial L}{\partial \ddot\theta} - \dot\theta\frac{d}{dt}\frac{\partial L}{\partial \ddot\theta}\right] + \dot\theta\frac{d^2}{dt^2}\frac{\partial L}{\partial \ddot\theta},$$

. . . .

$$\overset{(n+1)}{\theta}\frac{\partial L}{\partial \overset{(n)}{\theta}} = \frac{d}{dt}\left[\overset{(n)}{\theta}\frac{\partial L}{\partial \overset{(n)}{\theta}} - \overset{(n-1)}{\theta}\frac{d}{dt}\frac{\partial L}{\partial \overset{(n)}{\theta}} + \ldots + (-1)^{n-1}\dot\theta\frac{d^{n-1}}{dt^{n-1}}\frac{\partial L}{\partial \overset{(n)}{\theta}}\right]$$

$$+ (-1)^n\frac{d^n}{dt^n}\frac{\partial L}{\partial \overset{(n)}{\theta}};$$

all of the required form. By addition, collecting terms diagonally,

$$\frac{dL}{dt}=\dot{\theta}\left[\frac{\partial L}{\partial\theta}-\frac{d}{dt}\frac{\partial L}{\partial\dot{\theta}}+\frac{d^2}{dt^2}\frac{\partial L}{\partial\ddot{\theta}}\dots+(-1)^n\frac{d^n}{dt^n}\frac{\partial L}{\partial\overset{(n)}{\theta}}\right]$$

$$+\frac{d}{dt}\dot{\theta}\left[\frac{\partial L}{\partial\dot{\theta}}-\frac{d}{dt}\frac{\partial L}{\partial\ddot{\theta}}+\dots+(-1)^{n-1}\frac{d^{n-1}}{dt^{n-1}}\frac{\partial L}{\partial\overset{(n)}{\theta}}\right]$$

$$+\frac{d}{dt}\ddot{\theta}\left[\frac{\partial L}{\partial\ddot{\theta}}-\frac{d}{dt}\frac{\partial L}{\partial\dddot{\theta}}+\dots+(-1)^{n-2}\frac{d^{n-2}}{dt^{n-2}}\frac{\partial L}{\partial\overset{(n)}{\theta}}\right]+\dots$$

Thus with any number of variables,

$$\frac{dL}{dt}=\Sigma\left[\Theta_0\,\dot{\theta}+\frac{d}{dt}(\Theta_1\dot{\theta}+\Theta_2\,\ddot{\theta}+\dots\Theta_n\,\overset{(n)}{\theta})\right], \quad . \quad (7)$$

where

$$\left.\begin{aligned}\Theta_0&=\frac{\partial L}{\partial\theta}-\frac{d}{dt}\frac{\partial L}{\partial\dot{\theta}}+\dots, \quad \Theta_1=\frac{\partial L}{\partial\dot{\theta}}-\frac{d}{dt}\frac{\partial L}{\partial\ddot{\theta}}+\dots\\ \Theta_2&=\frac{\partial L}{\partial\ddot{\theta}}-\frac{d}{dt}\frac{\partial L}{\partial\dddot{\theta}}+\dots, \qquad \Theta_n=\frac{\partial L}{\partial\overset{(n)}{\theta}}\end{aligned}\right\}, \quad (8)^*$$

If then we put

$$F_\theta=-\Theta_0, \;\; E=-L+\Sigma(\Theta_1\dot{\theta}+\Theta_2\ddot{\theta}+\dots+\Theta_n\,\overset{(n)}{\theta}), \quad (9)$$

the result (7) is expressed by

$$\frac{dE}{dt}=\Sigma\,F_\theta\,\dot{\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

But if L has the form $\frac{df}{dt}$ where f is a function of $\theta\,\dot{\theta}\dots\overset{(n)}{\theta}$, then L or

$$\frac{df}{dt}=\frac{\partial f}{\partial\theta}\dot{\theta}+\frac{\partial f}{\partial\dot{\theta}}\ddot{\theta}+\dots+\frac{\partial f}{\partial\overset{(n)}{\theta}}\overset{(n+1)}{\theta},$$

and

$$\frac{dL}{dt}=\frac{d}{dt}\left(\frac{\partial f}{\partial\theta}\dot{\theta}+\frac{\partial f}{\partial\dot{\theta}}\ddot{\theta}+\dots+\frac{\partial f}{\partial\overset{(n)}{\theta}}\overset{(n+1)}{\theta}\right),$$

which has the form of (7) with

$$\Theta_0=0, \;\; \Theta_1=\frac{\partial f}{\partial\theta}, \;\; \Theta_2=\frac{\partial f}{\partial\dot{\theta}}, \dots \quad \Theta_{n+1}=\frac{\partial f}{\partial\overset{(n)}{\theta}}. \quad . \quad (11)$$

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* Or $\Theta_n=\frac{\partial L}{\partial\overset{(n)}{\theta}}$, and $\Theta_r=\frac{\partial L}{\partial\overset{(r)}{\theta}}-\frac{d\Theta_{r+1}}{dt}$ from $r=n-1$ down to $r=0$.

These values make L equal to $\Theta_1\dot{\theta}+\Theta_2\ddot{\theta}+\ldots$ (or Σ with more variables), *i. e.* the value of E found by the process (9) is zero, and also F_θ or $-\Theta_0$ is zero. [Or we may show that

$$\frac{\partial L}{\partial \overset{(n+1)}{\theta}}=\frac{\partial f}{\partial \overset{(n)}{\theta}},\quad \frac{\partial L}{\partial \overset{(r)}{\theta}}=\frac{\partial f}{\partial \overset{(r-1)}{\theta}}+\frac{d}{dt}\frac{\partial f}{\partial \overset{(r)}{\theta}},\quad \frac{\partial L}{\partial \theta}=\frac{d}{dt}\frac{\partial f}{\partial \theta},\qquad (12)$$

where the middle form applies in all cases but the first and last. The construction of Θ's by (8) or the footnote leads then to the above result.]

Thus if L is a kinetic potential of any order a function E is derivable from it by the direct process in (9), which will have the character of energy, *i. e.* its rate of increment may be expressed as a rate of working of forces F. But if $L=\frac{df}{dt}$, f defined as above, then the forces concerned and the value of E derived from L all vanish.

The term then by which P differs from Kelvin's kinetic potential contributes nothing to force or to the expression for energy. As applied to L the formula * gives

$$E=\Sigma\dot{\theta}\frac{\partial L}{\partial\dot{\theta}}-L=2T+I-(T-K+I)=T+K,$$

since I is a linear function of $\dot{\theta}$, and K does not contain $\dot{\theta}$. Therefore P and L when used as kinetic potentials yield the same forces, and a correct value of the energy.

A minor example of the principle of this section is the equivalence of $\dot{x}y$, $-x\dot{y}$, and $\frac{1}{2}(\dot{x}y-x\dot{y})$ as kinetic potentials, forms occurring in different estimates of I for a circular cylinder. The case where f is linear in velocities, and so $\frac{df}{dt}$ has a part linear in accelerations and another part quadratic in velocities, seems likely to be of common occurrence.

An important example is the electromagnetic formula for volume distribution given in Lorentz, *Encykl. Math. Wiss.* v. ii. p. 160, viz.

$$\int(\tfrac{1}{2}\Sigma a^2-\tfrac{1}{2}\Sigma X^2)d\tau=\int\tfrac{1}{2}(\Sigma Fu/V-\psi)\rho\,d\tau-\frac{1}{2V}\frac{d}{dt}\int\Sigma X\,F\,d\tau.$$

An example of both sections is furnished by Green's

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* We have also $E=L-\Sigma\kappa\frac{\partial L}{\partial\kappa}$. On the use of a kinetic potential of this type, and the coefficients in I, compare Phil. Mag. July 1908.

theorem, when the equation

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2\phi}{\partial z^2}=\frac{1}{\mathrm{V}^2}\frac{\partial^2\phi}{\partial t^2}$$

holds in space external to moving surfaces S, viz.

$$\int\left(\overline{\frac{\partial\phi}{\partial x}}\Big|^2+\overline{\frac{\partial\phi}{\partial y}}\Big|^2+\overline{\frac{\partial\phi}{\partial z}}\Big|^2-\frac{1}{\mathrm{V}^2}\overline{\frac{\partial\phi}{\partial t}}\Big|^2\right)d\tau=-\int\phi\frac{\partial\phi}{\partial\nu}d\mathrm{S}-\int\frac{1}{\mathrm{V}^2}\frac{\partial}{\partial t}\left(\phi\frac{\partial\phi}{\partial t}\right)d\tau$$

$$=-\int\phi\frac{\partial\phi}{\partial\nu}d\mathrm{S}-\int\frac{v_\nu\phi}{\mathrm{V}^2}\frac{\partial\phi}{\partial t}d\mathrm{S}-\frac{d}{dt}\int\frac{\phi}{\mathrm{V}^2}\frac{\partial\phi}{\partial t}d\tau. \quad . \quad . \quad (13)$$

When half the left-hand member is used as a kinetic potential, its effective section is given by surface integrals.

§ 3. For a compressible fluid or gas in irrotational motion equation (1) is replaced by

$$\int\frac{dp}{\rho}+\frac{\partial\phi}{\partial t}+\tfrac{1}{2}\Sigma u^2=f(t),$$

and the volume integral is to be taken after multiplication by ρ. When compressibility is admitted we must recognize the existence of energy associated with compression, and separate the pressure from this element of intrinsic energy. Thus using $\rho v=1$ as in thermodynamics,

$$\rho\int\frac{dp}{\rho}=\rho\int v\,dp=\rho\left(vp-\int p\,dv\right)=p-\rho\int p\,dv=p+\rho\mathrm{U}\text{ say.}$$

The integral then stands

$$\int\left(p+\rho\mathrm{U}+\rho\frac{\partial\phi}{\partial t}+\frac{\rho}{2}\Sigma u^2\right)d\tau=0, \quad . \quad . \quad (14)$$

where $\int\rho f(t)d\tau$ is neglected for the same reason as before. In lieu of (3), recognizing the variability of ρ, we have

$$\frac{d}{dt}\int\rho\phi\,d\tau=\int\frac{\partial}{\partial t}(\rho\phi)\,d\tau-\int\rho v_\nu\phi\,d\mathrm{S}+\int\rho v_\nu\kappa\,d\sigma. \qquad (15)$$

Again

$$\int\left(\rho\Sigma u\frac{\partial\phi}{dx}-\phi\frac{\partial\rho}{\partial t}\right)d\tau=\int\left\{\rho u\frac{\partial\phi}{\partial x}+\ldots+\phi\frac{\partial}{\partial x}(\rho u)+\ldots\right\}d\tau$$

$$=-\int\rho v_\nu\phi\,d\mathrm{S}+\int\rho\frac{\partial\phi}{\partial\nu}\kappa\,d\sigma,$$

which in conjunction with (15) makes

$$\frac{d}{dt}\int\rho\phi\,d\tau=\int\rho\frac{\mathrm{D}\phi}{\mathrm{D}t}d\tau+\int\rho\left(v_\nu-\frac{\partial\phi}{\partial\nu}\right)\kappa\,d\sigma. \quad , \quad (16)$$

or we have (4) repeated without modification. If we write (14) as

$$\int\left(p+\rho\frac{\mathrm{D}\phi}{\mathrm{D}t}\right)d\tau=\int(\tfrac{1}{2}\Sigma u^2-\mathrm{U})\rho\,d\tau,$$

and add (16) we get

$$\int p\,d\tau+\frac{d}{dt}\int\rho\phi\,d\tau=\int(\tfrac{1}{2}\Sigma u^2-\mathrm{U})\rho\,d\tau-\int\rho\left(\frac{\partial\phi}{\partial\nu}-v_\nu\right)\kappa\,d\sigma,\ (17)$$

a result differing from (5) only in the term containing intrinsic energy.

A change in the position of a barrier σ gives rise to no ambiguity in the kinetic potential, for it means an equal change in the estimate of each side of equation (17), and the added term has the form $\frac{df}{dt}$. It is in fact $\frac{d}{dt}\int\rho\kappa\,d\tau$, where the integral extends to the space bounded by the two positions of the barrier and a strip of S.

For the case of sound originated by the vibration of a solid some simplification is possible. We omit κ in (17) write $\rho=\rho_0(1+s)$ and treat s as small. We have then

$$\rho\mathrm{U}=p_0\left(s+\frac{\gamma}{2}s^2\right),$$

while $$-\frac{\partial\phi}{\partial t}=\frac{\gamma p_0}{\rho_0}s=\mathrm{V}^2s,$$

and the second term in $\rho\mathrm{U}$ becomes $\frac{\rho_0}{2\mathrm{V}^2}\left(\frac{\partial\phi}{\partial t}\right)^2$. This taken with $\int\frac{\rho}{2}\Sigma u^2\,d\tau$, if ρ_0 is put for ρ, gives

$$\frac{\rho_0}{2}\int\left\{\overline{\frac{\partial\phi}{\partial x}}\Big|^2+\overline{\frac{\partial\phi}{\partial y}}\Big|^2+\overline{\frac{\partial\phi}{\partial z}}\Big|^2-\frac{1}{\mathrm{V}^2}\overline{\frac{\partial\phi}{\partial t}}\Big|^2\right\}d\tau.$$

In applying (13) to this expression we may omit the second surface integral as of the third order of small quantities, and the effective part is therefore $-\frac{\rho_0}{2}\int\phi\frac{\partial\phi}{\partial\nu}d\mathrm{S}$. The first part of $\rho\mathrm{U}$ is $\int p_0 s\,d\tau$, or as $(1+s)d\tau=d\tau_0$ element of original volume, if p_0 and ρ_0 are constant the integral is $p_0\int(d\tau_0-d\tau)$, and the second factor is the total diminution in volume of air. Thus if we alter the meaning of τ and τ_0, so that they represent the whole volume of the *solid*, τ_0 corresponding to the state of rest, the effective part of the kinetic potential is

$$L = -\frac{\rho_0}{2}\int\phi\frac{\partial\phi}{\partial\nu}dS - p_0(\tau-\tau_0). \quad . \quad . \quad . \quad (18)$$

Finally, if there is vortex motion the existence of a function corresponding to pressure is dependent on the vortex equations being satisfied. The integral $\int p\, d\tau$ may continue to behave as a kinetic potential, though possibly the character of the latter may be modified by the conditions for the existence of a pressure-function.

XXXVIII. *On Reflexion from Glass at the Polarizing Angle.* *By* Lord RAYLEIGH, *O.M., Pres.R.S.**

ACCORDING to Fresnel's theory the polarization is complete when light is reflected at the Brewsterian angle ($\tan^{-1}\mu$) or, as we may put it, light vibrating in the plane of incidence is not reflected at all at the angle in question. It has long been known that this conclusion is but approximately correct. If we attempt to extinguish with a nicol sunlight reflected from ordinary glass, we find that at no angle of incidence and reflexion can we succeed. It is difficult even to fix upon an angle of minimum reflexion with any precision.

The interpretation of these deviations from Fresnel's laws is complicated by uncertainties as to the nature of surfaces of transition from one medium to another. It is certain that many, if not all, surfaces attract to themselves films of moisture and grease from the surrounding atmosphere, and the opinion has been widely held that even in the absence of moisture and grease solid bodies are still coated with films of condensed air. Other complications depend upon possible or probable residues of the polishing material used in the preparation of optical surfaces. It was mainly for these reasons that I gave much attention some years ago† to the case of reflexion from *water*, where at any rate there was no question of a polishing powder and atmospheric moisture could introduce no complication. It was found that Jamin's results, up to that time considered standard, were entirely vitiated by films of grease. Special operations are necessary to remove these films. When proper precautions are taken, the intensity of reflexion at the polarizing angle may be less

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* Communicated by the Author.

† Phil. Mag. xxxiii. p. 1 (1892); Scientific Papers, iii. p. 496.

than $\frac{1}{1000}$ of what Jamin observed. It appeared, however, that the cleanest surfaces were not those which gave the least reflexion. At the highest degrees of purity the light again began to undergo reflexion, though to a very limited amount. The effect had changed *sign*.

The contamination which produces the effects observed by Jamin is but slight, regarded from any other than the optical or capillary point of view. The thickness of the film of olive oil which suffices to stop the movements of camphor fragments deposited upon water, is 2×10^{-7} cm., or about $\frac{1}{300}$ of λ_D. But such a film, or even a much thinner one, entirely disturbs the delicate balance upon which depends the absence of reflexion at the polarizing angle.

For a long time I have intended to make an examination of the corresponding phenomena when light is reflected from a surface of *glass*. I was prepared for complications depending upon moisture and grease, but thought that perhaps I could deal with them. As to the thickness of the films there is little definite information. Theory* indicates that they are likely to be persistent. A long while ago Magnus established the conclusion "that all substances, however different they may be, are raised in temperature when air comes in contact with them which is moister than that surrounding them, and that they are depressed in temperature when they are exposed to air which is drier than that by which they are surrounded" †. His experiments included glass, quartz, mica, caoutchouc, metals, and many other substances. In the case of glass, or rather cotton silicate, definite estimates have been given by Parks ‡, deduced from actual increases of weight. He finds thicknesses of the order $1{\cdot}0 \times 10^{-5}$ cm., about 50 times that of the greasy films which stop the camphor movements upon water and profoundly modify the reflexion of light at the polarizing angle. Even if we allow a good deal for the fact that these films were formed from a saturated atmosphere, enough will remain to explain much optical disturbance.

The deviation from Fresnel's formulæ is best explained in terms of Jamin's k, representing the ratio of reflected amplitudes for the two principal planes when light, incident at the angle $\tan^{-1}\mu$, is polarized at 45° to these planes. According to Fresnel $k = 0$, but Jamin showed that it may assume small finite values, positive or negative. The experimental method employed for the present purpose was

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* Phil. Mag. xxxiii. p. 220 (1892); Scientific Papers, iii. p. 523.

† Phil. Mag. xxvii. p. 245 (1864).

‡ Phil. Mag. v. p. 518 (1903).

substantially the same as in the former observations upon water, and can only be sketched briefly here. Sunlight reflected horizontally from a heliostat was caused to traverse the polarizing nicol mounted in a circle which allowed the rotation to be read to a minute of angle. After reflexion from the plate under examination the light traversed in succession a quarter-wave-plate of mica and the analysing nicol and was then received into the eye, either directly, or with the intervention of a small telescope magnifying about twice. A green glass was also often introduced in order to mitigate chromatic effects. Both the mica and the analysing nicol were mounted so as to be capable of rotation about the direction of the reflected ray.

The theory of the method is as follows. Fresnel's expressions S and T (*sine*-formula and *tangent*-formula) give the ratios of the reflected to the incident vibrations, for the two principal planes; and their *reality* indicates that there is no change of phase in reflexion (other than 180°). The *ellipticity* is represented by the addition to T of $i\mathrm{M}$, where M is small and $i=\sqrt{(-1)}$. Thus if the incident light be polarized in the plane making an angle α with the principal plane, the reflected vibrations may be represented by

$$(\mathrm{T}+i\,\mathrm{M})\cos\alpha, \quad \mathrm{S}\sin\alpha.$$

By the action of the mica, suitably adjusted, a relative change of phase $\frac{1}{2}\pi$ is introduced. This is represented by writing for $\mathrm{S}\sin\alpha$, $i\,\mathrm{S}\sin\alpha$. The vibration transmitted by the analyser, set at angle β, is then

$$\cos\alpha\cos\beta(\mathrm{T}+i\mathrm{M})+i\mathrm{S}\sin\alpha\sin\beta\;;$$

and the intensity of this is

$$\mathrm{T}^2\cos^2\alpha\cos^2\beta+(\mathrm{M}\cos\alpha\cos\beta+\mathrm{S}\sin\alpha\sin\beta)^2.$$

In order that the light may vanish, we must have both $\mathrm{T}=0$ and

$$\mathrm{M}+\mathrm{S}\tan\alpha\tan\beta=0,$$

the first of which shows that the dark spot occurs at the Brewsterian angle, while $\tan\alpha\tan\beta$ gives the value of M/S, viz. the k of Jamin. Accordingly if β be set to any convenient angle (such as 45°) and α be then adjusted so as to bring the dark spot to the central position, the product of the tangents of α and β, each measured from the proper zeros, gives k.

In practice it is not necessary to use the zeros. Set β, *e. g.* to $+45°$, and find α; then reset β to $-45°$. The new value of α would coincide with the old one were there no ellipticity; and the difference of values measures α upon a doubled scale. If α' be the second value, so that the difference is $\alpha'-\alpha$, then

$$k=\tan\tfrac{1}{2}(\alpha'-\alpha),$$

or with sufficient approximation in most cases

$$k=\tfrac{1}{2}(\alpha'-\alpha).$$

The sign of $\alpha'-\alpha$ is reversed when the mica is rotated through a right angle, and the absolute sign of k must be found independently.

The subjects of observation have been principally two plates, of which the first is of black glass, *i. e.* glass containing sufficient absorbing material to be opaque. When first examined on May 24 (1907) it had been lying in a box for many years. Carefully cleaned by washing and wiping, it gave $\alpha'-\alpha=+5^\circ$, β as throughout being $\pm 45^\circ$. On polishing rather protractedly with rouge, it gave $\alpha'-\alpha=+35'$, a large reduction. Blowing at the surface while under observation with a stream of chemically dried air had very little effect.

Want of sunshine prevented further observations until Aug. 3, when $\alpha'-\alpha$ was found to be about $+1^\circ$. Treatment with rouge reduced this to $+40'$, and so far as appeared neither heating (with the idea of removing grease) nor treatment with specially moist or specially dry air made much difference. But on further repolishing with rouge the ellipticity practically disappeared. There was no certain change in the position of the dark spot when β was altered between $\pm 45^\circ$.

It seemed that the earlier treatments with rouge had been inadequate. In the last application the polisher was of paper cemented to glass and impregnated with the rouge. After polishing, the glass was breathed upon and carefully wiped with a cloth. In subsequent operations this procedure was always followed.

Further observations showed that even on Aug. 3 the polishing had not been carried far enough. On Aug. 7 $\alpha'-\alpha$ was made to change sign, being reduced (algebraically) to $-10'$ or $-22'$. This was about the limit. Even in this condition the surface did not seem sensitive to moisture, much to my surprise. And it was matter for further surprise when it appeared that 24 hours' exposure to the air of the room—no chemical operations were in progress—sufficed to carry the surface back to the positive side with $\alpha'-\alpha=+10'$, increased in a few days to $+40'$. These changes of sign were observed not only with the black glass, which on the evidence of its polarizing angle is a flint, but also with a piece of patent plate prepared by roughing the hind surface and varnishing it with a cement of nearly the same index. It may be mentioned that another piece of patent plate became good on treatment with hydrofluoric acid and polishing with rouge upon a *soft* tool. After deterioration by exposure the negative values of $\alpha'-\alpha$ could not be recovered by merely cleaning the plate with moisture and wiping; actual repolishing was necessary. The natural inference is that even within 24 hours the substance of the glass is actually attacked by the gases of the atmosphere.

As I was leaving home for some time I arranged an experiment to see whether careful protection would save a glass surface from the above described deterioration, which might probably be attributed to moisture and carbonic acid. Accordingly on Aug. 22 the black glass, giving $\alpha'-\alpha=-14'$, was put away in a tube containing potash and closed, probably airtight, with a rubber cork. On Oct. 15, nearly two months later, the glass was taken out and (with surface untouched) gave $\alpha'-\alpha=-6'$, still on the negative side. The difference of values, though doubtless real, is perhaps no more than may be attributed to moisture and carbonic acid imprisoned with the glass. Four days later the readings gave $+35'$. The plate glass put away at the same time with potash in another tube with $\alpha'-\alpha=-19'$ was examined after two months, on Oct. 19, and gave $\alpha'-\alpha=+4'$, so that in this case the protection seems to have been less efficient.

A large number of further observations were made upon both glasses with the object of ascertaining, if possible, how much of the change which ensues after repolishing is due to a film of foreign (greasy) matter deposited from the atmosphere and how much to an alteration of the glass itself. The negative condition, lost in a day or two after repolishing, is in part recovered under the operation of a careful wiping with moisture, but only to a limited extent. Full recovery requires actual repolishing. It is of course possible that even the mild treatment by wiping may attack the very thin film of altered glass which is all that we can suppose to have been formed in so short a time; but on the whole the evidence pointed to two kinds of contamination, one removable by wiping and the other requiring the more drastic treatment with rouge. In spite of some easily understood irregularities, it appeared that the full effect of wiping was easily produced and that repetition could carry the process no further. The same conclusion is favoured by the results of heating the plate pretty strongly. The same kind of recovery in the direction of the negative condition could thus be attained, but never to the full extent. In some experiments the plate was purposely contaminated. Thus on Nov. 1 a repolished plate at $-13'$ was exposed to the smoke of burning greasy waste, after which $\alpha'-\alpha$ was $+46'$. A very thorough treatment by wiping took it back to $-6'$, but only after repolishing could the original condition $(-10')$ be nearly recovered. In another experiment a stream of air which had passed over petroleum was directed against a repolished surface, but the effect was only momentary. As regards surfaces which have stood a week or two, I think there can be no doubt but that the glass itself has been seriously attacked.

The results here recorded are in many respects very different from what I had anticipated—especially the comparative insensitiveness to grease and moisture. It must be remembered, however, that a surface finished by wiping and in contact with air is certainly contaminated with water and probably with grease. In spite of this it is possible to have the reflexion *free from ellipticity.* As regards grease we may perhaps argue from the manner in which the breath is deposited. A freshly split surface of mica receives the moisture of the breath as an almost invisible film, showing the colours of thin plates as it evaporates, but nothing of the appearance ordinarily associated with dew and dependent upon an irregular deposition. I am not sure whether glass has ever been observed in this condition*, but experience from the days of wet collodion photography convinces me that a wiped glass does not so behave. The best that can be attained is a uniform dull grey appearance, such as under a magnifier would exhibit lenticular drops.

The conclusion which suggests itself is that even a recently repolished surface, which may exhibit but small ellipticity, is in a highly complicated condition. Grease itself may be comparatively inoperative optically on account of its index approximating to that of the glass. But why varying degrees of moisture should make so little difference is not apparent. Surface phenomena generally offer a wide field for investigation, which might lead to results throwing much needed light upon the constitution of matter.

Terling Place, Witham.

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* Possibly the path of an electric discharge over a glass surface may be a case in point.

XXXIX. *The Variation of Manganin Resistances with Atmospheric Humidity.* *By* F. E. Smith, *A.R.C.Sc.* (From the National Physical Laboratory.) *

IN the issue of 'The Electrician' dated June 14th, 1907, Drs. Rosa and Babcock published an article of great interest under the above title. A long series of measurements on manganin resistances was given, and it was shown that the higher resistances exhibited a yearly cycle corresponding to the variations in the relative humidity of the atmosphere. Later †, Drs. Jaeger and Lindeck published results proving that the variations of many high resistances at the Reichsanstalt were quite negligible even when the humidity was believed to have appreciably changed. That the humidity variations at Washington were not very abnormal has been shown by Dr. Rosa ‡, and it appears, therefore, that some shellaced coils remain approximately constant with varying humidity, while others change by considerable amounts. Indeed, Dr. Rosa emphasizes the point, that of the resistances examined by him the coils of nominally equal value did not change by equal amounts.

The changes in resistance of the manganin standards of the National Physical Laboratory have been reported on from time to time, and we have also stated that small changes in the resistances of 1 ohm coils have been detected within twenty-four hours. On the publication of the paper by Drs. Rosa and Babcock, we were, therefore, convinced that some of the changes we had observed were due to variations in atmospheric humidity, and shortly afterwards we proceeded to measure the effect of humidity on various standard coils.

The first coil experimented with was one of 10,000 ohms of manganin, of the Reichsanstalt form, and made by O. Wolff of Berlin. It was placed inside a box through which passed two well-insulated copper leads connected to mercury cups, to which also the leads of the coil were connected. The metal cylinder surrounding the coil was removed so that the shellac was fully exposed to the atmosphere. The box was made practically air-tight by coating it on the outside with paraffin wax, and the humidity inside the box was varied by introducing a large quantity of fused calcium chloride, or by the insertion of water contained in large crystallizing dishes. The temperature could be varied by placing the box inside a large electric oven, but it was not allowed to exceed 35° C. Measurements of resistance were made at an approximately constant temperature of 17° C.

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* Communicated by Dr. R. T. Glazebrook, F.R.S.

† 'The Electrician,' Aug. 2, 1907. ‡ 'The Electrician,' Nov. 15, 1907.

After the 10,000 ohm coil had been in the box for 8 days in an atmosphere dried with fused calcium chloride, its resistance was identical with its value in an atmosphere of 60 per cent. relative humidity. When water was substituted for the calcium chloride and 20 days had elapsed, the resistance of the coil was 7 parts in 100,000 *lower* than before; but on opening the box and exposing the coil to the outer atmosphere, the resistance rose to to its normal value within 20 minutes. We concluded, therefore, that the low value was a result of leakage, and we suspected the presence of a thin film of moisture on the ebonite. In some later experiments such a film was visible, and the main leakage was undoubtedly that between the current leads of the coil and the metal cylinder on which the coil is wound. The gap between the leads and the cylinder is about 5 mm. In the experiments cited above the temperature of the box and its contents was raised to 35° C., but as this appeared to be a doubtful procedure, all subsequent experiments with coils in saturated atmospheres were made at the temperature of the air.

We next placed the 10,000 ohm coil in an atmosphere dried with phosphoric anhydride, and after the expiration of 30 days its resistance was again measured. It was 2 parts in 100,000 lower than normal. Afterwards, acting on a suggestion from Dr. Rosa, the coil was sealed inside a glass beaker, at the base of which either fused calcium chloride, or phosphoric anhydride, or water could be placed. Before sealing (when a dry atmosphere was desired) the beaker and its contents were placed for 8 hours in an atmosphere at low pressure—the pressure recorded being 3 cms. of mercury. After the coil had been exposed for 4 days to the action of an atmosphere dried with phosphoric anhydride, the resistance was 1 part in 100,000 lower than normal, and after being exposed for 4 days in an atmosphere approximately saturated with water, the resistance was 11 parts in 100,000 low. The latter effect was again found to be due to leakage, for on exposing the coil to the air of the room the resistance between the current leads rose in the following manner:—

Before exposure to air of room, resistance low by 0·011 p. cent.
After

3	minutes	,,	,,	,,	,,	0·008	,,
4	,,	,,	,,	,,	,,	0·005	,,
5	,,	,,	,,	,,	,,	0·004	,,
6	,,	,,	,,	,,	,,	0·003	,,
12	,,	,,	,,	,,	,,	0·002	,,
25	,,	,,	,,	,,	,,	0·001	,,

The first coil experimented with exhibited, therefore, no appreciable change in resistance with change in humidity.

Our next experiments were made with five other standard coils and some resistance-coils in boxes, but before giving the results obtained with them, it may be of interest to give an idea of the amount of moisture absorbed by the shellac coating a resistance-coil.

Mr. Melsom, who has constructed very many standard coils, shellaced a metal cylinder of the same size as those used in the winding of standard coils of the Reichsanstalt pattern, and afterwards he baked it and treated it in the same way as standard coils are treated. After remaining for 10 days in a desiccator containing phosphoric anhydride, this shellaced cylinder weighed 51·2614 grams, and after being hermetically sealed for 10 days in a beaker containing a little water at 17°·0 C. its weight was 51·2816 grams; an increase of 0·02 gram. It appears that, after calibration, such a cylinder might be used as an hygrometer.

The other standard coils examined are five in number. One of these, No. 2449, is by O. Wolff, Berlin; and the remaining four were made by Mr. Melsom in accordance with the Reichsanstalt specification. In Table I. the results are recorded. The value of the resistance in air having a relative humidity of about 60 per cent. at 17° C. is taken in each case as the unit, and the variations from this value, when the coils were placed in atmospheres approximately dry and approximately saturated, are given in parts in 100,000. The time during which a coil was exposed to the action of a particular atmosphere is indicated at the head of a column, and

Table I.

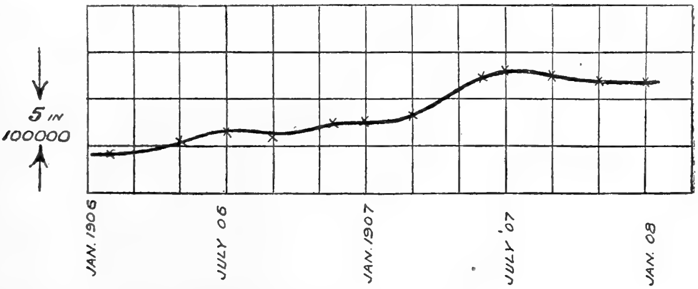
Coil.	Nominal Value.	Atmosphere dried with P_2O_5 for					Atmosphere saturated with water for						Change.
		3 days	4 days	5 days	6 days	10 days	2 days	4 days	6 days	10 days	18 days	24 days	
L. 19...	ohms 10	−15	−16	−18	−17	−18	+2	+3	+6	+18	+23	+23	+41
L. 143...	10	−1	−2	−2	−4	−3	+23	+36	+38	+38	+36	+37	+40
L. 140...	100	−9	−13	−17	−14	−16	+20	+25	+38	+40	+48	+48	+64
L. 139...	1000	−3	−2	−2	−1	−2	+16	+17	+30	+35	+35	+37	+39
2449 ...	1000	−2	−2	−4	−2	−3	+6	+8	+8	+9	+11	+11	+14

the probable increase in resistance when a coil is taken from a dry to a saturated atmosphere at 17° C. is given in the last column.

Here we have positive evidence of changes in standards of the best construction; and the fact that the coil made by O. Wolff is affected by varying humidity to a less extent than the coils made by Mr. Melsom points either to a difference in the shellac varnishes employed, or to an effect due to the ageing of the varnish, or both. The changes recorded in Table I. are comparable with those given by Drs. Rosa and Babcock.

It is of interest to compare the changes in resistance from Jan. 1906 to Jan. 1908, of one of these coils with the humidity change given in Table I. For this purpose the coil L. 19 is chosen because it has been kept under very close observation. In comparing the changes it is necessary to bear in mind that during the period 1906–8 the coil L. 19 was kept in oil, and hence the variations of atmospheric humidity would have an appreciably less effect on the shellac, and hence on the resistance, than when the coil was exposed to the air. The observations on L. 19 for 1906–8 are summarized in the form of a curve, from which it will be seen that the resistance has gradually increased since Jan. 1906 by about 8 parts in 100,000; that maxima occur about July each year, and that it is improbable that the change in resistance due to humidity variations has exceeded 2 parts in 100,000, or one-twentieth of the change recorded for the same coil in Table I. Observations on other manganin coils, immersed in oil, indicate maximum changes in their resistances, due to variations in atmospheric humidity, of the order of 1 part in 100,000.

Curve showing variation in 10 ohm manganin resistance L. 19.



Of air-cooled manganin coils coated with shellac, a number in boxes, by R. W. Paul and by O. Wolff, have been measured from time to time, and the seasonal changes of resistance—especially in the case of the Paul box—must have been very small, certainly less than 1 part in 10,000.

The floor of the standardizing room at the National Physical Laboratory is about four feet below the outer ground-level, and the room is maintained at a temperature not less than 17° C. In the summer months the temperature rises at times to 20° C. We have no records of the hygrometric state of the air of the room over long periods of time, but a series of observations has been commenced.

In Table II. the results are given of some measurements on manganin coils in a box by Messrs. Nalder Bros. The outer case was removed, and a larger one substituted for it. In this larger box, water, fused calcium chloride, or phosphoric anhydride could be placed, and the air inside the box could be heated by an electric lamp and stirred by a small motor-driven fan. The shellaced cylinder, previously referred to, was also hung inside the case, and was weighed from time to time to roughly determine the hygrometric state of the atmosphere.

TABLE II.

Observations on Coils in Nalder Box 3921.

Coils.	Nominal Value	Atmosphere dried with P_2O_5 for			Atmosphere saturated with water for			Maximum change.
		2 days	6 days	20 days	2 days	4 days	20 days	
	ohms.							
4000 3000 2000 1000 } ...	10000	−3	−5	−6	+9	+16	+17	23
1000	1000	0	0	0	+1	+ 3	+ 3	3
400 300 200 100 } ...	1000	−2	−5	−6	+1	+ 6	+ 7	13
100	100	−1	−2	−4	+1	+ 3	+ 5	9
40 30 20 10 } ...	100	0	0	−2	+2	+ 5	+ 5	7
Weight (in grams) of shellaced cylinder		51·265	51·264	51·263	51·280	51·281	51·283	

The range of the box is from 4000 ohms to 1 ohm. Measurements were made of some individual coils and of some in series, as indicated in col. 1, Table II. The change in resistance is given in parts in 100,000, the values in an atmosphere of about 60 per cent. relative humidity at 17° C. being taken as unit values.

Table III. gives the variations in resistance of some coils in box No. 2385 by O. Wolff, the results of the observations being in chronological order. It is noteworthy that when the box-coils were measured in an atmosphere dried by P_2O_5, the resistance of the three higher coils diminished by appreciable amounts, but the 1000 and 100 ohm coils remained practically constant. When, however, the atmosphere was converted into one saturated with moisture, the 100 ohm coils alone remained approximately constant in resistance; the value of the other coils *fell* by very considerable amounts. Although this fall was probably entirely due to leakage, it persisted, in a diminished degree, after exposure of the coils to a normal atmosphere for thirty days.

Table III.

Observations on Coils in Wolff Box No. 2385. Unit Values in an atmosphere of about 60 per cent. relative humidity at 17° C.

Coils.	Nominal Value.	Atmosphere dried with P_2O_5 for				Water.	Normal Atmosphere.		
		2 days	3 days	7 days	10 days	4 days	1 day	10 days	30 days
50000 &c.	ohms. 100000	–25	–31	–36	–38	–2100	–220	–33	–15
10000 *β*	10000	–27	–40	–56	–59	– 630	–310	–71	–25
10000 *α*	10000	–20	–25	–33	–35	– 520	–265	–77	–18
1000 *β*	1000	0	0	– 1	– 2	– 58	– 31	– 6	– 2
1000 *α*	1000	0	0	0	– 2	– 61	– 22	–10	– 4
100 *β*	100	– 2	0	0	– 1	0	+ 2	0	0
100 *α*	100	0	0	– 2	– 2	+ 1	+ 2	+ 1	0

In the case of this box the humidity effect is seen only in the change of resistance resulting when the coils were transferred from a normal atmosphere into a dry one. When the saturated atmosphere was substituted, the leakage effect quite masked over any effect due to elongation of the wire by expansion of the shellac.

It will be seen that our observations do on the whole support the conclusions arrived at by Drs. Rosa and Babcock, and that coils hermetically sealed, or coated with a varnish which does not absorb moisture, must have an advantage over manganin coils coated with shellac. The fact that some high-resistance coils exhibit the "humidity effect" to a negligible extent only, points to the possibility that a shellac varnish may be prepared, which, after baking, is not appreciably hygroscopic.

XL. *Minimum Spark Potentials.*

By JOHN E. ALMY, *Ph.D.*[*]

RECENT work of Earhart[†], Shaw[‡], Hobbs[§], and Kinsley[||] dealing with spark potentials for very short spark-gaps seem to show that the spark-discharge may take place at potentials far below the so-called "minimum spark-potential." These results, so signally at variance with the results of Carr[¶] and others, who have found every evidence of a minimum value of potential, below which it was impossible to obtain a discharge with any spark-gap or any gas pressure whatever, seem to require further careful investigation.

At first, two spark electrodes were mounted upon an interferometer of the Fabry-Perot type, one electrode being carried upon the table that carries the movable plate of the interferometer, the other being fixed adjacent to the second plate of the interferometer. The supports were fairly rigid, being of massive brass plates, reinforced. In attempting to use electrodes which were segments of a sphere of 5 cm. radius, and later, using spheres of 1 cm. radius, it was noted that a discharge, or at any rate a short-circuit of the discharge circuit, was obtained with potentials considerably below the "minimum potential" (about 350 volts in air at atmospheric pressure), but that when this occurred the electrodes were invariably drawn together and remained fused together; while in case the potential was raised above the minimum potential this fusing together of the electrodes rarely if ever results. It sometimes happened that with

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[*] Communicated by the Author.

[†] Earhart, Phil. Mag. [6] i. p. 147 (1901).

[‡] Shaw, Proc. Roy. Soc. lxxiii. p. 337 (1903).

[§] Hobbs, Phil. Mag. [6] x. p. 617 (1905).

[||] Kinsley, Phil. Mag. [6] ix. p. 692 (1905).

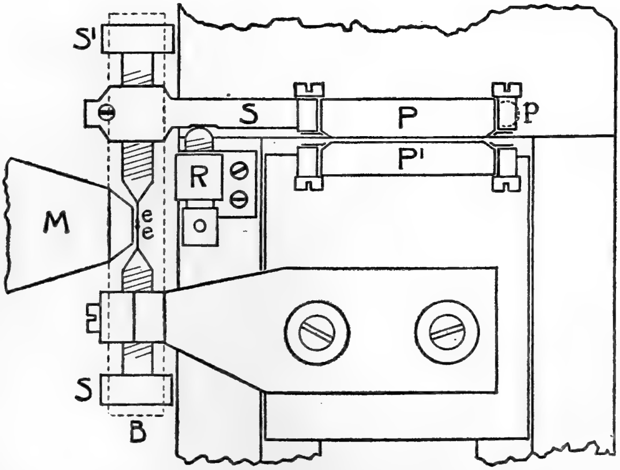
[¶] Carr, Proc. Roy. Soc. lxxi. p. 374 (1903).

potentials near 350 volts a rapid series of discharges or short-circuits would occur, accompanied by a humming note, very like that of the Trevelyan rocker; evidently the electrodes were set in rapid vibration by the electrostatic force between the charged electrodes. Clearly the supports were not sufficiently rigid.

This phenomenon suggests the possibility that what have been considered spark-potentials for very short sparks may not have been at all the potentials required to give a disruptive discharge through the gas between the electrodes, but were rather the potentials necessary to give sufficient electrostatic attraction between the electrodes to cause a displacement equal to the spark-gap, thus bringing the electrodes in contact. If this be true, the potential required to effect a discharge, with these short distances, would be a function of the size of the electrode, especially if that size were comparable in magnitude to the spark-gap.

In order to investigate this question the following apparatus was devised: Spherical electrodes of minute dimension were obtained by fusing in the oxy-hydrogen flame the end of fine platinum wire, ·0057 cm. in diameter; the smallest spheres thus formed had a radius very approximately ·0035 cm. and were essentially true spheres. Two such electrodes were mounted on the interferometer, as shown in fig. 1 (horizontal section). The electrodes *e e* are carried on screws that thread very tightly through the steel supports; one support is rigidly clamped to the moving carriage of the interferometer,

Fig. 1.



being insulated by ebonite; the second, S, is carried on the frame which carries one plate of the interferometer, this plate, P, being supported on a post, *p*, about which, as a vertical axis, it is free to rotate but for the stop R, which was made as rigid as the other parts of the apparatus. To take up "back lash" and any looseness in the adjustment of parts, a number of strong indiarubber bands, B B, were stretched around the electrodes pressing upon the screw heads, *s s*; a high-power microscope M, placed horizontally, made possible the careful alignment of the minute electrodes, and enabled one to follow visually the course of effects. Without the rubber bands it was impossible to get the system sufficiently rigid so that the electrodes were not visibly moved when potentials near 300 volts were applied to spark-gaps of a few wave-lengths of sodium light; with the bands in place the separation of the electrodes follows promptly the displacements of the bands of the interferometer, and that the rubber bands did not affect the accuracy of the interferometer in the measurement of the spark-gap, at least so far as the motion of the interferometer plates is concerned, was shown by determinations of the wave-length of sodium light, in which the same values were obtained with and without the rubber bands in place.

The electrical system used was the usual one; a battery of storage-cells gave 1200 volts potential, this was connected through a cadmium-iodide-amyl-alcohol resistance to earth; the spark-gap and a Weston voltmeter, in parallel, were shunted on this resistance with movable electrode in the iodide solution, so the potential applied to the spark-gap could be varied at will and read off directly. For a time, an auxiliary circuit with 2·2 volts and a galvanometer were used to detect short circuit of the spark-gap, but the settings made in this way proved less definite and capable of repetition than those made with from 10 to 20 volts on the regular spark circuit. The method of procedure was usually this: With the electrodes clearly in contact at the start, they were moved apart by steps of ·1 wave-length (Na), testing with the 10 volts for a short circuit *after* each step; as soon as open circuit was obtained the electrodes were then separated by a certain number of wave-lengths and the potential gradually raised to a value somewhat less than the "minimum potential"; if, after waiting a sufficient interval, this potential failed to give a discharge, the spark-gap was decreased by a wave-length and again tested; when this process had been repeated until the spark-gap was unquestionably extremely small and had been subjected to the high potential several minutes with no evidence of discharge, the potential was reduced to 10 volts and the distance measured through which the electrodes needed to move to give short circuit. For example, using two platinum spheres each approximately ·007 cm. in diameter the following observations are noted :

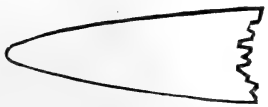
Applied Potential.	Spark-gap.	Remarks.
325 volts.	1 wave-length.	No spark.
275 ,,	·8 ,,	,,
310 ,,	·4 ,,	No discharge.
310 ,,	·55 ,,	No discharge, potential applied 5 minutes.
340 ,,	·6 ,,	Discharge occurred.
340 ,,	1·5 wave-lengths.	,, ,,
340 ,,	2·5 ,,	A single spark occurred but no second could be obtained at that potential.
365 ,,	same.	Second spark occurred.
340 ,,	3 wave-lengths.	A single spark.
340 ,,	5 ,,	,, ,,
410 ,,	10·5 ,,	Discharge repeatedly.

Using spheres of unequal size, with diameters ·008 cm. and ·0057 cm. the following results were obtained :

280 volts ; no discharge ; gap measured ·8 wave-length.
310 ,, ,, ,, ·7 ,,
335 ,, ,, ,, ·6 ,,
350 ,, discharged ; ,, ·6 ,,

Next a pair of steel needles were substituted for the minute spheres. Needle-points are by no means geometrically pointed, but are usually more approximately parabolic, in the axial section. The appearance of the needles used, as seen in the microscope, is shown in fig. 2; the diameter at a distance from the tip equal to the radius of curvature at the tip was approximately ·0007 cm. With two such electrodes the following observations dealing with spark-gaps of less than a wave-length of sodium light were made :

Fig. 2.



320 volts applied ; no discharge ; gap measured ·9 wave-length.
330 ,, ,, ,, ,, ·7 ,,
330 ,, on 5 minutes, no discharge ; gap ·5 ,,
330 ,, applied ; no discharge ; gap measured ·25 ,,

By taking a definite spark-gap and gradually increasing the applied potential until a discharge, or short-circuit, resulted, the following observations were made:

Spark-gap, ·15 wave-length; at 270 volts circuit closed, no discharge was observable in the microscope.
Spark-gap, ·2 wave-length; at 345 volts circuit closed, electrodes were found to be fused together.
Spark-gap ·35 wave-length; at 360 volts a spark passed, clearly visible, circuit remained opened for lower potentials.

The evidence seems conclusive that with spark-gaps down to at least ·3 wave-length of Na light, that is, ·0000177 cm. *a potential of* 330 *volts is not sufficient to produce discharge through air at atmospheric pressure*, while 360 volts is sufficient to do so.

It is of interest to notice the nature of the discharge with these minute spark-gaps. Through the microscope (magnifying about 500 times), the discharge that occurs with potentials near the "minimum potential" is seen to be a quiet luminous glow discharge, the luminescence beginning at a point somewhat back from the needle tip, completely surrounding the needle and extending back along the needle (one electrode only), exactly similar to the negative glow around a cathode in gas at low pressure. But at the tip of the needle no luminosity was evident. While with higher potentials a brilliant, concentrated, discharge passed in a more limited path, appearing in the microscope much like a long arc-discharge results. With a gap of several wave-lengths on a few occasions the passing of scintillating particles (dust or metallic ?) from one electrode to the other was noticed; once or twice this occurred with potentials below the "minimum," but could not be repeated. The following observations made with steel needles as electrodes are illustrative (p. 461).

It seems conclusive from the observations given that, at any rate when minute electrodes, comparable in size to the size of the spark-gap, are used, there is a "minimum potential" below which, no matter what the spark-gap, a true spark-discharge does not take place. And there seems large probability that Paschen's law of inverse proportionality of spark-length to gas pressure is equally applicable to spark-gaps shorter than that corresponding to the "minimum potential." Some work has been done to verify this, with fair success at pressures below atmospheric; at atmospheric pressures the distances concerned are so extremely small that the problem of determining the sparking potential, when the discharge is compelled to pass through the short path, is one of great difficulty. The results obtained will be given in a later paper.

Spark-Gap (wave-lengths).	Potential (volts).	Remarks.
·4	345	No discharge.
·3	345	,,
	350	Glow discharge.
1·0	345	No discharge.
	350	Glow discharge.
1·5	345	No discharge.
	350	Glow discharge.
2·5	345	No discharge.
	350	Glow discharge.
4·0	345	No discharge.
	350	Glow discharge.
7·5	320	Scintillation: ceased immediately.
	350	Glow discharge; continuous.
	440	Arc discharge produced.
9·0	490	Arc discharge; no glow obtained.
10·0	505	,, ,, ,,
12·5	530	,, ,, ,,
15·0	600	,, ,, ,,

Considering the electrostatic force which exists between two large electrodes brought within such minute distances as were used by Earhart, Shaw, and Hobbs, it seems not wholly improbable that the strains sufficient to bring their electrodes into contact may have occurred with potentials less than the "minimum." So that the potentials that produce a short circuit in the spark-gap were simply those required to give the requisite displacement of the electrodes.

In connexion with this question of short sparks, attention may be called to the fact that Earhart[*], and Shaw[†], in recent work upon spark potentials in liquid dielectrics have apparently made no attempt to ensure absence of dust or other foreign particles from the liquids tested. True, Earhart gives as argument for this disregard the fact that the spark-potential for the second and succeeding sparks was the same as the first, but that is, in truth, evidence showing that the dust *already present does* affect the discharge potentials. It is well known that the passage of a spark in any insulating oil invariably results in the formation of carbon particles, and these particles collect between the electrodes, and it hardly seems probable that the presence of particles of so

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[*] Earhart, Phys. Rev. xxiii. p. 358 (1906).

[†] Shaw, Phil. Mag. [6] p. 317 (1906).

good a conducting material as carbon in the spark-gap could be entirely without effect upon the discharge. Rather, it seems likely that the particles present before the first spark were as effective as carbon particles. The writer* has shown clearly that the passage of a spark through an oil does very materially affect the potential required to produce the discharge. So that, valuable as the results of Earhart and Shaw are as representing the actual working conditions which usually obtain, they may not be taken to represent the potentials necessary to produce spark discharges through the distances given, in the pure liquid.

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XLI. *The Greenhouse Theory and Planetary Temperatures.*

By Frank W. Very†.

When Tyndall, as the result of his measures of the absorption of terrestrial radiation by water-vapour, assured us that the removal of moisture from its atmospheric covering would plunge the British Isles into a more than Arctic winter, he directed attention to that which, next to the solar radiation itself, is the most potent factor in terrestrial climate. In a general way this is now universally recognized; but we have not yet arrived at unanimity as to the details of the process by which this protective agency works, or of their applicability to other worlds than ours.

Never having had any experience with gases devoid of convection, nor with solids lacking thermal conductivity, it is perhaps hardly safe to speculate as to how such substances would or would not behave; but if a guess may be hazarded on the subject of Professor Poynting's ideal greenhouse‡, one would suppose that if the background were absolutely nonconducting, unless it were a perfect reflector, in which case it would not be heated at all, the heating effect of solar rays would be increased in something like the proportion of six to one even without any glass. For if we suppose cubical particles, each containing a cubic centimetre of perfectly absorbing and conducting substance, to be maintained in the sun's rays at an excess of 10° above an initial temperature of 300° A., and then reduce the thickness of the normal absorbing

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* Almy, *Ann. der Phys.* [4] i. p. 508 (1900).

† Communicated by the Author.

‡ J. H. Poynting, "On Prof. Lowell's Method for Evaluating the Surface Temperatures of the Planets," Phil. Mag. [6] vol. xiv. p. 749, December 1907.

layer from 1 cm. to $\frac{1}{1000}$ cm., the radiating surface being only one-third as much as before, we should have, if there were no loss of heat by convection, three times the thermal effect, giving an excess of 27°·5 by the fourth-power law. But if the thin strip were backed by nonconducting material, the radiating surface would be only one-sixth of that of the cube, while the thermal effect of the same solar radiation would be six times as great, and the excess would be 49°·4.

Now, where a layer of conducting material of indefinite thickness is to be heated, a day is too short a time to reach thermal equilibrium; but for an infinitesimal layer a day is relatively an infinite time; and since the glass of the greenhouse roof is supposed to let in rays which are transformed at the surface into others which cannot get out, or can get out only in small part, a fraction of the heat from inward radiation must be added to the heat of the infinitesimal layer at each radiant transfer from solid to glass and back, until the temperature of the superficial layer of the solid background is raised so high that it either begins to give out radiations which *will* penetrate glass, or until the glass emits an equal radiation. If the layer is really nonconducting, or what is the same thing thermally, if its thickness is infinitesimal and its radiation one-sided, or again, if the background conducts but has been exposed to insolation so long that the interior temperature gradient is zero at the surface, a second is long enough for the entire process; or if the glass transmits a little of the infra-red, and a single layer of glass is insufficient to give the maximum effect, additional ones will complete the realization of the maximum temperature in static equilibrium.

Now, as we are not making a world, but only an ideal, or perhaps I should say a transcendental greenhouse, there is nothing to hinder us from piling story on story until we get a greenhouse, let us say, fifty stories high. At first each added story will capture a little extra heat, and this will also go on accumulating until the absorption of the additional sheets of glass for the solar rays is greater than their power to obstruct the passage of radiation of long wave-length, and thus to increase the amount of heat trapped. By making our glass thin enough, however, we can entirely obviate this difficulty; for by making a greenhouse of one thousand stories, each covered with glass one one-thousandth as thick as that of the ordinary greenhouse, the absorption will be no greater, but the heat-trapping will increase up to a certain point in proportion to the number of chambers traversed. Such a structure will have a cumulative action resembling that of a bundle of imperfectly reflecting mirrors, which, if numerous enough, reflect as well as a more perfect one. In the present case, the mirror must be supposed to have the peculiar quality of being transparent to the ingoing radiation, and a perfect reflector of the outgoing rays; but with such a mirror, if it were possible to obtain it, there would be no possibility of stopping the accumulation of heat short of a temperature at which penetrating rays of solar quality are emitted.

With absorbent, instead of reflective layers, the temperature can only increase until, in the steady state, the roof radiates out as much as the sun sends in. But since the roof then radiates greatly inward to the background, the latter is receiving the direct solar rays as before there was a roof, and also an equal amount of returned radiation. Hence the thermal effect is doubled. The maximum heat-trapping effect is reached when the inmost layer of the roof and the background reach the same temperature, or when equal amounts of energy are interchanged between these surfaces according to Prévost's law of exchanges. The condition is represented in Poynting's equation for the greenhouse effect,

$$\frac{\mathrm{R}}{\mathrm{S}}=\frac{t+a/n}{t_1+(n-1)a_1/n}{}^{*}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if $t=1$, $a=0$, $t_1=0$, $a_1=1$, and $n=2$, when $\mathrm{R/S}=2$. This is of course the maximum increment of thermal energy which it is possible to get by means of a greenhouse provided simply with an absorbent covering. The more perfect our heat-trapping device becomes, the nearer will be the approach to this ratio. If the number of chambers is not indefinitely great, n must be a little larger than 2, because each successive chamber in the outward direction is at a little lower temperature, and radiation outward, being towards a colder surface, exceeds radiation inwards.

Having demonstrated the properties of our ideal glass house, I might leave the subject with the remark that at first blush neither it nor Professor Poynting's greenhouse bears the remotest resemblance to our actual complex world. But if the temperature of an ideal planet all depends on hypotheses, let us introduce into our discussion assumptions which make for warmth rather than cold; because evidence drawn from astronomical observations indicates that there is abundant warmth at the surfaces of the more distant planets. I shall endeavour to show that the higher temperatures agree better with facts of observation and with theory.

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* t and a denote the transmission and absorption of solar rays (S), and t_1, a_1 the same for ground radiation (R), while $1/n$ is the fraction of glass radiation sent downward.

If we look a little further into the matter, perhaps we shall find that my greenhouse raised to the thousandth power is not so much of a *reductio ad absurdum* as one might suppose; for have we not increasing evidence that matter is really discontinuous, or that it is a form consisting of innumerable chambers? Thermal energy is transferred from molecule to molecule in the interior of a body by a process which involves a time-factor and a discontinuous mechanism. Restore these by giving our background conductivity, and we have again the analogue of the thousand-story greenhouse in the capacity of matter for storing up heat, quite apart from the atmospheric effect.

Short of a duplicate thermal effect, there is no reason why various mechanisms of this sort may not go on increasing in temperature until the emission of short-waved æther vibrations which will penetrate the outermost layers of the protecting roof limits the further acquisition of stored-up energy—that is, there would be none so long as we retain the further property which Professor Poynting assumes, that the atmosphere has no convection. This, however, is too wide a departure from actuality to be permissible in considerations which are to have any bearing on natural phenomena on this earth. Experiment has given the following relative losses of temperature by radiation and by convection: For a small thermometer, heated to 15° C. in sunshine, about three-tenths of the heat is lost by convection; but in a thin strip of blackened platinum similarly heated, the loss by convection is twice as great as that by radiation. Up to a temperature-excess of about 15° C., convective emission from a body of the size of a thermometer-bulb increases rapidly. After this, convection is more nearly a constant proportion of the total loss of heat. At high temperatures, radiation, which varies nearly according to the fourth power of the absolute temperature in solids, is increasingly potent to diminish heat, while the air becomes viscous, and convection is impeded; but for small differences of temperature at moderate temperatures, such as would exist in successive chambers of the multiple greenhouse, convection is of importance in assisting to limit the possible accumulation of heat.

I have tried the effect of successive enclosures of ordinary glass around a sun-thermometer, and find that there is very little heat gained after two or three layers have been added. But probably the progression would be more noticeable if glass of a very thin lamination could be procured. I have indeed used mica with some success.

In an experiment where a black-bulb thermometer in air was exposed to the sun's rays in an enclosure protected by three layers of thin glass, separated by air-spaces, I obtained a reading of 104° C., the shade temperature in the air being 35° C. The altitude of the sun was 50°, and the solar radiation was 1·30 small calories per square centimetre per minute (obtained with a mercury pyrheliometer). The temperature of the superficial layer of the soil was not taken, but is usually about 10° higher than the air temperature for the given altitude of the sun. Admitting that a layer of soil about 1 cm. deep was maintained at a temperature of 45° C. by the sun's rays, the retention of heat was augmented by three layers of glass in the ratio

$$\left(\frac{104+273}{45+273}\right)^4=1{\cdot}975.$$

This already approaches the theoretical duplicate ratio, and yet nothing has been allowed for heat-trapping by the atmosphere which, with a relative humidity of 42 per cent., must have been considerable. Hence the ground temperature was probably higher than 45° C.

If we take the excess of surface soil-temperature over air-temperature twice as large, making the surface temperature $35+20=55°$ C., the augmentation by the three layers of glass was

$$\left(\frac{104+273}{55+273}\right)^4=1{\cdot}744.$$

Even this gives a smaller heat-retaining power to the atmosphere than it usually possesses; but except on mountains the excess of surface temperature is seldom greater than 20° C. Be this as it may, the observation certainly shows that a solar radiation of 1·3 cal./cm.^{2} min. is competent to produce a temperature above that of boiling water; and if the solar constant is as large as 3·1 cal./cm.^{2} min., which I believe to be probable, the sun can give at the earth's distance a temperature of $\chi°$, where

$$\chi^4 : (104+273)^4=3{\cdot}1 : 1{\cdot}3,$$

or

$$\chi=468° \text{ A}.$$

Langley * obtained at his mountain camp on Mt. Whitney, in a double hot-box of his design, an excess of 98°·5 C. above shade temperature. No simultaneous actinometer readings were made; but by interpolation from those of other days

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* S. P. Langley, "Researches on Solar Heat," Professional Papers of the Signal Service, No. 15, Chap. 18, p. 166.

(Table 85, p. 98, *loc. cit.*), it may be inferred that the solar radiation at the same hour, $1^h\,40^m$ P.M., was usually about 1·84 cal./cm.^{2} min. For comparison with my observation, I will suppose the shade temperature to have been the same as mine, giving a reduced hot-box temperature

$$=35+98{\cdot}5+273=406^{\circ}{\cdot}5\ \text{A},$$

whence

$$\chi=\left\{\frac{3{\cdot}1}{1{\cdot}84}\times(406{\cdot}5)^4\right\}^{\frac{1}{4}}=463^{\circ}\ \text{A}.$$

These temperatures are also in approximate agreement with that which I have found for the moon at midday (454° A.)*. The moon, unlike the earth, has a sufficiently prolonged insolation to produce a steady state of temperature, and it has so little atmosphere that very little heat is conveyed to cold parts of the planet through convection currents.

Sun temperatures at planetary surfaces are very greatly modified by atmospheric agencies. In nature the effect of convection is very marked, for the atmosphere acquires its heat mainly by convection of hot air, as well as by evaporation of moisture from a heated surface, and by the distribution of these thermal increments by means of atmospheric circulation.

Atmospheric heating by the absorption of radiation is accomplished with especial efficacy in two layers—one high up, the other near the surface. The multiple greenhouse has therefore a further analogue ; for the incoming solar rays are most efficacious in warming the air in the upper layers of the atmosphere where these rays first meet the atmospheric moisture. A very considerable fraction of infra-red solar radiation is taken out by line and band absorption in the upper air. In passing through the first ten kilometres of air containing appreciable moisture, or what may be called the aqueous atmosphere, certain rays are struck out from the spectrum completely. These rays do not enter into our formula for atmospheric absorption. They have been lost completely and do not reach the earth's surface. Consequently the readings of actinometers which take no account of these lost rays, even after correction for the apparent absorption of the atmosphere determined by high and low sun comparisons, give only the solar radiation, minus an unknown line and band absorption. The solar radiant energy kept back

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* F. W. Very, "The Probable Range of Temperature on the Moon," Astrophysical Journ. vol. viii. p. 284, December 1898.

by those atmospheric constituents which have the first opportunity to exercise absorbent action, is used in increasing the temperature of the upper air, and is probably responsible for a large part of the excess of temperature above that which would be indicated by the adiabatic rate, which has been made known by the records of sounding balloons. The observations of Teisserenc de Bort, who was the first to confirm the existence of this hypothetical warm upper layer of air, have now been extended by the German sounding balloons to a height of 25 kilometres, to which height the aqueous atmosphere certainly sometimes ascends. Undoubtedly the height of the aqueous atmosphere is a variable quantity, subject to wide fluctuations which are partly responsible for the variations of surface temperature. In summer time, the lower part of the aqueous atmosphere stores up a great amount of heat, giving hot waves when descending currents prevail during periods of high barometer. In winter. on the contrary, the periods of high barometer may be attended by cold waves, because the heavily moisture-laden layer in immediate contact with the surface is swept away, and surface radiation escapes freely; but the cold would then be far more intense if it were not for the presence of the rarer layers of the aqueous atmosphere, which still remain as a warm layer at no great altitude, but are unable to affect surface temperatures much by direct radiation, since the emission of radiation by a gas through a deep layer of its own substance is small on account of its great absorptive power for its own radiation.

The second region of atmospheric heating by absorption of radiation is one near the surface where the infra-red radiations from either land or water are so thoroughly absorbed at certain wave-lengths that these cannot escape except by a slow process of absorption and reradiation many times repeated. In this respect also, the illustration of the multiple greenhouse is again valid, and surface temperatures would accumulate until they became unbearable, did not convection overturn the atmospheric heat-retaining structure.

The retaining action of an atmosphere for surface heat cannot be represented by so simple a device as that of a thin sheet of perfectly conducting glass, having the same temperature at its upper and lower surfaces. It seems to me that in part Professor Poynting's argument is irrelevant as regards the problem of the surface temperature of a planet without the inclusion of further details. If Professor Poynting will turn his great mathematical ability to the consideration of some of the numerous alternative hypotheses, it seems probable that a much wider range of possibilities may appear. Even if the complete differential equations cannot now be attempted, the problem can be taken up in sections, as he has done for a part of the process, investigating one influence after another separately, but of course recognizing that these will have mutual modifications which must be considered in the final summing up.

Take, for example, the climatic influences involved in the evaporation and condensation of water. M. Liais many years ago estimated that this process has a very large part in determining terrestrial thermal conditions. I will suppose, in illustration, that we seek the effect of this factor on the climate of Mars. Assuming that the barometric pressure is much smaller on Mars, a supposition for which there is good reason, evaporation of moisture at a given temperature will be more rapid, and condensation more difficult than here. Consequently, at that temperature, more moisture can exist in the atmosphere of Mars, diffusing to a great height, and still the relative humidity will remain low*. The smaller relative humidity diminishes the strength of the broad diffuse bands of aqueous absorption, but does not affect the line absorption. Since condensation of moisture is favoured by the presence of free ions to serve as nuclei of condensation, we should like to know something as to this condition on Mars. We do know that here, with abundance of moisture in the air, rain does not fall unless some widespread general condition of the atmosphere, which appears to be associated with its electrical state, is added to the other favouring factors. Telescopic observation of Mars shows a very considerable degree of persistence in the surface markings which indicates comparative absence of obscuring cloud, that is to say, there is less liability of rain, moisture remains long in the air, and the continuity of the protecting aqueous envelope is more complete. Though less heat is received, the final result, if more is stored, may be not very different in the two planets so far as this factor is concerned.

Professor Lowell† emphasizes the importance of albedo in

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* Since this was written, Mr. Slipher has obtained at the Flagstaff Observatory spectrograms of Mars showing intensification, not of the comparatively feeble "rain band" near D which has been the subject of much contention in the past, but of the much more powerful water-vapour band "*a*" in the extreme red. I have had the privilege of examining the original photographs, and can testify to the certainty of the evidence they bring of the presence of water-vapour in the atmosphere of Mars.

† Percival Lowell, "Temperature of Mars," Proc. American Acad. Arts and Sciences, vol. xlii. p. 651, March 1907.

determining a planet's temperature, and shows that a planet's albedo is largely atmospheric. This being so, since about a third of the sun's radiant energy resides in the visible spectrum where selective scattering is most effective, the earth, with its greater albedo, receives a smaller proportion of heat at its surface than Mars on this account. In the visible region of the spectrum, the radiant absorption by gases is small, and the blanketing action of the atmosphere *nil*, because there are no rays of this wave-length emitted by its heated surface; but the larger proportion of heat received from this part of the spectrum by the ground of Mars produces, if the absorbent and conducting properties of the surface are the same, a relatively larger radiation of infra-red rays outward, which is at the same time proportionally better preserved.

Land temperatures on this earth exceed those over water. Mars has the land climate. The heat-storing powers of the soil are also greater with a dry climate. Again, the conditions on Mars favour a greater thermal effect from the same amount of solar radiation. That the cumulative effect of so many factors acting in one direction can largely overpower a deficiency of that due to remoteness from the sun, is a conclusion which is at least permissible; and if computations founded on reasonable assumptions lead to results which are in good agreement with the seasonal indications deduced from the fluctuations of a snow-cap whose existence is far more probable than some of the hypotheses made in arguments against its possibility, it seems to me that the balance of the evidence inclines strongly towards Professor Lowell's conclusions.

In treating the subject of atmospheric selective depletion of radiation, a more accurate result might be obtained by treating the diffraction by air molecules, and the selective reflexion from dust separately; but without going into this refinement, an approximate knowledge of the reflective depletion of the solar rays falling on an air-covered planet can be reached if we admit that the transmission, so far as it depends on reflexion, varies as t_r^ϵ, where t_r is the reflective transmission for rays at the zenith, and ϵ is the air mass. The depletion will then be $1-t_r^\epsilon$, and the total reflective depletion for the entire surface of the sunlit atmosphere is

$$\Sigma(1-t_r^\epsilon)\times\Delta\cos\zeta,$$

where ζ is the sun's zenith distance. For $t_r=0{\cdot}6$,

$$\Sigma(1-t_r^\epsilon)\Delta\cos\zeta=0{\cdot}677,$$

which corresponds very nearly with the depletion for a solar altitude of 27°.

Bearing in mind that the discussion at this point does not relate to the line and band absorption which follow different laws, the value of $1-t_r$, or the atmospheric depletion by diffraction and selective or scattering reflexion, may be approximately as follows:—

By taking the spectral energy-curves given in my reduction of the Mount Whitney observations [*], and making a further reduction to sea-level, Professor Lowell obtains [†] for the light reflected by the air from sea-level upwards, the fraction 0·74. In the reduction to sea-level, observations made at different places and times, and with different instruments, were used, which is objectionable, but unavoidable, It is also desirable to differentiate the depletion in the infra-red into several kinds. I do not know that 0·74 is too large for the air-reflexion of visible rays, but we shall be taking a lower limit if we make it 0·6. It cannot be as much for the air above clouds. As clouds hang at very different altitudes in the air, no exact statement can be made as to the light reflected by the air before the sun's rays reach the cloud level. Let it be 0·3, and the reflexion from clouds 0·72, as has been given by observation. Then the light reflected from a cloudy area of the earth's surface will be $0·3+(0·72\times 0·7)=0·804$, giving the albedo of a half-clouded earth, $\frac{1}{2}(0·6+0·8)=0·7$. Only a small amount of infra-red radiation is reflected by the air. Let us say 0·2 for clear air, and 0·1 for the air above clouds. But the clouds also do not reflect the infra-red rays as well as they do the visible rays; for I have been able to determine the position of the sun bolometrically through clouds so thick as completely to hide it from the eye. Allowing that clouds may reflect the infra-red rays half as well as the luminous ones, infra-red reflexion from a cloudy area is $0·1+(0·36\times 0·9)=0·424$. One third of the rays being visible, the total reflexion over cloud is

$$(0·33\times 0·804)+(0·67\times 0·424)=0·549.$$

The reflexion by clear air is

$$(0·33\times 0·6)+(0·67\times 0·2)=0·332\ ;$$

and the mean reflexion from a half-clouded earth for the entire spectrum is $\frac{1}{2}(0·549+0·332)=0·44$, giving $t_r=0·56$.

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[*] U.S. Weather Bureau Publication No. 254, "The Solar Constant," fig. 1, p. 21.

[†] Proc. American Academy of Arts and Sciences, vol. xlii. p. 656 March 1907.

Professor Poynting objects* to Lowell's value for the reflexion of light by the air as being too large. "On another point," he says, "common observation appears, at any rate at first sight, to contradict Professor Lowell. He assumes that the loss in the visible spectrum radiation in its passage through the atmosphere is practically all due to reflexion, and he puts it down as about 0·7 of the whole in clear sky. If this were true the reflexion from the sky opposite to the sun would I think be vastly greater than it is. White cardboard reflects diffusely about 0·7 of sunlight. But when a piece of white cardboard is exposed normally to the sun's rays, it is several times brighter than the cloudless sky."

This is true if the white surface is compared with a deep-blue sky far away from the sun; but it is not always true for the sky near the sun, and the upward reflexion towards the sun is probably nearly proportional to the downward reflexion when the sky is only slightly hazy. I tried the following experiment on a day with hazy blue sky, whitish near the horizon:—The sun being at an altitude of 20° and shining on fresh snow, I measured with a wedge-photometer the visibility (*a*) of a wide area of bright background, and (*b*) that of a narrow dark bar projected on the same background, getting for

Sky near the Sun................	(*a*) 13·5 mag.	(*b*) 13·0,
Sky at horizon, azimuth 45° from sun ..	12·0	11·5,
Snow in sunshine....................	12·0	11·5.

Taking the ratio of brightness corresponding to the difference of magnitudes, the sky near the sun was four times as bright as the sky at the horizon; but the latter was as bright as the sunlit snow. I confess that I was surprised at the last equality, for the sunlit snow gave me the impression of greater brightness; but this impression is no doubt due to the absence of colour in the snow, while the blue tint of the sky gives one a conception that the sky-light is dimmer than it really is. The sky at the horizon was half a magnitude brighter, or 1·6 times as bright as the sky at an altitude of 20° and azimuth 90° from the sun.

A repetition of the experiment on another occasion gave me the following results:—The sky was a pale blue with a few fracto-cumuli, but without appreciable cirrus-haze. The observations were made through a slit 3 cm. wide, viewed at a distance of 1 metre by means of the wedge-photometer. The point in the sky selected for measurement was distant from the sun about four diameters, or far enough away for

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* Phil. Mag. [6] vol. xiv. p. 750.

the brightness to be nearly uniform. Mean altitude of sun = 28°.

Sky, 13·0 mag.	Snow 11·7 mag.	Sky, 12·8 mag.	Snow 11·8 mag.
13·4	in 11·4	13·0	in 11·6
13·2	Sun, 11·5	13·1	Sun, 11·7
13·0	11·3	13·1	11·8
12·8	11·8	13·0	11·8
Mean 13·08	11·54	13·00	11·74

Difference of magnitude, 1st set, Sky = +1·54 mag.
" " 2nd " " +1·26 "

The mean difference is sky = +1·4 magnitude, or the sky had 3·63 times the brightness of sunlit snow.

With a clear blue sky, I found for—

Sun's altitude = 30°, snow 1·6 times brightness of sky,
" " = 10°, sky 1·35 " " snow.

It appears from these comparisons that the discrepancy between the brightness of the sky and of a white sun-illumined surface is not as great as one is apt to guess.

If one stands with his back to the sun and compares the light reflected from the sky with that from a piece of white paper, the former comes principally from remote depths of air, and has suffered further depletion in returning thence to the eye. It is therefore not to be expected that the air should reflect as well as a piece of white paper held close to the eye.

It will no doubt be agreed that the depletion suffered by the sun's rays in the middle of the visible spectrum is not due to telluric absorption-bands, but results solely from diffraction and scattering reflexion. I measured the light from the sun, when it was about to set, and compared its intensity in the green of the spectrum with that which the same region had when the sun was 30° high. The intensity of green light from the nearly setting sun was 0·0000065 times that at the higher altitude. The relative air-masses were 2·0 and 24·4, that at the zenith being unity. The zenithal transmission corresponding to that for air-mass 24·4 was therefore

$$(0{\cdot}000\,0065)^{\frac{1}{24{\cdot}4-2{\cdot}0}} = 0{\cdot}587,$$

and the transmission at a middle altitude of 30° was $(0{\cdot}587)^2 = 0{\cdot}345$, or the depletion equal to 0·655, which must be further increased in a summation for the entire exposed hemisphere, becoming 0·690. This value is too small, because the reflexion from dust is to a certain extent independent of the air mass; but it represents fairly well the reflective depletion for the entire spectrum.

Although the above is only a single observation which would have to be repeated on many different occasions to give a thoroughly reliable result, it is at least something better than a guess. To this depletion must be added the band absorption which chiefly affects the infra-red spectrum, and may be taken for moderate altitudes above the horizon in temperate latitudes as $0·3 \times 2/3 = 0·2$, but which is probably twice as great for the entire earth with its moist tropics.

The radiation received from a zenith sun is $(A-B) \times t_r$, where A is the solar constant, and B is the band absorption. If A is 3 calories per square centimetre per minute,

$$(A-B)t_r = (3·0-0·6) \times 0·56 = 1·34 \text{ cal.},$$

a quantity which is not often exceeded at sea-level.

In regard to selective, reflective depletion of the solar rays, it is clear that radiation of every wave-length undergoes more or less superficial reflexion at the outside surface of suspended particles of dust, ice crystals, &c. This differs in no wise from the reflexion at the surface of a mirror, although if the particles be many-faceted, the rays will be reflected in many directions and may not be distinguishable from the diffuse reflexion from internal bubbles or other discontinuities in a transparent but turbid medium. This surface reflexion is a general one, or in the visible spectrum we should call it a colourless one. If the rays penetrate a little way into the substance before being reflected, certain rays may be absorbed, giving selective reflexion, which in the visible spectrum we call coloured reflexion. Melloni coined a special word for the selection of invisible rays, labelling it "thermochrose," but the distinction is not needed. Finally, molecules and particles whose dimensions are small relatively to the wave-length give selective diffraction which varies progressively with the wave-length. I have used the word depletion to cover losses by all of these processes without individual specification. Any part of the solar radiation which is reflected back into space can have no effect on planetary temperature. This precept is so obvious that it seems strange that it should be overlooked.

In considering the effect on climate it is not so easy to decide how we ought to treat the band absorption. So far as absorption occurs in the upper air, it raises its temperature, and this the more on account of the low density of the air at great altitudes. Any extra warmth in the higher layers of the atmosphere must have some effect in raising the temperature of lower ones. Heat transferred from earth to air is partly lost as radiation from air and cloud before being returned to earth. Whether the loss is counterbalanced by heat from absorption of solar rays in the upper air brought down to earth in descending air-currents as an accession to the potential temperature which is represented by the work stored up in a previous expansion, it might be difficult to determine; but quite a large part of the band absorption may be indirectly useful in enhancing surface temperatures. Professor Lowell cuts the Gordian knot by an ingenious method which dispenses with a knowledge of these data. Before passing to it, I wish to consider what Professor Poynting calls the "greenhouse effect" in planetary temperatures a little more in detail.

In Poynting's equation for the atmospheric greenhouse effect, $1/n$ is the fraction of the radiant energy absorbed by the air which is returned downwards. Of n Professor Poynting says: "I do not see how to estimate the distribution of the radiation from the air between the upward stream into space and the downward stream to the surface." This being so, I propose to substitute values for the other factors which are less problematical and determine n. Following Lowell, Professor Poynting has assumed $a_1=0{\cdot}5$, $a=0{\cdot}325$, $t_1=0{\cdot}5$, $t=0{\cdot}42$. From (1) we obtain

$$n=-\frac{a_1\mathrm{R}+a\mathrm{S}}{t\mathrm{S}-t_1\mathrm{R}-a_1\mathrm{R}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let $\mathrm{S}=3$ cal./cm.^{2} min.$=2{\cdot}1\times10^6$ ergs/sec., which distributed over the whole earth becomes one fourth of this, or $5{\cdot}25\times10^5$ ergs/sec. Taking the mean temperature of the whole earth as $\theta=288°$ A.,

$$\mathrm{R}=\sigma\theta^4=5{\cdot}32\times10^{-5}\times288^4=3{\cdot}66\times10^5 \text{ ergs/sec.}$$

Substituting these values in (2), $n=2{\cdot}43$, that is, less than half of the atmospheric radiation comes downwards; but the determination probably has little or no significance, because the storing effect of the atmosphere is not a purely radiant effect. In fact the radiation from the atmosphere to the earth is comparatively small, as I have shown in my "Atmospheric Radiation." Although much of the energy of terrestrial radiation absorbed by the air comes back to the ground, it does so largely by modes other than radiant, such as the condensation of water-vapour into rain. The greenhouse effect, using the term in a very wide sense, may still be attained, but by a very complicated process.

If we apply Poynting's equation in its strictly limited sense to my hot-box experiment, its use becomes legitimate. The following approximate values are close enough for illustration: Take $t=0{\cdot}8$, $a=0{\cdot}2$, $t_1=0$, $a_1=1$, $(\theta_s/\theta)^4=1{\cdot}744$. Substituting in the equation

$$(\theta_s/\theta)^4=\frac{t+a/n}{t_1+(n-1)a_1/n}, \quad . \quad . \quad . \quad . \quad (3)$$

$$n=1{\cdot}944/0{\cdot}944=2{\cdot}06,$$

which is in substantial agreement with Professor Poynting's supposition that one half of the radiation of the glass goes downward, although, of course, my experiment does not quite fulfil his requirement of a greenhouse of indefinite extent.

In the application of the formula of Arrhenius to the cloud-covered half of the earth's surface, Poynting says that Lowell "finds that this half only receives 0·2 of the radiation which the clear-sky half receives. The surface temperature under cloud should therefore be only $\sqrt[4]{0{\cdot}2}=0{\cdot}67$ of that under clear sky. If the latter is 300° A., the former is only about 200° A. Common observation contradicts this flatly, for the difference is at most but a few degrees." This only illustrates the inadequacy of a consideration of the problem from a purely radiant aspect. Suppose that the clouds are so dense that only one per cent. of solar radiation reaches the surface. Must we presume that the temperature will immediately fall to near the absolute zero? Not at all. The true surface temperature cannot be found unless the heat received be linked with the heat lost. This Lowell does, obtaining from his analysis of day and night temperatures on the earth a value of the relative emissivity of the earth, and finding that only about 16 per cent. of the heat received from the sun's rays in the day-time is lost by radiation into space in the twenty-four hours. What becomes of the rest? Obviously if so much heat is retained, the earth must be getting hotter. The answer to the question is that the earth *does* get hotter in summer, but the extra heat is lost in winter; and the entire process requires an estimate of the heat transferred from the summer to the winter hemisphere by the winds of the globe.

On p. 749 (*loc. cit.*) Professor Poynting says that Lowell "pays hardly any attention to the 'blanketing effect,' or, as I prefer to call it, the 'greenhouse effect' of the atmosphere."

It is true that Professor Lowell does not consider the greenhouse effect analytically and obviously, but it is nevertheless implicitly contained in his deduction of the heat retained, obtained by the method of day and night averages. The method does not specify whether the heat is lost by radiation or by some more circuitous process; and thus it would not be precise to label the retaining power of the atmosphere a "greenhouse effect" without giving a somewhat wider interpretation to this name. If it be permitted to extend the meaning of the term to cover a variety of processes which lead to identical results, the deduction of the loss of surface heat by comparison of day and night temperatures is directly concerned with this wider "greenhouse effect." The method employed by Professor Lowell is a good one, for it dispenses with a detailed knowledge which we may hope to possess eventually, but which, when found, cannot be incompatible with the conclusions deduced by the less circumstantial method. Thus the objection which Professor Poynting makes to the method where he says that Lowell "neglects both the surface radiation reflected down again and the radiation downwards of the energy absorbed by the atmosphere," seems to me to be, on the contrary, one of the strong points in its favour; because for its use it is not necessary that we should know these details. The transmission by cloud for solar and terrestrial radiation may not be the same; but if a complex of radiant and convectional processes which cannot be represented by so simple a formula as that of Arrhenius, gives a virtual equality of depletions under cloudy or clear sky, which can be represented by the statement that, though less heat is received under cloud, less is also lost and in about the same proportion, the precise part assigned to each fraction of the process does not affect the argument.

Reverting to my simile of the bundle of mirrors, transmitting some rays and perfectly reflecting others, may it not be possible to realize it? It is known that there are some transparent substances, such as quartz, which have bands of metallic reflexion in the infra-red spectrum. If there were gases in which such bands were sufficiently numerous in the infra-red without too seriously encroaching upon the visible part of the spectrum, it would be possible to obtain almost any increment of temperature at the surface of a planet covered by such selectively reflecting gases.

The major planets have atmospheres containing unknown and highly absorbent gases which produce bands in the visible spectrum, increasing in strength with the distances of the planets from the sun. These bands invade the red end of the spectrum, but diminish in width and blackness towards the shorter waves, and die out near the middle of the visible spectrum. This suggests that there may be present in the atmospheres of these planets substances having very numerous and intense absorption bands in the infra-red ; and if these bands are so strong that they give metallic reflexion for surface radiation, even the small amount of energy in the solar radiation on Neptune can be so largely stored up that a high surface temperature is maintained by the accumulated heat. The great inclination of the axes of the two outer planets, whereby large parts of their surfaces remain for long years in a state of arctic night, may serve in this case as a safety-valve by the .transferring of heat to cold regions by atmospheric circulation, thus preventing too great an accumulation in the sunward zones. I believe that this, though problematical, is a plausible explanation of the high temperatures which exist on the major planets, as evidenced by the vigour of their atmospheric circulation, the formation of cloud-belts, &c., which has driven some astronomers to maintain that these planets are much younger than the earth, although there is no reason for such a supposition, and much weighty evidence to the contrary.

If in equation (1), distinguishing between relative losses by reflexion and absorption, so that the completed equation (*vide* Poynting) is

$$R = tS + r_1R + \tfrac{1}{2}(aS + a_1R), \quad . \quad . \quad . \quad . \quad . \quad (1')$$

we put $t=0{\cdot}1$, $r=0{\cdot}7$, $a=0{\cdot}2$, $a_1=0{\cdot}01$, $r_1=0{\cdot}99$, $t_1=0$, we find for $n=2$,

$$R = 40\,S.$$

I will take for the maximum or steady temperature in sunshine at the earth's distance a mean of my three values, $1/3(468+463+454)=462°$ A. Then, since the inverse square root of Neptune's distance from the sun is 0·18, the sun temperature at Neptune is $462 \times 0{\cdot}18 = 83°$ A. $=\theta_s$, and

$$\theta_N = \sqrt[4]{40 \times (\theta_s)^4} = 323° \text{ A.} = +50° \text{ C.};$$

that is, it is possible for Neptune to have a torrid climate from the solar rays alone without owing anything to its own internal heat, and this without requiring any exceptional action of its atmosphere on luminous rays, or such as would be noticed in telescopic examination.

After what precedes, it will be seen that we cannot compare the heat-retaining powers of the two planets, unless we have reason to believe that the heat-retaining process is similar in the two bodies considered. Thus we cannot compare the greenhouse effect for the earth and Neptune ; but Mars and the earth appear to resemble each other so nearly that Professor Lowell's method for obtaining the surface temperature of Mars is appropriate.

In this method as applied to the earth, it is assumed that clouds transmit 20 per cent. of terrestrial radiation from a surface at sea-level, and clear air 50 per cent., values which are close enough as approximations. The mean of these being 0·35, if y is the radiant energy received at the earth's surface, and e the relative emission of radiation from that surface, the heat retained is equal to that radiated from the surface, or

$$\sigma\theta^4=\sigma(288)^4=y(1-0\cdot35\,e). \quad \ldots \quad . \quad . \quad . \quad . \quad (4)$$

Lowell introduces into this equation different values obtained by observation of the loss of temperature by nocturnal radiation with clear sky, and also under a cloudy sky; and thus obtains for e the value, $e=0\cdot4634$, whence

$$\sigma(288)^4=0\cdot838\,y.$$

By the ratio of retained heat deduced from my hot-box experiment, when compared with a possible maximum retention of heat of 2 to 1, we get

$$1\cdot744/2\cdot000=0\cdot872\,y.$$

We may conclude that something like 85 per cent. of the heat received from the sun's rays is retained at the earth's surface through the greenhouse effect of the atmosphere.

For the whole earth with its moist tropics, and including marginal zones where the solar rays pass through a great thickness of absorbent, the band absorption is probably about 0·4. If 0·7 of the solar radiations are reflected from the hemisphere exposed to the sun's rays, and if of the $(1-0\cdot7)\times(1-0\cdot4)=0\cdot18$ received, 85 per cent. are retained, the temperatures involved become according to the fourth-power law

$$\sigma(288)^4=\sigma(\theta_s)^4\times0\cdot18\times0\cdot85$$
$$=\sigma(\theta_s)^4\times0\cdot153,$$

whence $\theta_s=460°$ A.

In the last part of his paper, Professor Poynting makes "an attempt to represent the effect of day and night on the temperature of the earth"; but as he neglects the conduction of the ground, and assumes that "the surface has reached an equilibrium between receipt and expenditure of radiation," a condition which is never attained on the earth, since also he considers that a large amount of radiation is absorbed by the air, "nearly 1 with the setting sun," which is not the case, and as he then introduces hypothetical values of n, the reciprocal of the fraction of air radiation radiated downwards, the attempt cannot be regarded as successful. The band absorption which alone communicates heat to the air directly, remains but a fraction of the total depletion even at sunset. I doubt if the band absorption ever exceeds 0·5.

Since no reasonable modification of the constants will enable the simple formula for a glass greenhouse to fit the atmospheric conditions on our earth, the formula is inapplicable to problems of planetary temperature without extensive modifications, except perhaps in the conceivable case of a special reflective atmosphere.

Westwood, Massachusetts,
February 7, 1908.

XLII. *The Production of Small Variable Frequency Alternating Currents suitable for Telephonic and other Measurements. By* B. S. COHEN[*].

[Plates XVI.-XIX.]

INTRODUCTION.—The devices described in the latter part of this paper are the outcome of experiments carried out in the Investigation Branch of the Engineering Department of the National Telephone Company, in order to obtain suitable alternating currents both of simple and complex wave form to act as substitutes for the voice in telephonic measurements. Although primarily designed for this purpose, it is considered possible that the apparatus to be described is capable of more extended use.

A short summary of the methods known to the author of obtaining small alternating currents of the kind suitable for telephonic measurements may prove of interest as an introduction.

Statement of the problem.—The ordinary telephonic current is a few milliamperes at a potential of about 2 to 10 volts and is of complex wave form. The frequency of the fundamental harmonic generally lies between 100 and 300 complete periods per second, *i. e.* it varies from 100∼ to 300∼, the highest harmonic having a frequency of 4000∼ to 5000∼, although all harmonics above 1500∼ are comparatively unimportant. The average frequency of the whole wave is about 800∼. From consideration of these data it follows that the ideal device for supplying such alternating current is one which will give currents of any frequency lying between 100∼ to 500∼, singly or in combination. The output of this

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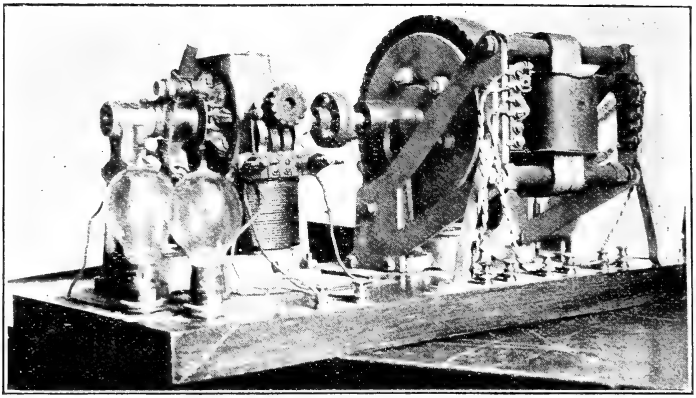
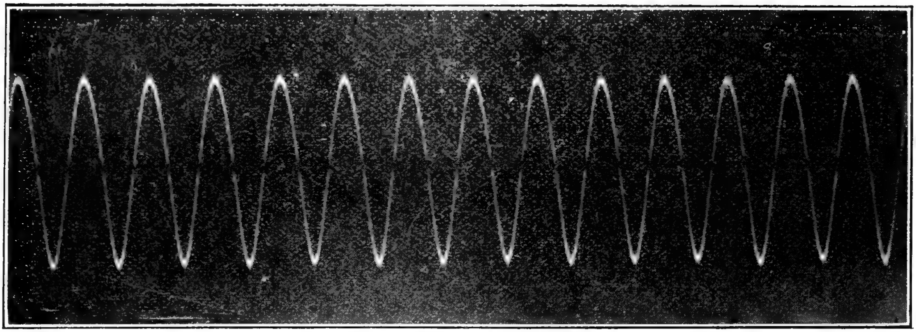
[*] Communicated by the Physical Society: read May 22, 1908.

Fig. 1.



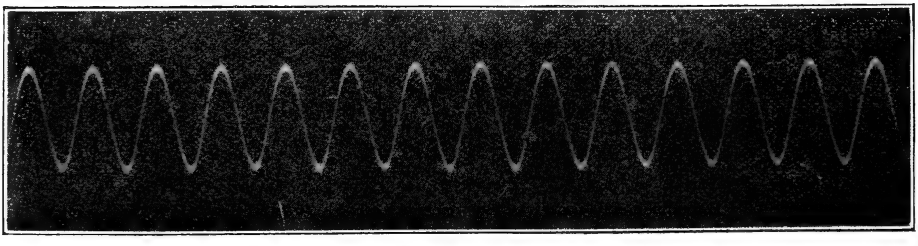
N. T. Co. Alternator.

Fig. 2.



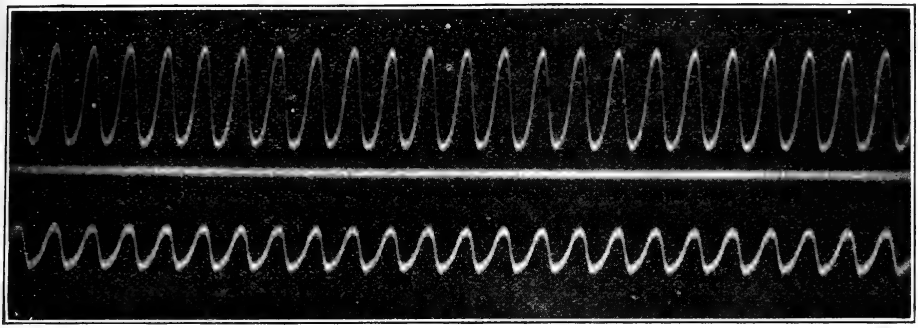
Unfiltered Wave.

Fig. 3.



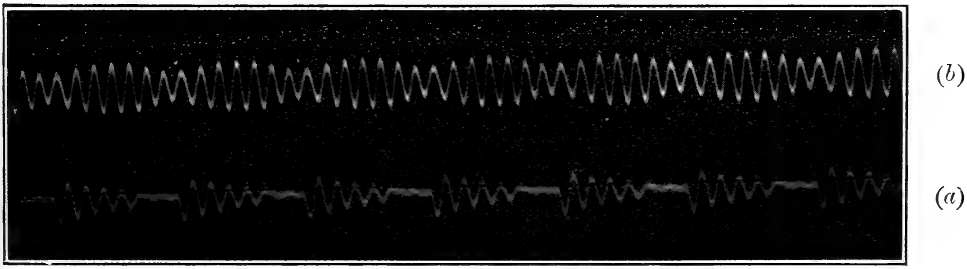
Filtered Wave.

Fig. 4.



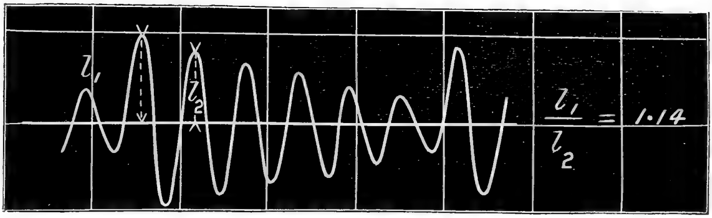
Waves in primary and secondary of humming telephone instrument.

Fig. 18.



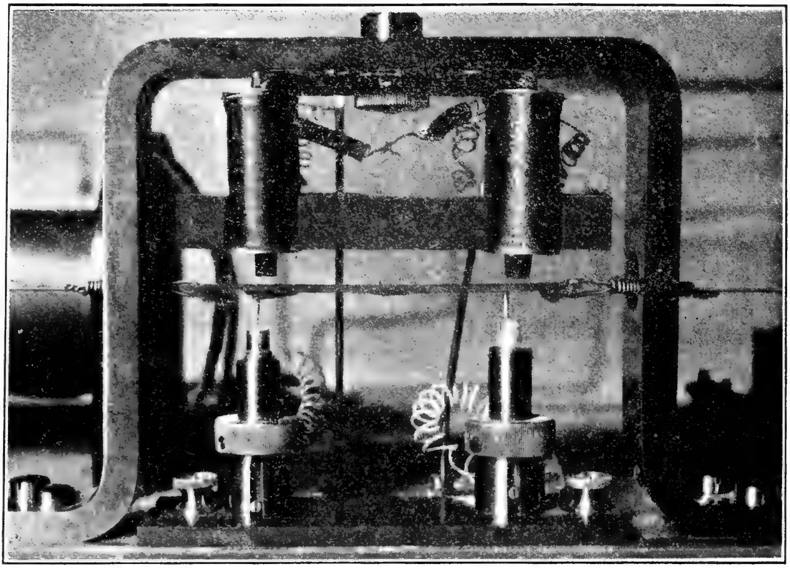
Wave Forms. Continuous oscillation circuit.

Fig. 19.

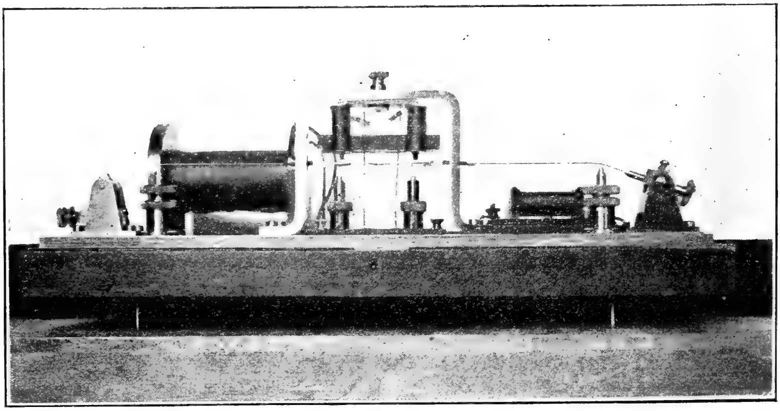


Mean Speech Wave.

FIG. 5.

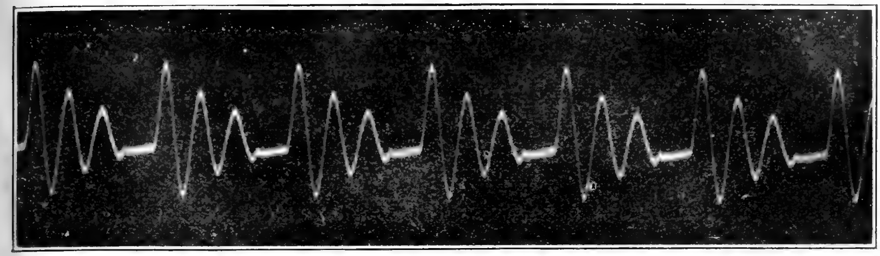


VIBRATING WIRE.
Details of mercury cups, etc.

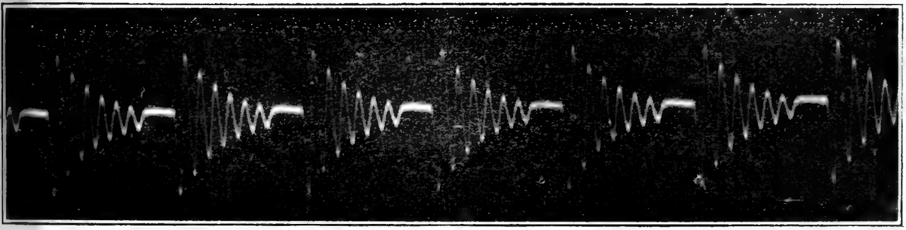


VIBRATING WIRE INTERRUPTER.
General View.

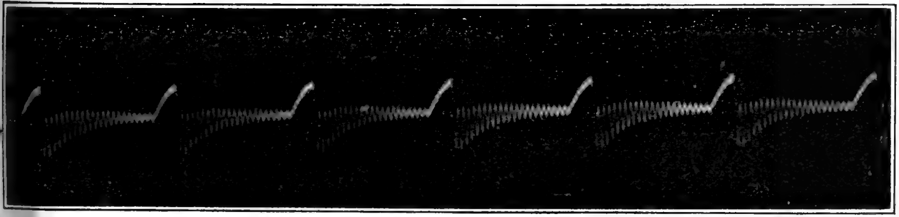
Fig. 7.



490 ~.



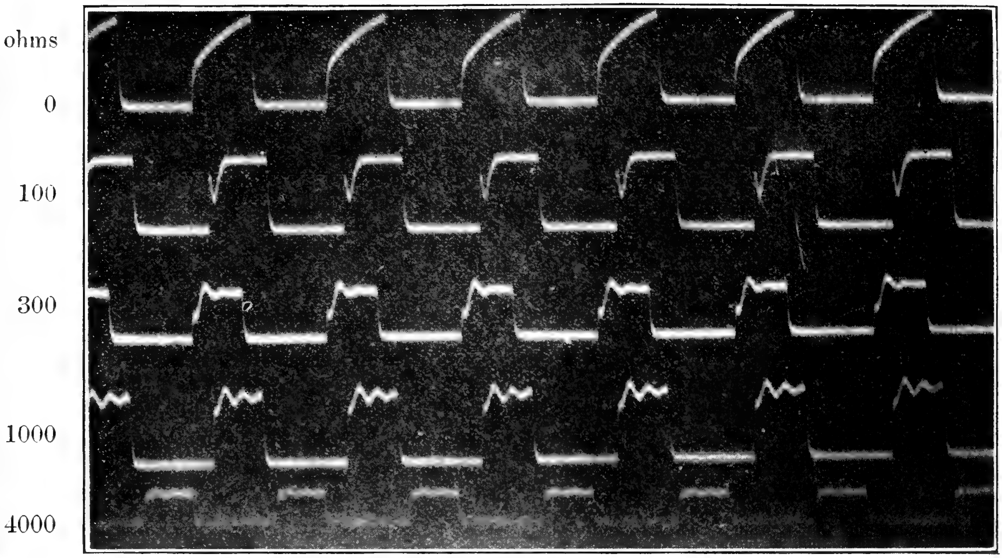
959 ~.



2880 ~.

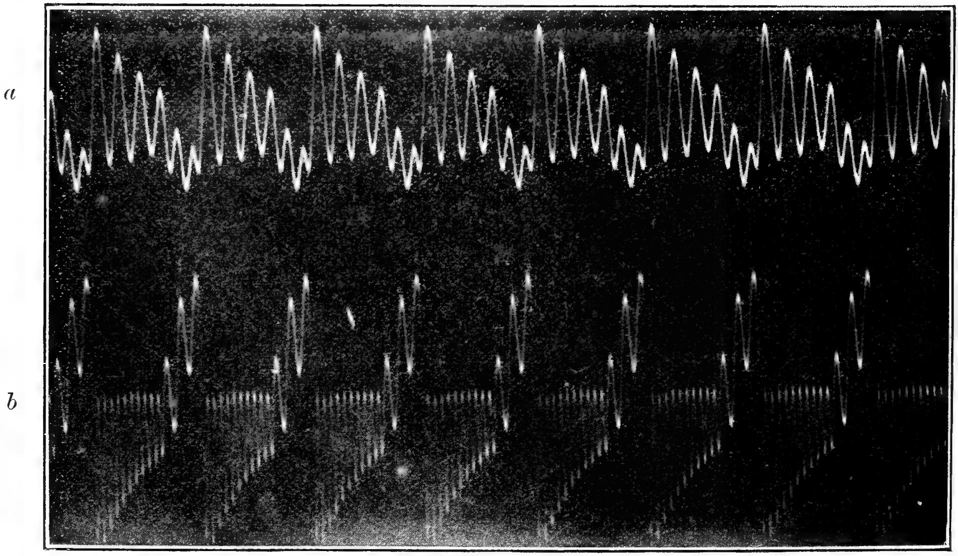
Single action circuit waves.

Fig. 9.



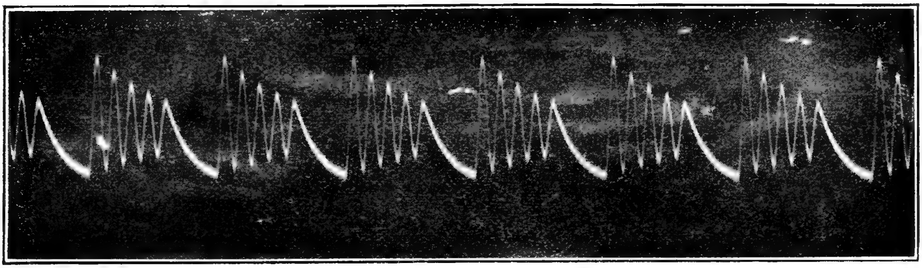
Effects of resistance in single action circuit.

Fig. 10.



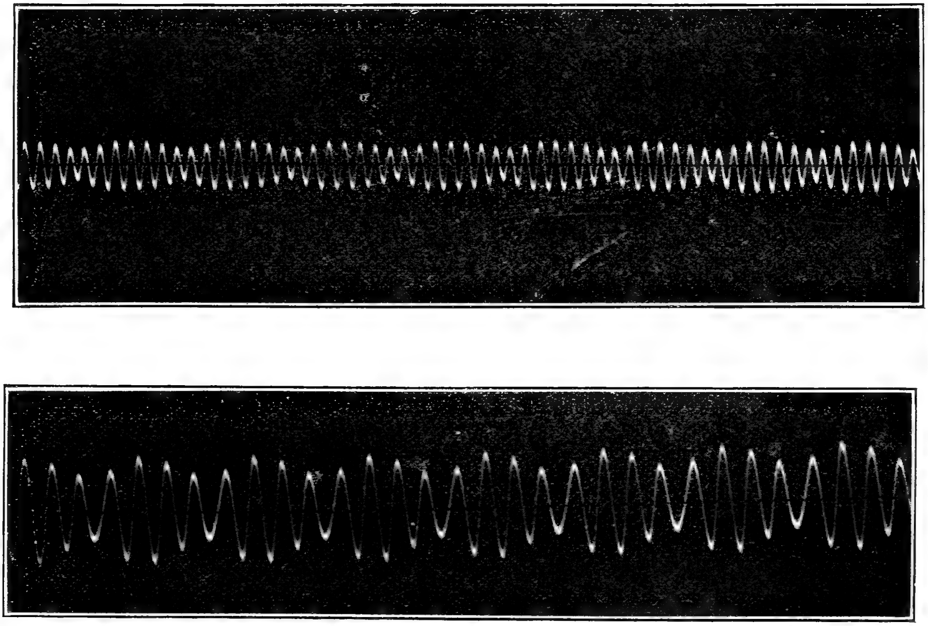
Double action circuit waves.

Fig. 12.



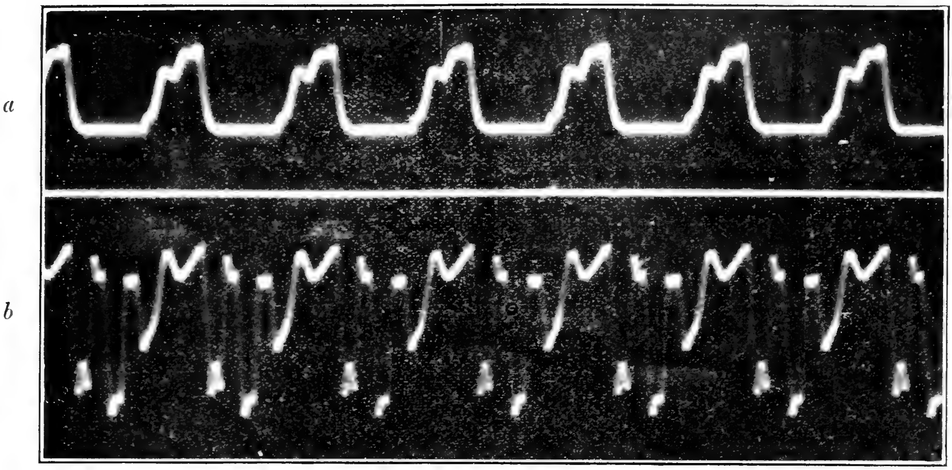
Assisting Waves.

Fig. 13.



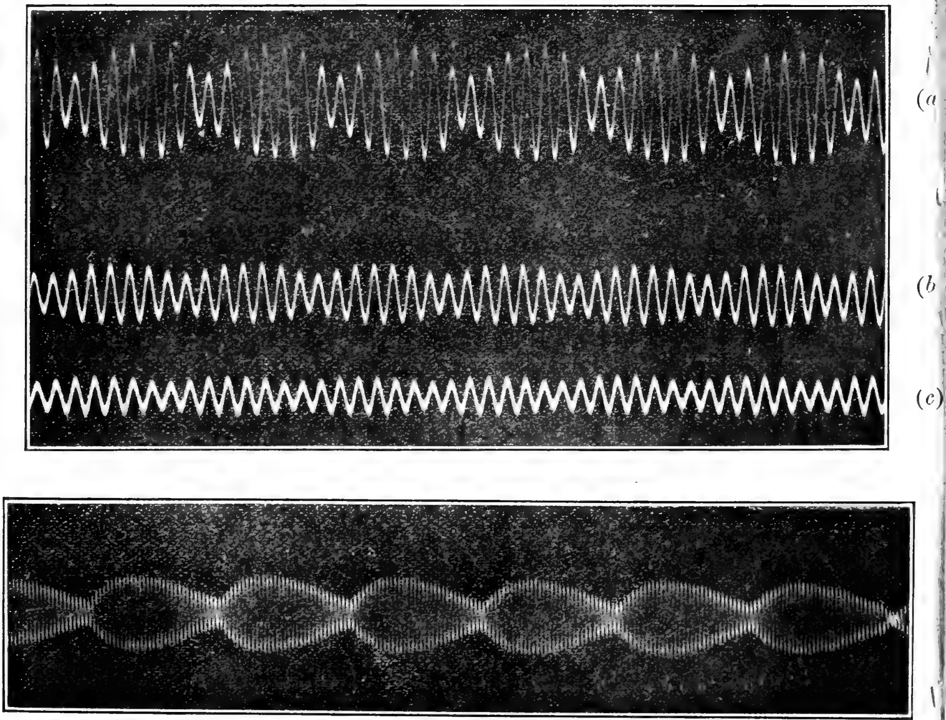
Opposing Waves.

Fig. 14.



Complex Wave Form.

Fig. 16.



Wave Forms. Modified double action circuit.

apparatus should be about 1 watt, and it is necessary that it should be capable of working uniformly over a fairly considerable period of time.

Simplicity and portability are also highly desirable.

Alternators.—A sine wave alternator coupled to a motor, the combination being capable of running at a constant speed for a considerable period, is a very useful form of apparatus for investigations in connexion with telephony. A suitable machine is, however, difficult to obtain.

The Western Electric Company build a machine with an output of about 30 watts at frequencies varying from 800∼ to 1800∼, and the wave form is stated to resemble a sine curve closely at all loads.

Messrs. Siemens and Halske also make a machine with an output of 3 or 4 watts at about the same frequencies. Both these machines are of the inductor type, the purity of the wave form being secured by the shape of the teeth and pole faces.

Mr. Duddell's work with high frequency alternators is well known. He has also made several medium frequency machines, one of which, with a wound rotor, gives an output of about 20 watts, but only runs up to about 500∼.

In the Investigation Department of the National Telephone Company we have built a small alternator of the inductor type on the lines of the Siemens machine. This is illustrated in Pl. XVI. fig. 1.

With a 30 volt battery connected to the field windings, the output is only about ·3 watt, but the wave form is fairly good, *i. e.* it approximates to a sine wave. By decreasing the air gap, the output can be considerably increased at the expense of the purity of the wave form.

With the best air gap (about ·015 mm.) the P.D., which is independent of the frequency, is 10·5 volts.

Fig. 2 (Pl. XVI.) shows the wave form of this machine when the frequency is 800∼. Measurements of the capacity of small mica condensers made with the current from this alternator on the assumption that it is a pure sine wave, are accurate to within about 3 per cent., and this forms a very good test.

For more accurate measurements this machine has been used with a wave filter, consisting of series inductances of low effective resistance and parallel capacities, similar to that described by G. A. Campbell (Phil. Mag. March 1903). The wave form when at a frequency of 800∼ this filter is used is shown in fig. 3 (Pl. XVI.).

Humming Telephone.—The interaction between a receiver and a transmitter setting up an alternating current whose frequency depends on the free period of the apparatus can be utilized. The method, however, is untrustworthy, and the output small.

The wave form is also far from sinusoidal, as might be expected when it is considered that it is influenced by the action of the polarized electromagnet in the receiver. Fig. 4 (Pl. XVI.) shows the wave form using the local battery type of telephone instrument.

Mr. A. Campbell's modification of the humming telephone consists of a steel bar with a free period of the frequency desired, and this is set in motion by a polarized electromagnet, which has attached to it a light microphone, which maintains the interaction and supplies current to the external circuit through a transformer. This apparatus is more reliable than the humming telephone. The output, however, is limited by the transmitter, and the wave form is similar to that of the ordinary humming telephone *.

Organ Pipes etc.—Organ pipes, other wind instruments, and tuning forks sounding in transmitters, were experimented on for a short time, and might under certain conditions give satisfactory results. It is difficult to avoid trouble, however, with all such arrangements, owing to irregularities introduced by the transmitters and to their limited output.

Vibrating Wire Interrupters.—The vibrating wire interrupter described by Wien, Orlich, Campbell, and others, has when suitably modified given very satisfactory results, and I propose to describe a special form of this apparatus †. It has been found very difficult to construct a vibrating wire which will run reliably at a frequency much above 300∼, and I have been unable to find references to wires which could be maintained in vibration at a frequency higher than 500∼. The output is also very limited, and the frequency difficult to determine and vary.

In order to overcome these drawbacks the instrument illustrated in fig. 5 (Pl. XVII.) has been designed. The upper figure shows details of the mercury cups and electromagnet, and the lower figure gives a general view of the whole instrument. The wire is steel, 1·06 mm. in diameter, and supports a soft iron armature which is maintained in vibration by an electro-

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* For further particulars of these devices see Note by R. Appleyard, Elect. Rev. pp. 57 & 656, vol. xxvi. 1890; Paper on Humming Telephones, F. Gill, Journal I. E. E. vol. xxxi. 1901; A. Campbell, Proc. Royal Soc. p. 208, June 12th, 1906; J. E. Taylor, Journal I. E. E. p. 396, vol. xxxi. 1901; F. Dolezalek, *Zeitschrift für Instrumentenkunde*, p. 240, Aug. 1903.

† (1) Max Wien, Wied. *Ann.* xlii. p. 593 (1891).
do. do. xliv. p. 681 & p. 689 (1891).
(2) Orlich, *Electrotechn. Zeitsch.* vol. xxvi. (1903).

magnet with a laminated core of stalloy, which is an alloy of iron much used in electrical work, a mercury cup and a platinum wire contact. The wire is provided with a tension adjuster, and will run steadily at frequencies varying from 100∼ to 250∼

The frequency of the alternating output is quite independent of the wire frequency, and is obtained by means of a separate circuit, mercury cup, and contact. The mercury cups are made from glass tube 4 mm. in internal diameter, and these are enclosed in brass tubes to which the mercury is connected by means of a platinum wire fused into the glass. The cups thus made slip into brass adjustable carriers from which they can readily be removed for cleaning purposes, and the carriers admit of a fine vertical adjustment.

Experiments have been made with cups of varying diameter. Those with the smallest diameters gave the best results.

It would appear that the mercury in the small cups remains much steadier under the action of the vibrating contact than in those of larger diameter, owing possibly to the greater surface-tension effect.

Single Action Circuit.—Several forms of oscillating circuit have been used of which the two principal ones may be described as "single action" and "double action" respectively.

Fig. 6.—Single Action Circuit.

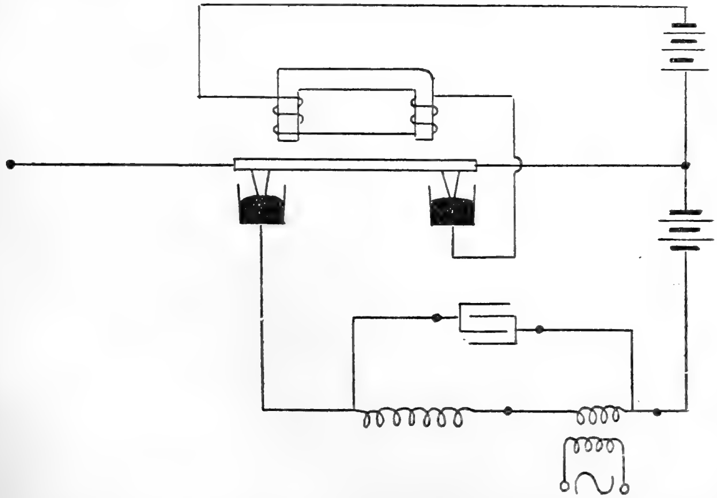


Fig. 6 shows the single action circuit and also the wire driving circuit. The latter requires no explanation. The former consists of a platinum contact and mercury cup which in the make contact position connects a battery to a capacity in parallel with an inductance and transformer primary.

On the break between the cup and contact an oscillation occurs in the circuit.

By this method a series of damped trains of oscillations of any frequency can be produced, the trains following each other with the frequency of the wire vibrations.

Theory of Action.—Oscillations will occur when $\frac{R^2}{4L} < \frac{1}{K}$, their frequency being given by $\frac{1}{2\pi}\sqrt{\frac{1}{LK} - \frac{R^2}{4L^2}}$. With the values of L, K and R used, the last term can be neglected and formula becomes $\frac{1}{2\pi}\sqrt{\frac{1}{LK}}$.

The total output in watts, excluding all losses, will be the energy stored, divided by the interval of time between each succeeding train of waves.

The equation to the line joining the peaks of the damped waves is $Y = e^{-\frac{aR}{2L}}$, so that for small damping L must be large and R small, which also gives the maximum output.

In one of the circuits used the inductance is ·037 henry, and its effective resistance which is practically invariable over the range of frequency used is 10 ohms. (These figures include the resistance and inductance of the primary of transformer.)

Fig. 7 (Pl. XVII.) shows an oscillogram of damped wave trains produced in the manner just described.

The three frequencies are 490~, 959~, and 2880~ produced by using the three capacities, 2·88 mfd, ·8 mfd, and ·1 mfd respectively.

The frequency of the vibrating wire was 90~ in all three cases. It will be observed that only part of a complete train is utilized in the lower frequency waves.

Problem of Output.—The transformer used in this circuit is a small one of the telephone type, with a few turns and a somewhat loose coupling. By reason of this, variations in the frequency and damping of the output caused by variations of the load on the secondary affecting the effective self-induction of the oscillating circuit are rendered small, but at the same time the output is reduced.

In cases where the load is constant it is possible to use a more efficient transformer and so obtain a considerable increase in the output.

It is worthy of mention that in the apparatus as constructed, the chief storage of energy occurs in the coil and not in the condenser. The single action circuit has proved of value for telephonic purposes.

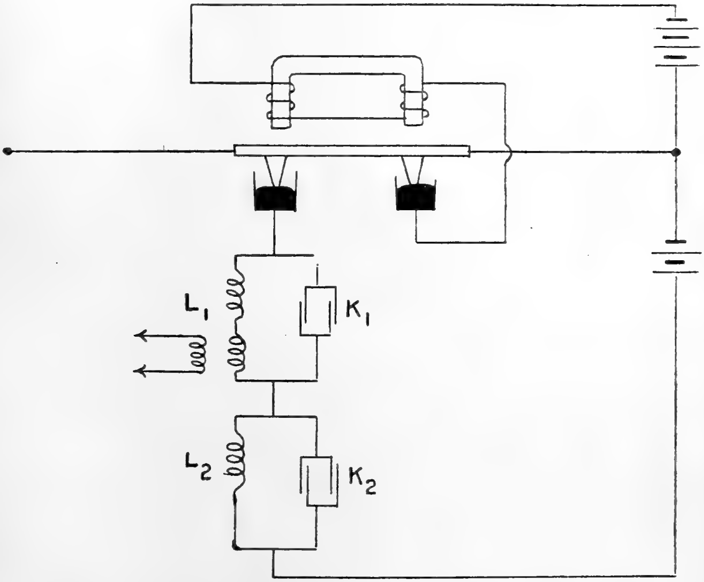
Double Action Circuit.—The double action circuit previously referred to is illustrated in fig. 8.

This circuit, unlike the single action one, gives a pronounced oscillation on the make contact, as well as on the break.

On referring back to fig. 6 it will be seen that no oscillation can occur on the make contact as the battery short-circuits the oscillating circuit during that period.

By introducing resistance into the battery circuit, however, an oscillation on the make contact can be obtained in addition to the break oscillation. This oscillation is of the frequency of the main oscillating circuit.

Fig. 8.—Double Action Circuit.



Although the results might have been predicted theoretically, the following series of oscillograms (Pl. XVIII. fig. 9) are inserted as they show in a rather interesting manner the effect of insertion of resistance.

This series shows the variations obtained in the make contact oscillations in a circuit as shown in fig. 6, when the resistance in series with the battery (which is of negligible internal resistance) is varied from 4000 to 0 ohms.

The make oscillation is most evident when the resistance is reduced to 1000 ohms.

At 300 ohms the oscillation begins to appear during the current rise on the make contact, whilst at 100 ohms the oscillation is entirely confined to the rise during the make contact.

The resistance is still large enough to cause the current to rise very quickly to its maximum value, thus giving a nearly square shouldered wave.

As the resistance is still further reduced the current takes longer to rise to its maximum value and at the same time the oscillation is reduced, until ultimately at 0 ohms the familiar current rise curve with no superimposed oscillation is produced.

In the double action circuit as illustrated (fig. 8) a capacity shunted by an inductance is introduced in place of the simple resistance. This somewhat modifies the action of the circuit. If the inductance L_2 is inserted as shown in the figure and the capacity K_2 omitted, the effect is to give an oscillation on the make contact, the frequency of which is determined by the combined inductance of L_1 and L_2 and the capacity K_1. When the capacity K_2 is added a similar effect is produced. The resulting make frequency being due to the combined effect of both inductances and capacities. The break oscillation will be that due to L_1 and K_1 only.

Fig. 10 (Pl. XVIII.) shows two waves produced by this circuit. The following small table gives the necessary data:—

Wave.	Values of				Frequency of oscillation :	
	L_1 henrys.	L_2 henrys.	K_1 mfds.	K_2 mfds.	make contact.	break contact.
a	·037	·037	1·67	·167	1020~	715~
b	·037	·037	·167	1·67	1020~	2160~

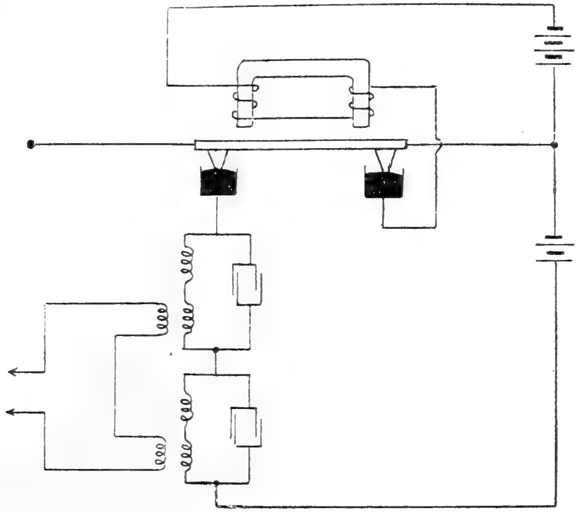
Double Action Circuit with two Transformers.—By inserting a second transformer in circuit as shown in fig. 11, two separate and distinct oscillations can be obtained. If the circuits are similar two separate waves will be produced the shape of which will be exactly similar.

By joining up the two secondaries so that these two waves either assist or oppose each other, some interesting results are obtained.

Fig. 12 (Pl. XVIII.) shows two 900 ~ break oscillations assisting one another. The make oscillations oppose each other and are therefore wiped out, the result being to give a wave exactly similar to that obtained with the single action circuit, but with about double the amplitude.

When the secondaries are joined up so that the break oscillations oppose each other, whilst the make oscillations assist, the result, if these oscillations are equal in frequency but unequal in amplitude, is to give a continuous and more or less uniform wave.

Fig. 11.—Double Action Circuit with Two Transformers.



The first wave in fig. 13 (Pl. XVIII.) shows the effect of opposing two 850∼ oscillations, and the second the effect with two 490∼ oscillations. The continuous waves resulting are 850∼ and 490∼ respectively.

The regularity of the continuous wave can be best modified by slightly varying one of the inductances, which have air cores by inserting in the cores one or two strands of fine iron wire.

It is obvious since the output depends on the difference between the two circuits that it will not be large. To increase the output, different inductances for each of the two circuits can be used, and the capacities adjusted so as to get the same frequency in each circuit.

It is of course impossible to obtain a pure sine wave by this method, and the extent of the impurity has not yet been examined analytically. Some tests have, however, been made by using these waves for measurement purposes. These are given further on.

At 300 ohms the oscillation begins to appear during the current rise on the make contact, whilst at 100 ohms the oscillation is entirely confined to the rise during the make contact.

The resistance is still large enough to cause the current to rise very quickly to its maximum value, thus giving a nearly square shouldered wave.

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When the secondaries are joined up so that the break oscillations oppose each other, whilst the make oscillations assist, the result, if these oscillations are equal in frequency but unequal in amplitude, is to give a continuous and more or less uniform wave.

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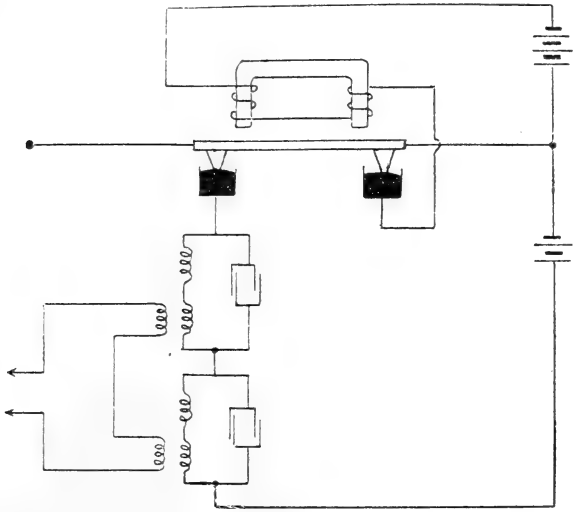

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It is obvious since the output depends on the difference between the two circuits that it will not be large. To increase the output, different inductances for each of the two circuits can be used, and the capacities adjusted so as to get the same frequency in each circuit.

It is of course impossible to obtain a pure sine wave by this method, and the extent of the impurity has not yet been examined analytically. Some tests have, however, been made by using these waves for measurement purposes. These are given further on.

the point just makes contact on the mercury surface, a spark is observed.

If then the distance between the mercury and the contact is slowly decreased, a series of sparkless points will be reached which are very sharply defined, as when such a point is reached, a variation either way of about ·07 mm. gives the sparking condition again.

The writer has not so far made any investigation into the reason for this action.

It is, however, most probable that this action is partly mechanical as at the sparkless points the vibrating surface of the mercury seems to be set in a rigid condition.

Use of continuous Waves for Absolute Measurements.—The wave forms illustrated in fig. 13 (Pl. XVIII.), fig. 16 (Pl. XIX.), and fig. 18 (Pl. XVI.) might conceivably be accurate enough for use when making absolute, as opposed to merely comparative, measurements.

The following table gives some results arrived at by measuring the current and p.d. with standard condensers subjected to these waves.

Wave form used.	Frequency.	Standard Capacity tested.	Percentage error.
Wave similar to that illustrated in fig. 13	1442	·167	−1·8
	854	·33	−1·7
	523	1·0	−1·0
Wave similar to that illustrated in fig. 16 (*a*)	833	·167	+3
	1442	·167	+4·2
Wave similar to that illustrated in fig. 18 (*b*)	833	·33	+2·4
	833	·167	+1·8
	1440	·167	+ ·5

These results were determined by inserting a non-inductive resistance of known value in series with the condenser, taking the potential-difference across both by means of a sensitive electrostatic voltmeter, and then calculating the capacity by the formula $A \,.\, 10^{16}/pV$, where A and V are the effective values of the charging current and potential-difference respectively. This is very satisfactory as very little time was spent in adjusting the waves.

So far as these tests go it would appear that the amount of the departure from the sine shape in these continuous waves is comparatively inconsiderable.

Telephonic Measurements.—The special form of vibrating wire described was primarily designed for telephonic measurements; and although the tests carried out in this direction are far too extensive to describe in any detail in this paper, a brief outline may perhaps be given.

Telephonic measurements are now mainly carried out by expressing the attenuation of speech-waves in any line circuit or apparatus in terms of the attenuation over a given length of a certain type of cable line settled on as a standard.

It has been found that the words representing the numbers 1, 2, 3, 4, 5, embody all the frequencies of telephonic importance, and these numbers are invariably used for testing purposes.

Inspection of the oscillograms of these five words as spoken by a number of persons shows that they may be approximately represented by fig. 19 (Pl. XVI.), which is given by the equation

$$\begin{aligned} y = {}& \cdot 29 \sin pt + \cdot 32 \sin 2pt + \cdot 39 \sin 3pt + \cdot 55 \sin 4pt \\ & + 1\cdot 06 \sin 5pt + 6\cdot 5 \sin\left(6pt - \frac{\pi}{2}\right) - 1\cdot 06 \sin \\ & 7pt - \cdot 56 \sin 8pt - \cdot 39 \sin 9pt - \cdot 32 \sin 10pt \\ & - \cdot 29 \sin 11pt, \end{aligned}$$

where $p = 2\pi \times 145.$

The general resemblance of this wave to some of those produced artificially, see figs. 7 and 12, is obvious on inspection.

It has been found that by replacing the human voice and transmitter by the vibrating wire producing these waves, and by using the correct frequencies, similar results to those produced by the voice can be obtained.

Having obtained a satisfactory substitute for the human voice, it is next necessary to replace the ear and receiver by some measuring instrument.

Simple measurements of the comparative current attenuation over the standard line and the line or apparatus under test do not give accurate results, and it was suggested by my assistant Mr. A. J. Aldridge, to whom I take this opportunity for expressing my indebtedness for considerable help given in carrying out the investigations embodied in this paper, that direct measurements of the comparative volumes of sound issuing from the telephone receiver could be made by allowing the receiver to sound into a transmitter connected up in the usual manner to a battery and induction-coil, and to measure the current in the secondary of the induction-coil.

This method has been found to solve most of the difficulties, and with the vibrating wire at the sending end of the line and at the other end of the line a receiver sounding into a transmitter, the latter being connected to a barretter used as an alternating current milliammeter, it has been found possible to carry out comparative telephonic measurements with greater accuracy than with the voice and ear, owing to the elimination of the personal equation and the greater sensibility to volume variation of the apparatus used.

This method can be used for such diversified tests as comparison of loaded with unloaded lines, comparison of standard and non-standard apparatus, such as receivers, transmitters, induction-coils.

Conclusion.—Apart from telephonic measurements, the modified vibrating-wire interrupter may possibly have a field for both comparative and absolute electrical measurements, and especially for use with the vibration galvanometer. The ease with which the frequency can be varied together with the steadiness of the resulting wave and the simplicity of the apparatus are certainly great recommendations. The author must express his indebtedness to the National Telephone Co. for the facilities afforded to him, to Dr. A. Russell for great help in the revision of this paper, to Mr. A. Campbell for references to humming and vibrating wires, and a tribute must also be paid to the oscillograph which has been of such great assistance in these investigations.

XLIII. *Notices respecting New Books.*

The Collected Mathematical Papers of J. J. Sylvester. Volume II. (1854–1873). Cambridge: At the University Press. 1908.

Oeuvres de Charles Hermite. Tome II. (1858–1872). Paris: Gauthier-Villars. 1908.

IT is fitting that these important continuations of the collected papers of two great contemporaries should be noticed together. To a large extent they worked along the same lines of analysis; and in the papers of each there are frequent references to the researches and results of the other. It is needless to point out in these days the great influence exercised on mathematical development by both Sylvester and Hermite. The former was characterized by an extraordinary exuberance of mathematical imagination. Who but a Sylvester, for example, could have discovered in the arduous course of discussing the equation of the fifth degree, that Music might be "described as the Mathematic of sense, Mathematic as Music of the reason—the soul of each the same!" Of the 110 papers which fill the English mathematician's volume, many are mere notes; of the many others which are substantial additions to knowledge special mention might be made of two. The one is the "Trilogy" on the real and imaginary roots of algebraic equations (Phil. Trans. 1864), including proofs of Newton's rule. The other is the interesting extension of Poinsot's representation of the rotation of a solid body, a paper which contains some very elegant geometrical reasoning.

The most outstanding papers in the French volume are the great memoir on the equation of the fifth degree, which was published at intervals in the *Comptes Rendus* during 1865 and 1866, and the essay or so-called Note on the Theory of Elliptic Functions, which originally formed part of the 6th edition of Lacroix's 'Differential and Integral Calculus' (1862). This second volume is adorned with a fine and evidently characteristic portrait of Hermite at the age of fifty. For their continued labours in editing the writings of Sylvester and Hermite, the respective editors, H. F. Baker and Emile Picard, deserve the thanks of the whole mathematical world.

An Elementary Treatise on Theoretical Mechanics. By J. H. JEANS, F.R.S. Boston: Ginn & Co. 1907.

THIS is a thoroughly sane book on Dynamics, just such in fact as we should look for at the hands of Professor Jeans. The opening chapters deal in a clear Newtonian manner with the simple principles at the foundation of the science, and up to the middle of Chapter IV. no serious demand is made on the mathematical powers of the student. In this chapter, which treats of the statics of particles, the equilibrium of the flexible string or chain is discussed. This early introduction of the belaying-pin and the catenary has much to commend it:—*e. g.*, they give easily realizable problems for the first use of the calculus. The next two chapters deal with the statics of rigid bodies and centres of gravity; and then in Chapter VII. we have a clear discussion of the principle of Work, including virtual work, conservation of energy, and the conditions for stable and unstable equilibrium. The treatment is admirable. The illustrations are well chosen and sufficient for the purpose; and there is no unnecessary wielding of the mathematical weapon. The simpler problems of motion under constant forces and of motion of systems of particles having been disposed of, the remaining chapters are characterized by a distinctly more advanced mode of treatment. Towards the end of the book the student is not spared, and many a reader who has, so to speak, cycled steadily up the incline to Chapter X. will begin to feel a steepening gradient as he essays the last two stages. Indeed it is not a mere question of a steeper ascent, it is ascent into a wholly different atmosphere. The symmetrical spinning top is a hard enough nut to crack for a student to whom most of the book is new; but the generalized methods of Lagrange and Hamilton are a much more severe test of the mathematical capacity of the reader. We are at one with Professor Jeans in his reasons for introducing this sketch of the higher dynamics. It will appeal strongly to the few students who have the requisite ability; and for those who have not a more detailed discussion would be equally useless. In a book in most respects so admirable, why does the author persist in using the misleading phrase "coefficient of elasticity"? Thomson and Tait's "coefficient of restitution" is much to be preferred, and moreover falls into line with Professor Jeans's own appropriate phrase "impulse of restitution." The whole section headed "Elasticity" ought indeed to be revised, especially in those parts in which the word elasticity itself appears. Each chapter ends with a number of problems which have the merit of being essentially practical.

XLIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 200.]

March 18th, 1908.—Prof. W. J. Sollas, Sc.D., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Carboniferous Rocks at Loughshinny (County Dublin), with an Account of the Faunal Succession and Correlation.' By Charles Alfred Matley, D.Sc., F.G.S., and Arthur Vaughan, B.A., D.Sc., F.G.S.

After an introduction recalling the succession at Rush, already described by the authors, a detailed account is furnished of the various sections in the Loughshinny area. About 1100 feet of Carboniferous rocks are exposed. They consist mainly of limestone, but also include a thick mass of conglomerate and many intercalated beds of shale and chert. The rocks have been much folded, and to some extent faulted. The lowest rocks belong to some part of the *Dibunophyllum*-Zone, the higher range through *Cyathaxonia*-Beds into *Posidonomya*-Limestones and shales of Pendleside age. The Lane Conglomerate may be on or near the horizon of the Rush Conglomerate. Local decalcification has caused the more or less complete disappearance of some of the *Cyathaxonia*- and *Posidonomya*-Limestones. The following table (p. 495) gives the position and correlation of various members of the sequence.

The region was close to an old shore-line of the Carboniferous-Limestone Sea, the actual position of which appears to have been almost parallel to, and a short distance seaward of, the present coastline between Rush and Skerries.

The paper closes with faunal lists from the various subdivisions and exposures, and an account of the faunal succession and correlation, both by the second author.

Stratigraphical Zones.	*Thickness in feet.*	*Palæontological Zones.*	*Correlation with the Rush area.*
Loughshinny Black Shales.	110	Upper *Posidonomya*-Zone. (P_2)	Not represented.
Posidonomya-Limestone Group.	260	Lower *Posidonomya*-Zone. (P_1)	Do.
Cyathaxonia-Beds (base not seen).	200	*Cyathaxonia*-subzone (locally divisible into D 3*b* D 3*a* but overlapping).	*Cyathaxonia*-Beds of Bathing-Place & Giants Hill.
(Gap)	(Gap)		
Dibunophyllum - Limestone.	100	Upper *Dibunophyllum*-Zone. (D_2)	Curkeen - Hill Limestone.
(Gap)	(Gap)		
Holmpatrick Limestone.	180	? D (of unknown position).	? Carlyan Limestone.
Lane Conglomerate.	200		? Rush Conglomerate-Group.
Lane Limestones.	60		? Rush Slates (top part only).

2. 'A Note on the Petrology and Physiography of Western Liberia (West Coast of Africa).' By John Parkinson, M.A., F.G.S.

The country is low-lying, with a gradual rise northward from shore-level, and rivers mature in character with alluvial flats raised above flood-level. Where the River Tuma falls into the River St. Paul the remnant of a hanging valley can be seen. Flat-topped ridges and isolated hills trending parallel to the foliation of the gneiss are characteristic of the country around Sanoyei and Boporo. There is a striking absence of late deposits of old gravels and sands.

In the southern part of the district there are indications of a series of garnetiferous gneisses, tremolite-schists, kyanite-schists or gneisses, garnet-graphite-gneisses, etc., associated with others of granitic type, the latter being apparently free from microcline and containing a pleochroic pyroxene. These rocks are replaced in the north by biotite-gneisses and hornblende-schists, which have an approximate and singularly constant east-and-west (magnetic) strike in their foliation. Microcline is common. These old crystalline rocks are cut by an extensive series of basalts and ophitic dolerites, resembling so closely the post-Cretaceous dykes of Southern Nigeria, that it is difficult to avoid the conclusion that they are of the same age.

April 15th.—Dr. J. J. Harris Teall, M.A., F.R.S.,
Vice-President, in the Chair.

The following communications were read:—

1. 'The Geological Structure of the St. David's Area (Pembrokeshire).' By J. Frederick N. Green, B.A., F.G.S.

With a view to the elucidation of controverted points in the geology of the St. David's area, the author has mapped the district in considerable detail on the 6-inch scale. The Cambrian rocks, the succession of which is well known, were first traced and were found to be greatly faulted. The faults have been followed into the underlying volcanic tuffs (Pebidian), and the succession within the intervening blocks of country determined and pieced together. In this way the Pebidian has been subdivided into fourteen horizons, with a total visible thickness of over 3000 feet. The tuffs are described in some detail, and the subdivisions classified into four series—the lower two of which are composed chiefly of trachytic pebbles in a chloritic matrix, and are usually separated by a peculiar schistose quartz-felspar-porphyry sill. The third series is composed of fragments of rhyolite and hälleflinta in a silicified matrix, and the topmost now principally consists of highly-sheared schistose beds. The volcanic fragments throughout the Pebidian are rolled, and have often undergone changes before deposition; thus the tuffs appear to be mainly, if not wholly, detrital.

By the aid of this succession, an unconformity between the Pebidian and the Cambrian is demonstrated, the position of the basal Cambrian conglomerate on the volcanic series varying by at least 1000 feet. The red coloration of the beds immediately underlying the conglomerate is due to staining.

The schistose sill has been traced into the porphyritic margin of the St. David's granophyre (Dimetian), to which it is allied petrographically; and it is inferred that the granophyre is a laccolitic intrusion in the Pebidian. The boundaries between the granophyre and the Cambrian are prolongations of faults proved in the latter; except at one point in the well-known Porthclais district, which, on account of its importance, has been mapped on the scale of 25 inches to the mile. A trench specially opened at this point exposed basal Cambrian rocks resting upon a denuded surface of the granophyre, which is therefore of pre-Cambrian but of post-Pebidian age.

The relationships of the basic igneous rocks west of St. David's, which have hitherto been held to be Pebidian lavas, are discussed, and the conclusion is reached that they are all post-Cambrian intrusions. Finally, it is suggested that the word Pebidian should be revived as a general term.

2. 'Notes on the Geology of Burma.' By Leonard V. Dalton, B.Sc., F.R.G.S.

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XLV. *Another Method of Measuring large Molecular Masses.*

By WILLIAM SUTHERLAND[*].

IT has already been proposed to find the masses of molecules, which are too large for the ordinary methods, by determining their radii from their velocities of diffusion or their velocities in electrolytic conduction (Phil. Mag. [6] ix. p. 781 and xiv. p. 1). These methods have been applied to the large molecules of egg albumin and globulin. In the latter paper it was shown that they yield for the radius of the hydrogen molecule an absolute value agreeing well with that given by the kinetic theory of gases. The latter paper contains incidentally also another method of finding large molecular masses which will be worked out in the present communication and applied briefly to experimental data for certain peptones, casein, and globulin. The theoretical equation (13) of that paper gives the following connexion between the molecular conductivity λ and the concentration of a solution containing n gram-molecules per cm.^{3} of a solute whose molecule yields n_1 positive ions of valency ν_1 and n_2 negative ions of valency ν_2, the conductivities of the ions at infinite dilution being Λ_{01} and Λ_{02}, and at concentration n being Λ_1 and Λ_2:

$$\lambda_0\eta_0/\lambda\eta = 1+2\pi(\Lambda_1+\Lambda_2)C\nu_1\nu_2\{n(n_1+n_2)/h\}^{\frac{1}{3}}/3KI\lambda_0, \qquad (1)$$

in which C is a constant, η_0 is viscosity of solvent, η of solution, h is the mass of the atom of hydrogen, K is the

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[*] Communicated by the Author.

dielectric capacity of the solvent, I the force in the solvent which ionizes the solute completely at all concentrations, and λ_0 is generally identical with $\Lambda_{01}+\Lambda_{02}$. In applying equation (1) to the refined measurements of Kohlrausch and his pupils on very dilute aqueous solutions I showed that $\nu_1\,\nu_2$ did not suffice to express the whole dependence upon valencies, and that seemingly a factor $(\nu_1+\nu_2)^2$ is introduced by 1/I. Moreover, Kohlrausch has recently preferred to treat λ as linear in $n^{\frac{1}{2}}$ rather than in $n^{\frac{1}{3}}$, which was his discovery of years ago. I believe this discrepancy arises in the assumption made in calculating λ from the experimental measurements that the conductivity of the water is not altered by the presence of the solute. Now in the Molecular Constitution of Aqueous Solutions (Phil. Mag. [6] xii. p. 1) I showed that the H ions of acids and the OH ions of alkalies ionize H_2O powerfully. It is possible therefore and probable that other ions ionize H_2O to a small extent, variable with the concentration. Probably a very careful discussion of Kohlrausch's measurements would clear up the discrepancy between his experiments and (1) and would give the law of the ionization of H_2O by all ions. Equation (1) is well verified by measurements on solutions which are not too dilute, though even with them $\nu_1\nu_2(n_1+n_2)^{\frac{1}{3}}$ does not suffice to give the whole of the dependence upon valency. But on the other hand equation (1), as it stands, expresses the valency rule discovered inductively by Ostwald from his experiments on dilute solutions of the Na salts of pobybasic acids (*Ztschr. f. physik. Chem.* i. and ii.). The form in which Ostwald's valency rule is expressed by Bredig (*ibid.* xiii.) is equivalent to $d\lambda/dn=\nu_1\nu_2\phi(n)$, where $\phi(n)$ is a function of the concentration the same for all solutes. This is the result obtainable from (1) by differentiation. Thus (1) is in agreement with a large body of experimental evidence. But (1) for dilute solutions may be written approximately

$$\lambda_0/\lambda=1+2\pi(\Lambda_{01}+\Lambda_{02})\mathrm{C}\nu_1\nu_2\{n(n_1+n_2)/h\}^{\frac{1}{3}}/3\mathrm{KI}\lambda_0. \qquad (2)$$

But a better value of the coefficient of $n^{\frac{1}{3}}$ can be obtained by improving the reasoning by which λ_0 comes into the right-hand side of (1). In (1) λ_0 measures the rate at which a positive ion and a neighbour negative one tend to relax the strain produced in them by electric force. But it will be better to regard each ion relaxing at its own rate, and so to replace $1/\lambda_0$ by $1/\Lambda_{01}+1/\Lambda_{02}$. If in the usual way we are going to compare solutions of equivalent and not equimolecular concentrations, we have m the number of gram equivalents per cm.^{3} equal to

$$n(n_1\nu_1+n_2\nu_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

So the relation between λ and m is

$$1/\lambda=\{1+2\pi C(\Lambda_{01}+\Lambda_{02})^2\nu_1\nu_2(n_1+n_2)^{\frac{1}{3}}m^{\frac{1}{3}}/3h^{\frac{1}{3}}(n_1\nu_1+n_2\nu_2)^{\frac{1}{3}} \\ \mathrm{KI}\Lambda_{01}\Lambda_{02}\}/(\Lambda_{01}+\Lambda_{02}). \quad . \quad (4)$$

For brevity we write this :—

$$1/\lambda=1/(\Lambda_{01}+\Lambda_{02})+bm^{\frac{1}{3}}, \quad . \quad . \quad . \quad . \quad (5)$$

where

$$b=2\pi C\nu_1\nu_2(n_1+n_2)^{\frac{1}{3}}(\Lambda_{01}+\Lambda_{02})/3h^{\frac{1}{3}}(n_1\nu_1+n_2\nu_2)^{\frac{1}{3}}\mathrm{KI}\Lambda_{01}\Lambda_{02} \quad (6)$$

and is the immediate subject of study.

In the important case of the Na salt of a ν_2-basic acid we have $n_2=\nu_1=1$, $n_1=\nu_2$, and

$$b=2\pi C\left(\frac{n_1+n_2}{2n_1}\right)^{\frac{1}{3}}\frac{\nu_1}{\Lambda_{01}}\frac{\nu_2}{\Lambda_{02}}\frac{\Lambda_{01}+\Lambda_{02}}{3h^{\frac{1}{3}}\mathrm{KI}}. \quad . \quad . \quad . \quad . \quad (7)$$

The experimental material from which Ostwald discovered his valency rule affords a suitable test for this theoretical deduction. It will be noticed that b, the coefficient of $m^{\frac{1}{3}}$, depends not only on $\nu_1\nu_2$ but also upon both Λ_{01} and Λ_{02}, whereas in Ostwald's rule there is no mention of this latter dependence. The reason for Λ_{01} and Λ_{02} not entering into Ostwald's statement of his rule is that he worked only with Na salts, so that Λ_{01} was constant, and that although he worked with acids with basicity ranging from 1 to 6, there was a rough tendency for $\{(n_1+n_2)/2n_1\}^{\frac{1}{3}}(\Lambda_{01}+\Lambda_{02})/\Lambda_{02}$ to be constant and so to disguise the dependence on Λ_{02}. In testing our equations we shall first apply (5) to Ostwald's data for the sodium salt of nicotinic or β-pyridine carboxylic acid C_5H_4NCOOH converting them from the Siemens unit of resistance, which he used, to the ohm. I find $\Lambda_{01}+\Lambda_{02}=89{\cdot}8$, and $b=0{\cdot}0838$, which give the following comparison :—

$1/10^3m$	32	64	128	256	512	1024
λ exp.	72·9	75·4	78·0	80·3	82·4	84·0
λ calc.	72·6	75·6	78·1	80·3	82·0	83·6

By availing himself of the carboxyl substitution compounds of pyridine up to pyridine pentacarboxylic acid, Ostwald obtained a series of similar ions with ν_2 ranging from 1 to 5, and by means of the sodium mellitate $C_6(COONa)_6$ he carried his investigation up to $\nu_2=6$. The following table contains the values of $\Lambda_{01}+\Lambda_{02}$ and b which I have calculated from Ostwald's data, as given by Bredig (*loc. cit.*), after I have converted them to the ohm as unit. The substances represented by their formulas are the sodium salts of pyridine-monocarboxylic acid, -tricarboxylic, -tetracarboxylic, and -pentacarboxylic acids, the place of the -dicarboxylic acid being taken by that of phenylpyridine-dicarboxylic acid, and the 6-basic salt being hexasodium mellitate :—

TABLE I.

	$C_5NH_4CO_2Na$.	$C_5NH_2C_6H_5(CO_2Na)_2$.	$C_5NH_2(CO_2Na)_3$.	$C_5NH(CO_2Na)_4$.	$C_5N(CO_2Na)_5$	$C_6(CO_2Na)_6$.
$\Lambda_{01}+\Lambda_{02}$...	89·8	106·1	144·8	166·5	192·1	204·2
b	0·0838	0·1257	0·1450	0·1796	0·2197	0·2830

From the data of Kohlrausch Λ_{01} for Na at 25° C. is 51·2, so that for the ions of these six acids we get for Λ_{02} the values 38·6, 54·9, 93·6, 115·3, 140·9, and 153·0. We have now all the data necessary for testing the implication of (7) that

$$b(\Lambda_{02}/\nu_2)\{2n_1/(n_1+n_2)\}^{\frac{1}{3}}/(\Lambda_{01}+\Lambda_{02}) \text{ is to be constant.} \qquad (8)$$

Here are the products × 10^4 for the six Na salts :—

361 358 358 363 382 423

We shall take the product to be 0·036 at 25°, becoming $0·036\times1·18=0·0425$ at 18°. The factor $\{2n_1/(n_1+n_2)\}^{\frac{1}{3}}$ enters through the necessity for expressing as uniform a distribution as possible throughout the solution of the nn_1 positive ions, each charged with ν_1 electrons, and the nn_2 negative ions, each charged with ν_2 electrons. Mathematically it is difficult to specify such a distribution; it is still more difficult to make physical allowance for the effect of the different magnitudes of the charges. If we leave out $\{2n_1/(n_1+n_2)\}^{\frac{1}{3}}$ the products × 10^4 are

361 325 313 311 322 353

On the whole then the theoretical deduction (7) is verified by experiment, and Ostwald's valency rule in its amended form as given by (7) is established upon a theoretical physical basis. By its means the ratio Λ_{02}/ν_2 can be found for an ion which has Λ_{02} too small to be measured with sufficient accuracy in the ordinary way. From this ratio the volume of the large slow ion can be found by one of the methods which I have proposed and applied for the measurement of large molecular masses. In the paper on Ionization in Solutions and Two New Types of Viscosity (*loc. cit.*), it was shown that for element ions this method is expressed for 18° C. by the equation

$$\frac{1}{B^{\frac{1}{3}}\Lambda_0}=\frac{0{\cdot}0365}{B^{\frac{2}{3}}}+\frac{0{\cdot}0022}{\nu(1+10{\cdot}5/B^{\frac{2}{3}})}, \quad . \quad . \quad . \quad (9)$$

in which B is the volume of a gram-atom of valency ν. For the fatty acid ions from the acetic CH_3COO up to $C_5H_{11}COO$ the same formula holds except that 0·0022 is replaced by 0·0097, ν of course being 1. While for these five ions the formula expresses the experimental facts closely, yielding Λ_0 to 1 per cent., it fails for formic acid for which it makes Λ_0 too large by 18 per cent. Now for the pyridinecarboxylic acids I find that at 18° C., assuming that at 25° Λ_0 is 1·18 times its value at 18°,

$$\frac{1}{B^{\frac{1}{3}}\Lambda_0}=\frac{0{\cdot}00547}{B^{\frac{2}{3}}}+\frac{0{\cdot}0097}{\nu(1+10{\cdot}5/B^{\frac{2}{3}})}. \quad . \quad . \quad (10)$$

In the second term this is identical with the previous result for the fatty acid ions, the valency ν appearing specifically, as it does in the case of the element ions. But the coefficient of the first term on the right is only 0·15 times that for the fatty acid ions and the element ions. I take this striking result to be due to the fact that pyridine is a base giving a markedly alkaline reaction. The N atom in it carries a special electron pair ♭♯, and the positive electrons of the acids derived from pyridine have their inductive effects mostly confined within the pyridinecarboxylic ions by this pair ♭♯. Now the first term on the right originates in viscosity caused by the electron of the ion acting inductively on the molecules of the solvent. But if the induction is confined within the ion mostly, then the viscosity of electric inductive origin must become relatively small. In the paper just cited I gave reason for theoretically expecting this variable effect in large ions, and was surprised not to find it in the fatty acid ions. It appears now that the paraffin residue C_nH_{2n+1} does not affect the inductive action in the solvent appreciably until in the formic ion it is reduced to H, whence the exceptional behaviour of the formic ion. It is very satisfactory in these circumstances to find the ordinary viscous resistance to the pyridinecarboxylic ions expressed by the same term as applies to the fatty acid ions with fulfilment of the additional theoretical condition that ν must appear as in (10) with values ranging from 1 to 6. In the following table are compared the values of Λ_{02} previously derived in this paper from the experimental data with those derived from (10) and multiplied by 1·18 to convert from 18° to 25°. The values of B the limiting volume of a gram-ion are derived from the data of Table IV. of Further Studies on Molecular Force (Phil. Mag. [5] xxxix. p. 1). B for certain elements has the approximate values C 8, H 4, N 8, and O 6. The substances are taken in the same order as in Table I. of the present paper.

TABLE II.

B..............	98	172	121	138	155	176
Λ_{02} exp.	38·6	54·9	93·6	115·3	140·9	153·0
Λ_{02} calc.	37·8	55·8	95·9	117·3	136·3	151·9

It ought to be mentioned that the theoretical considerations here used have led to very different values for Λ_{02} from those found by Bredig from the application of Ostwald's original valency rule and other empirical considerations. For example, Bredig gives the ionic conductivity of the ion of pyridinepentacarboxylic acid as 89·2 in the Siemens unit, equivalent to 94 with the ohm, to be compared with the 140·9 of Table II. above, and there are similar differences with the other ions though they tend to vanish when $\nu=1$. The fact that the values Λ_{02} exp. in Table II. agree with those given by (10) is favourable to the conclusion that the theory has led to more correct limiting values Λ_{02} than Bredig could obtain at the time when he collected and calculated the wealth of data in his paper.

We can now see how the foregoing considerations lead to a new method of measuring large molecular masses, or more strictly large ionic masses from which the related molecular masses can be inferred. If the mass of an ion is large and ν is not large, then the ionic velocity, say Λ_{02}, is small compared with $\Lambda_{01}+\Lambda_{02}$, which is measured experimentally and is liable to error comparable with Λ_{02}, thus involving Λ_{02} in very considerable error. But if b is measured and used in (8) along with the measured $\Lambda_{01}+\Lambda_{02}$ it gives Λ_{02}/ν_2 which in (10) gives B. The conditions of the solution are best understood by re-writing (10) in the following form :—

$$\frac{\nu}{B^{\frac{1}{3}}\Lambda_0}=\frac{0\cdot00547\nu}{B^{\frac{2}{3}}}+\frac{0\cdot0097}{1+10\cdot5/B} \quad . \quad . \quad . \quad . \quad (11)$$

Here there is a second unknown ν in addition to B. But it occurs as factor of a term which is small when ν is small. So the values of B can be calculated for such small values of ν

as 1, 2, and 3. To each value of B corresponds a value of the gram-molecular mass of the ion. But the equivalent mass of the ion is generally known from a titration, and this compared with the values of M shows what must be the right value of ν, and so the right value of M is obtained. But (10) applies strictly only to the pyridinecarboxylic acids, where there is an amphoteric union of basic and acid properties. We may assume (10) and (11) to apply approximately to other amphoteric ions. The first term on the right is uncertain, being for the pyridinecarboxylic acids only 0·15 of the value for the fatty acids, but for the case of ν not large it is of minor importance. Indeed, in these equations if we neglect the first term on the right we get a form of relation corresponding to the relation $\nu/B^{\frac{1}{3}}\Lambda = K/280$, K being dielectric capacity of ion, which I used when first proposing to find the mass of an ion from its conductivity. For the large organic ions $K = 2$ nearly. When ν is large we shall have to proceed in a similar way with (11), but more warily. It will be best then to illustrate the method by applying it to some typical cases.

The most interesting group is that of the peptones shown by Siegfried and his pupils to be definite chemical substances (*Ber. d. Deutsch. Chem. Ges.* xxxiii.; *Zeitsch. f. physiolog. Chem.* xxxv., xxxviii., xlv.). The following are the names of these, their simplest formulas by analysis, and the corresponding provisional molecular weights along with equivalents discussed below.

			Equivalent	
			as acid.	as base.
Trypsinfibrinpeptone α ...	$C_{10}H_{17}N_3O_5$	259	157	290
,, β ...	$C_{11}H_{19}N_3O_5$	273	197	397
Pepsinfibrinpeptone α ...	$C_{21}H_{34}N_6O_9$	515	248	370
,, β ...	$C_{21}H_{36}N_6O_{10}$	533		
Pepsinglutinpeptone	$C_{23}H_{39}N_7O_{10}$	573	320	470
Trypsinglutinpeptone	$C_{19}H_{30}N_6O_9$	486		

These are all amphoteric, but their acidic character is more pronounced than their basic. The equivalent weights for four of them both as acids and bases have been measured by Neumann according to the ingenious method of electric titration devised by Sjöqvist (Neumann, *Zeitsch. f. physiolog. Chem.* xlv. p. 216; Sjöqvist, *Skand. Archiv. f. Physiolog.* v. 1895). This method depends upon the exceptionally large electric conductivities of the H ion of acids and of the OH ion of alkalies. Suppose a normal solution of HCl has a normal solution of NaOH added to it in instalments, the specific electric conductivity of the mixture being measured after each addition. At the point of exact neutralization the conductivity will be a minimum, namely, that of a normal solution of NaCl. If more NaOH solution is added, the conductivity increases till with an infinite amount it becomes that of normal solution of NaOH. The experimental method of using the method to find the equivalent weight of an acid is to start with a solution of NaOH 0·05 normal, as in Sjöqvist's investigation with albumin, and then to add the acid in instalments till it is present in great excess. Then if the results are graphed with amount of acid as abscissa and electric conductivity as ordinate, they give in the simplest cases two straight lines meeting at the point of minimum conductivity, whose abscissa gives the amount of acid required to make a known volume of 0·05 normal solution of the acid. In the more complex cases the graph does not give the two ideal straight lines near the point of minimum conductivity, but forms a curve with the two straight lines as fairly decided asymptotes. If these asymptotes are produced till they meet, their point of intersection gives the required datum. Neumann tested the method on glycocoll NH_2CH_2COOH and asparagine $C_2H_3NH_2CONH_2COOH$ both as acids to NaOH and bases to HCl, and obtained by electric titration results agreeing with their known equivalents. Applying the method then to four of Siegfried's peptones, Neumann obtained the results given above under the headings "equivalent as acid, as base." These do not stand in any simple intelligible relation to the provisional molecular weights. The situation is a suitable one for applying the methods of the present paper. Neumann measured the equivalent conductivities of the four Na peptonates at strengths 1/32 and 1/1024 normal, as given in the next table along with the values of $\Lambda_{01}+\Lambda_{02}$ and b in (5) derived from them. His values of the conductivity of HCl correspond to the temperature 21°·5, according to Kohlrausch's latest data. At this temperature Λ_{01} for Na is 47, by which we obtain Λ_{02} for the peptone ions. Then by means of (8) with $(0·036+0·0425)/2=0·03925$ as the appropriate constant for 21°·5, and with tentative values of $n_1/(n_1+n_2)$, we calculate Λ_{02}/ν_2 as given in the table, and so we obtain ν_2.

Table III.

Peptone.	λ(32).	λ(1024).	$\Lambda_{01}+\Lambda_{02}$.	Λ_{02}.	b.	Λ_{02}/ν_2.	ν_2.
Trypsinfibrin α ...	72·98	90·76	102	55	·1246	29·2	1·88
,, β ...	82·2	104·7	120	73	·121	35·4	2·06
Pepsinfibrin α I. .	72·3	101·9	126	79	·186	23·2	3·4
,, II.	77·5	106·6	129	82	·163	27·1	3·02
Pepsinglutin	75·8	105·5	128·5	81·5	·172	25·6	3·18

It is to be noticed that four out of the five values of ν are nearly integers, while that for the first specimen of pepsinfibrin peptone α is nearly 3·5. Such a fractional value might appear if a peptone was split up by NaOH into two ions, one of valency 3, the other 4. That there is a splitting of the peptone molecule we shall see immediately. But for the four cases where ν_2 is nearly a whole number we shall replace its value in the table by the nearest whole number, with which we shall then divide the tabulated value of Λ_{02} to get the following amended values of Λ_{02}/ν_2 for the four peptones in the above order:—

ν_2.	2	2	3	3
Λ_{02}/ν_2 ...	27·5	36·5	27·3	27·2

These valencies are the same as Neumann found by the use of Ostwald's empirical valency rule. To use the values of Λ_{02}/ν_2 in (11) for finding B we must reduce them to 18° by dividing by 1·09 and then we get

	Peptone.			
	Trypsinfibrin α.	Trypsinfibrin β.	Pepsinfibrin α.	Pepsinglutin.
B	150	83	144	144

The valencies of these ions must represent the number of COO groups they contain, so that $144/3=48$ represents the volume of a COO group in a trivalent peptone ion, together with the volume of the atoms associated with it. But B for COO is 20, so that the volume of an equivalent of a trivalent peptone ion is about $2\frac{1}{2}$ times the volume of COO, so its mass will be roughly $2\frac{1}{2}$ times that of COO, which is 44. Thus we find the order of magnitude of an equivalent to be about 110 at the most, and this is much smaller than 248 and 320 found by Neumann by electric titration for the trivalent peptones. It is plain then that we have to do with a splitting up of the peptone molecule by NaOH. Suppose M to be the molecular mass of peptone, which is split into n_2 ions of valency ν_2 and mass p, and a neutral residue of mass r, then $M=n_2p+r$, and the equivalent by titration is $M/n_2\nu_2=p/\nu_2+r/n_2\nu_2$. This $r/n_2\nu_2$ is the difference between our rough maximum of 110 found above for p/ν_2 and 248 or 320 for $p/\nu_2+r/n_2\nu_2$. It is important, then, to look into the values of B as closely as we can. In the trivalent ion with $B=144$ 3000 would contribute 60 to B. Knowing the amino-acid character of the peptones we may assume that possibly an NH_2 group is associated with one COO group or two, if two they contribute 32 to B. In B there remains only 52 to account for, which is most easily done by assuming the presence of C and H groups, which for the trivalent ion in peptones give $HCCH_2COO(CHNH_2COO)_2$ as a typical formula, having B=144. The actual formula must be decided by chemical analysis of the acid ions when separated from the residue. But as regards the two peptones yielding trivalent ions we can assert that the molecular mass of pepsinfibrinpeptone α must be a multiple of 515, the minimum possible by analysis, and also a multiple of three times 248, the equivalent found by electric titration. The smallest number which satisfies these conditions within the limits of experimental error in determining the equivalent is $515 \times 3 = 1545$, which would give an equivalent of 257, the experiments giving a possible range from 234 to 262. In the same way the molecular mass of pepsinglutin peptone must be a multiple of 573 and also of 3×320. In this case 5×573 satisfies the conditions, since 2865/9 gives an equivalent of 317, while the experimental range is from 317 to 328. Treating the divalent ions in the same way, we find for the ion of trypsinfibrinpeptone α such a formula as $(CHNH_2)_4(COO)_2$, for which B is 152 instead of 150, and for pepsinfibrinpeptone β ions the formula $C(NH_2)_2(COO)_2$, for which B is 80 instead of 83. For α the molecular mass is to be a multiple of 259, and also of 2×157. The number 1295 is the lowest satisfying the conditions nearly, since 1295/8 gives an equivalent 162, the experimental value ranging from 157 to 164. For the β form the molecular mass is a multiple of 273, and also of 2×197, and 2730 meets the case. We have not obtained perfectly definite molecular masses for the peptones, because we have found that we really deal only with the acid ions split from the peptone molecule, and are without definite experimental information as to the mass of the neutral residue. The HCl compounds of peptone are not so definite in their behaviour as the NaOH compounds, so that Neumann's experiments with them do not enable us to add anything of importance to the foregoing. The molecular mass of the peptones seems to be of the order 1400 or 2800. If we use the estimated molecular masses for the four peptones along with the masses of the ions in $M = n_2 p + r$ for calculating r, we get the values 1111, 2214, 479, and 1806. Apparently these residues are important substances still of considerable complexity.

In this connexion it will be useful to consider briefly the molecular conductivities of aqueous solutions of the peptones found by Neumann, these being calculated by him according to Siegfried's formulæ above, as if these gave correct molecular masses. I find that his results can be expressed by the formula

$$\lambda=a+c/n^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where a and c are parameters characteristic of each peptone, and have the following values:—

Peptone.

	Trypsinfibrin α.	Trypsinfibrin β.	Pepsinfibrin α. commercial.	Pepsinfibrin α. Börkel.
a	10·2	10·56	12·7	8·78
c	0·0549	0·0275	0·0187	0·016

The following comparison is given to show how the formula expresses the experimental facts:—

Trypsinfibrinpeptone α.

1/1000 n.	8	16	32	64	128	256	512	1024
λ exp. ...	15·88	18·01	20·44	23·70	28·82	36·99	49·23	66·51
λ calc. ...	15·11	17·14	20·02	24·09	29·84	37·98	49·48	65·76

To explain the formula we may assume that the parameter a represents the molecular conductivity of a salt whose variation with concentration is not detectable at these dilutions in the presence of the rest of the peptone. The difference between 12·7 for the commercial sample of pepsinfibrinpeptone and 8·78 for Börkel's preparation may be ascribed to soluble impurity in the commercial sample. But in the other cases a may originate in some organic salt of an amine base which is split off from the peptone upon solution in water. Then the term $c/n^{\frac{1}{2}}$ arises from the conductivity of the acids separated from the peptone by water. Ostwald's dilution law for organic acids at high dilution makes their conductivity proportional to $1/n^{\frac{1}{2}}$. I have suggested that this law of Ostwald's originates in the organic acids consisting of double molecules which are partly dissociated by water according to the law, the dissociated molecules being completely ionized and the undissociated not at all. Thus, then, the formula (12) shows that either peptone is an organic acid or has organic acids split off from it, and that the single acid or mixture of acids forms so dilute a solution that its molecular conductivity can be accurately represented by $c/n^{\frac{1}{2}}$. With an amount of ionized dissociated di-acid proportional to $1/n^{\frac{1}{2}}$ the molecular conductivity ought to be proportional to $\Lambda_0/n^{\frac{1}{2}}(1+bm^{\frac{1}{3}})$, where m is the actual concentration of the organic ions. The fact that this term $bm^{\frac{1}{3}}$ does not appear in (12) proves that the actual concentration of the organic ions is too small to make it appreciable. This is exactly what we should expect of such acids as we have found to form Na salts when peptone is neutralized with NaOH. The phenomena of diffusion with peptones and their compounds must be considerably complicated by the ionizations which take place with them. The result of Kühne that pepsinpeptone diffuses only half as slowly as glucose (twice as fast) seems incompatible with the results of the present paper (see Cohnheim's *Chemie der Eiweisskörper*, p. 87). The diffusion of the peptones is worth thorough investigation for its bearings upon the whole physical chemistry of digestion.

By this method we shall now investigate the Na salts of globulin and casein. For Hardy's data for the conductivity of solutions of Na globulin I have found the following formula to hold with the units used in this paper (Proc. Roy. Soc. B. lxxix. p. 146):—

$$\lambda = 22 + 1/(0{\cdot}005 + 3{\cdot}1\,m^{\frac{1}{3}}). \quad . \quad . \quad . \quad (13)$$

At infinite dilution this gives $\lambda = 222$, which is a little greater than the 218·4 of Kohlrausch for NaOH at 18° and infinite dilution. The remarkable point about this formula is the functioning of one half of the Na in quite a different capacity from the other, shown by the term $22 = 44/2$ which is independent of the concentration. Moreover, although at infinite dilution the conductivity is nearly that of NaOH, at ordinary finite dilutions it is much smaller than that of NaOH because the coefficient 3·1 is so large. This large coefficient is due to the globulin whose ions involve the half of the Na ions and all the OH ions in a greater viscosity of electric origin. The globulin ions act as an electric brake upon the electrically driven OH ions and half of the Na ions. Thus although the experiments with Na globulin are not yet refined enough in practice and theory to yield directly the conductivity of the globulin ion, they give us the viscosity of electric origin due to the globulin ion, and thus enable us to find its conductivity and volume by the methods of the present paper, if we accept Hardy's conclusion that ν_2 is probably 2. Let us write (13) in the general form

$$\lambda = \Lambda_{0b}/2 + 1/\{1/(\Lambda_{0b}/2 + \Lambda_{0a}) + bm^{\frac{1}{3}}\}, \quad . \quad . \quad (14)$$

where Λ_{0b} represents the conductivity of the positive ion like Na, and Λ_{0a} represents that of OH. Probably Λ_{02} the conductivity of the globulin or similar ion ought to appear on the right side as an additional term, but it is best omitted till it emerges clearly from the experiments. For NH_4 globulin this formula holds just as for Na globulin. I shall now show that it applies to Na and NH_4 casein, thereby strengthening considerably the validity of its form and interpretation. The data for the caseinates were obtained by Sackur (*Ztschr. f. physik. Chem.* lxi. 1902) at 25°. For Na casein they give $\Lambda_{0b}/2=28\cdot15$, $\Lambda_{0b}/2+\Lambda_{0a}=219\cdot3$, and $b=1\cdot678$. The sum of 28·15 and 219·3 is 247·4, while λ for NaOH at 25° and infinite dilution is 247·2. Kohlrausch's value for $\Lambda_{0b}/2$ at 25° is 25·6, so perhaps 28·15–25·6 represents a tendency for Λ_{02} for casein to make its appearance. The following comparison shows the applicability of (14) to Na casein:—

1/1000 m ...	40	80	160	320	640
λ exp.	46·5	51·3	56·2	63·0	69·5
λ calc.	46·8	51·1	56·4	62·5	69·7

For NH_4 casein $\Lambda_{0b}/2=38\cdot4$, $\Lambda_{0b}/2+\Lambda_{0a}=231\cdot5$, and $b=1\cdot634$. For Hardy's NH_4 globulin at 18° the corresponding values are 29, 208·3, and 2·3, this last number differing unaccountably from the 3·1 for Na globulin.

It is necessary to form some conception of the way in which half of the positive ions in these solutions are exempt from the resistance of viscosity of electric origin. The case becomes clearer if we consider first the simpler one of the HCl compound of globulin for which (*loc. cit.*)

$$1/\lambda=1/384\cdot6+0\cdot9\,m^{\frac{1}{3}}. \quad . \quad . \quad . \quad . \quad (15)$$

Here at infinite dilution the conductivity is 384·6, which is almost the 384·0 for pure HCl, while 0·9 for b is so large that it must be due to large globulin ions. It seems, then, that HCl in water ionizes the globulin molecule into a positive and a negative globulin ion which we shall denote by the symbols G_b and G_a. The solution of globulin in HCl is a mixture of solutions of G_bCl and G_aNa, which are both completely ionized at all concentrations, so that at infinite dilution the conductivity is the sum of those for H, Cl, G_a, and G_b. But $\Lambda_{0a}+\Lambda_{0b}$ is too small compared with $\Lambda_{01}+\Lambda_{02}$ for HCl to be found from ordinary conductivity experiments, and therefore does not appear in (15). But to find the effect of the globulin ions on the value of b we may reason in the following manner. So far I have not considered the molecular conductivity of mixtures in general, though the subject ought to illustrate some of the details of viscosities of electric origin. But for the matter in hand we may formulate a simple approximate theory for our mixture of globulin compounds thus:—As the ions pass one another we shall have cases where G_b has G_a for its neighbour, and also others where Cl is its neighbour, and similarly with G_a. It is as if we had to do with a mixture of G_aG_b, G_bCl, G_aNa, and HCl. The slowly moving ions G_a and G_b cause most of the viscous resistance of electric origin; we shall assume that they cause it all. To find the appropriate $1/\lambda_0$ for introducing in the righthand side of (1) we note that with pure G_aG_b we should use $1/\Lambda_{0a}+1/\Lambda_{0b}$, say $2/\Lambda_0$, and with pure G_aNa $1/\Lambda_{0a}+1/\Lambda_{01}$, so that a mean value suitable for G_a would be $(3/\Lambda_0+1/\Lambda_{01})/2$, which is nearly $3/2\Lambda_0$. So for G_b we should get $3/2\Lambda_0$. With Λ_0 as a sort of mean value for both globulin ions we have $1/\lambda_0$ represented by $3/2\Lambda_0$.

Hardy has shown (Journ. of Physiology, xxxiii. p. 251) that the valency of globulin is probably even, so we shall try 2 as its simplest likely value, according to my globulin paper (*loc. cit.*). Now G_a when associated with G_b as its neighbour would give 2×2 for $\nu_1\nu_2$ in (2) or (6), and when associated with Na would give 2×1. Hence for the mean value of ν for its neighbour we take 3/2, and we can now adapt (8) to the case we are considering by introducing into its righthand side Λ_{01} or 44 for Na, which was omitted as a factor in comparing Na compounds amongst themselves. Hence for the mean globulin ion of assumed valency 2 we have

$$b(\Lambda_0/2)\{2n_1/(n_1+n_2)\}^{\frac{1}{3}}/(3/2)^2=0{\cdot}0425\times44. \quad . \quad (16)$$

As each HCl produces two globulin ions, m should be replaced by $2m$ for G and H or Cl, and so the proper value of b to use in this equation is the mean of $0{\cdot}9$ and $0{\cdot}9/2^{\frac{1}{3}}$. The appropriate value for $\{2n_1/(n_1+n_2)\}^{\frac{1}{3}}$ is the mean of those for $n_1=n_2=2$, and $n_1=2$, $n_2=1$, or 1·050. These give $\Lambda_0/2=4{\cdot}965$, and so $\Lambda_0=9{\cdot}93$, while Hardy's direct measurement by the method of Lodge shows that it is about 10. With 4·965 for Λ_0/ν in (11) we get $B=9506$. Hence, with x for the number of C atoms in the globulin ion, by means of the following percentage composition of globulin and the values of B for the atoms

	C.	H.	N.	O.	S.
Per cent.	52·71	7·01	15·85	23·32	1·11
Atomic B	8	4	8	6	18

we get the equations $12\,x=0{\cdot}5271$ times the mass of the globulin ion (H=1), and

$$x\left\{8+\frac{12}{52{\cdot}71}\left(4\,.\,\frac{7{\cdot}01}{1}+8\,.\,\frac{15{\cdot}85}{14}+6\,.\,\frac{23{\cdot}32}{16}+18\,.\,\frac{1{\cdot}11}{32}\right)\right\}=\mathrm{B}. \quad (17)$$

These give $x=512$ and the molecular mass of the globulin ion as 11650, so that its equivalent is 5825. With HCl Hardy found the equivalent of globulin to be 5560, the sharper results with NaOH indicating 5000. Thus the value of *b* has given us values of Λ_0 and of the equivalent of globulin in excellent agreement with the direct determinations of experiment. There is good reason for believing, then, that the valency of the globulin ions produced by HCl in water is 2 and their molecular mass (weight) is 10000 (nearly). The formula for the globulin ion is $C_{512}H_{817}N_{132}O_{170}S_4$.

Returning to the cases of the globulin and the casein compound formed with NaOH we find the marked peculiarity that half of the Na ions move unaffected by viscosity of electric origin, while the other half of the Na ions and all the OH ions are affected by it to an unexpected extent. For NaOH globulin $b=3{\cdot}1$, whereas for HCl globulin it is 0·9. For NH_4OH globulin it is 2·3, whereas we should expect the NaOH and NH_4OH compounds to have nearly the same value, as they do in the case of casein. If there were an excess of NaOH it would show almost the conductivity of pure NaOH, the ions of the excess appearing to escape the large viscosity due to the globulin. In reality, of course, all the Na and all the OH ions would move under a reduced average viscosity of electric origin, but the effect is the same as if those equivalent to the globulin suffered the full viscosity due to it, and those in excess moved as if free from that viscosity. But in the actual case half of the equivalent Na behaves as if free from the viscosity caused by the globulin. Here, then, we must have an arrangement of the Na, the OH, and the globulin ions, such as leaves half of the Na ions unconstrained by electric force from the rest of the ions. This arrangement, being different from the homogeneous distribution assumed in our theory, must be the cause of the increase in the value of *b*. But though in our ignorance of this arrangement we are not able to calculate from *b* the value of Λ_0, and that of B for the globulin ion in presence of NaOH, we can use the values of *b* to compare the sizes of the ions of globulin and casein. We must first reduce the value of *b* for NaOH casein from 25° to 18° by the factor 1·18, thus $1{\cdot}678\times1{\cdot}18=1{\cdot}98$, and then with 3·1 for *b* in NaOH globulin we have B for casein nearly $(1{\cdot}98/3{\cdot}1)^3$ times B for globulin. If we take 10000 for the mass of the globulin ion in presence of NaOH, we have that of the casein ion $10000\ (1{\cdot}98/3{\cdot}1)^3$ nearly or 2605. With the percentage composition of casein, C 53·07, H 7·13, N 15·64, O 22·60, S 0·76, and P 0·80, and with 16 for the atomic B of P we can write down the corresponding formula for the casein ion, but it is better to derive this from the experimental equivalent of casein, as is done below.

If $\nu = 2$, as in the case of globulin, the equivalent of casein is 1302. Now Laqueur and Sackur found 1135 for the equivalent of casein in its NaOH compound using phenolphthalein as indicator. The calculated result, as regards order of magnitude, is in satisfactory agreement with this. Hence the casein ion appears to be divalent, and its molecular mass by titration is 1135×2 or 2270. According to the percentage composition of casein and 2270 for the mass of its ion the formula of its ion is half of $C_{200}H_{322}N_{50}O_{64}SP$, and as we have seen by analogy with globulin the casein ions must be derived in pairs from the casein molecule, the formula just given is the simplest possible according to physical considerations. It is also the simplest according to purely chemical considerations, as the S atom or the P atom cannot be divided. When we speak of the casein ion being half of this formula we mean the average casein ion, the S may go with one of the ions and P with the other, or both S and P may be in one ion and neither of them in the other, the mean ion always containing $\frac{1}{2}$S and $\frac{1}{2}$P. In the same way the formula of the globulin ion is half of $C_{1024}H_{1634}N_{264}O_{340}S_8$, which we take to be the formula for the globulin molecule. My previous estimate was dearly double this (*loc. cit.*). According to the theory of the colloidal state proposed by me in 'The Chemistry of Globulin' (*loc. cit.*) colloidal globulin and casein will have the molecules which are given by their formulas not present as free molecules, but as those three-dimensional patterns proposed to be called semplars, which are joined symmetrically to one another by some of the latent valencies of N and O being called into action. For a full account of many previous methods of estimating the mass of large protein molecules the reader is referred to *Die Grösse des Eiweissmoleküls* by F. N. Schulz (Jena, G. Fischer, 1903).

Melbourne, May 1908.

Fig. 2.

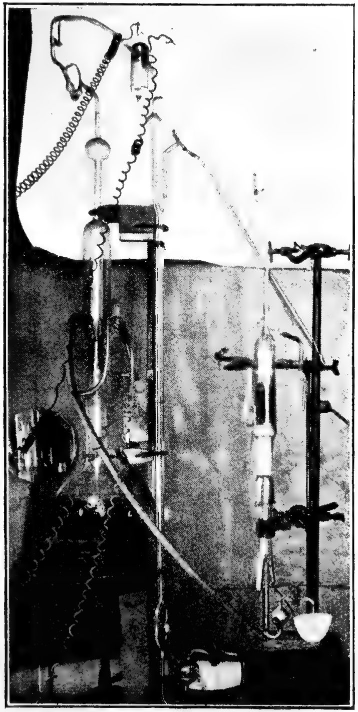
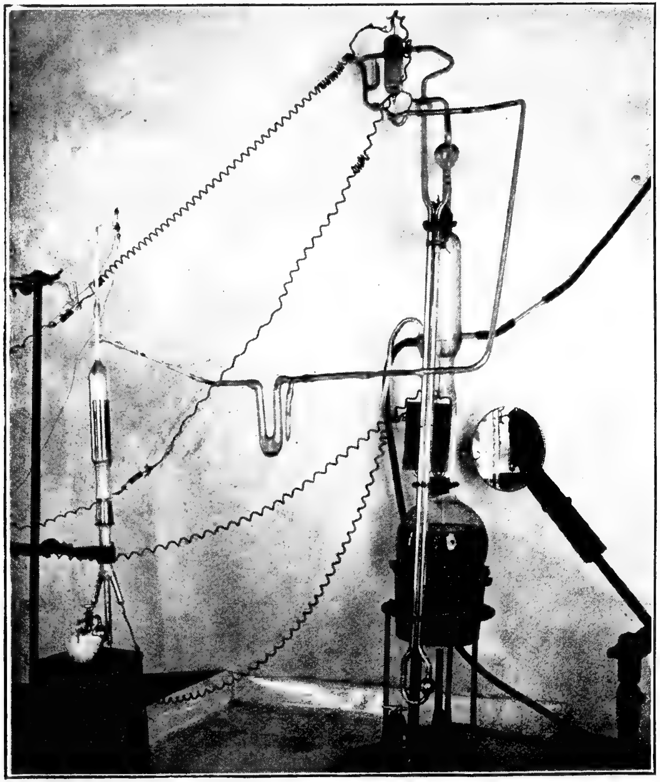


Fig. 3.



XLVI. *Attempts to detect the Production of Helium from the Primary Radio-Elements.* *By* FREDERICK SODDY, *M.A.*[*]

[Plate XX.]

THE question whether helium is a product of the radioactive changes of uranium and thorium has proved an extremely difficult one to settle experimentally. The work here described was commenced in 1905, and the results obtained, though by themselves of no significance as yet, appear to warrant the hope that all difficulties have been overcome, and now only a sufficiently long period of time and periodic testing are required to solve the problem. The quantities of helium that have been looked for throughout are of the order of a millionth part of a cubic centimetre, which is the amount present in only a fraction of a cubic centimetre of atmospheric air. From the first it was recognized that the difficulties in the way of ensuring that the observations had a real significance were so formidable, that mere qualitative detection or non-detection of helium, however definite or frequently repeated, would not of itself suffice to settle the question beyond all doubt. The objects of the experiments have been to obtain a quantitative estimate by the spectroscope of the amount of helium produced from uranium and thorium, or in the event of negative results to fix a definite limit to the quantity of helium that could not fail to have been detected under the conditions. To be quite sure, it is necessary to carry out a long series of consistent quantitative experiments, in which helium is detected with regularity when the time of accumulation is above, and not detected when the time of accumulation is below a certain period. These are only now being commenced. Whether the necessary certainty and perfection have been achieved for the results to bear a significant interpretation, only the results of future tests will disclose. All that can now be claimed is that a beginning has been made.

Theoretical Rate of Production of Helium.

At the commencement of the work radioactive theory afforded only a halting and as it now seems deceptive guide to the order of the amount of helium to be looked for in experiments of this character. The calculations were so indirect and so imperfect that it was hardly possible to say as the result of any given experiment that it definitely conflicted with what is theoretically to be expected. The

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[*] Communicated by the Author.

theoretical estimates formed from now available data are quite different from what were formed when the work was commenced, and the difference between the older and the newer estimates indicated by theory have steadily widened as the new data have been accumulated. Had the present data been available, the task would have appeared even more hopeless to attempt than it did at first, for the theoretical estimates of the rate of disintegration of the primary radio-elements have steadily decreased. Thus Professor Rutherford gave for the radioactive constant of uranium, in 1905, 10^{-9} (year)$^{-1}$ ('Radioactivity,' 2nd edition, p. 458), and in 1906 2×10^{-10} (year)$^{-1}$ ('Radioactive Transformations,' p. 158), while the present value, calculated by the same method as the last, from more recent data, has again been lowered to $1{\cdot}2 \times 10^{-10}$. Considering the nature of the quantity, the alteration does not appear very vital, but for the purposes of the present work the difference between the first and last value is just the difference between waiting six weeks and waiting a year between tests before sufficient helium to be detected accumulates. The first is practicable, the second is hardly so.

While, however, the quantitative estimates of the rate of production of helium have decreased, the general progress of radioactivity since the commencement of the work has increased the probability that helium is a product of uranium and thorium, and indeed of all radio-elements producing α-rays, to such an extent that it is difficult at the present time to maintain the opposite view. The chief evidence, of course, is derived from the elucidation of the nature of the α-rays by Rutherford; but strong support is also given by the way in which the atomic weights of uranium, radium, and polonium, the latter estimated from its probable position in the periodic table, conform to the simple supposition that each α-ray-producing change results in a reduction of the atomic weight by four units.

It would scarcely be profitable to discuss all the possibilities that have to be taken into consideration in attempting to arrive at the upper and lower limits of the rate of production of helium indicated by theory. It is better to make the most probable assumptions and to consider in which direction the rate would be affected if these assumptions are altered.

The value $1{\cdot}2 \times 10^{-10}$ (year)$^{-1}$, just referred to, is arrived at by the application of the disintegration theory in its simplest form, from the ratio of the quantities of uranium to radium in minerals and the rate of disintegration of radium.

Throughout the most recent value for the latter, $3{\cdot}48\times10^{-4}$ (year)$^{-1}$, given by Boltwood (Am. Journ. Sci., June 1908, p. 493), will be taken. Multiplying it by the most recent value ($3{\cdot}4\times10^{-7}$) for the ratio of radium to uranium in minerals (Boltwood, *loc. cit.* April 1908, p. 297), gives $1{\cdot}2\times10^{-10}$ (year)$^{-1}$, which may be taken as the present theoretical value for the rate of disintegration of uranium according to these data, and will be referred to as the "direct value." For thorium we have yet no such direct method, and the difficulties commence.

It is necessary, before any further progress can be made with the calculation, to introduce the assumption that the α-particle is an atom of helium, and to first deduce, from the rate of disintegration of uranium, the rate of production of helium, on the assumption that one atom of uranium gives rise to some definite number (N) of atoms of helium. As the α-radiation of uranium is apparently homogeneous, and produced in the apparently single change of uranium into uranium X, it is reasonable to assume at first that one atom of helium is produced from one atom of uranium, and therefore that the helium is one-sixtieth of the weight of uranium disintegrating. This gives 2×10^{-12} (year)$^{-1}$ for the rate of production of helium from uranium.

To find from this the rate of production of helium from thorium it suffices, on the assumptions made, to compare the relative α-radiation of uranium and thorium and the average velocities of the α-particle of uranium and thorium respectively. For present purposes perhaps a sufficient approximation is reached if we regard the relatively greater average velocity of the thorium α-particle as just compensating for the relatively higher specific α-activity of thorium. This gives the same rate of production of helium for both uranium and thorium, viz. 2×10^{-12} (year)$^{-1}$.

The unfortunate feature about this calculation is that it may not be allowable to calculate the ratio of the rate of disintegration of radium to that of uranium, from the ratio of their respective quantities in minerals, because it is uncertain that the disintegration theory in its simplest form applies. Rutherford has suggested tentatively, in order to bring actinium into the scheme of radioactive changes in pitchblende, that actinium may be a product of disintegration of uranium produced simultaneously with the radium series, and not in the direct line between uranium and radium. If this is true, in equilibrium the number of atoms of radium formed are but a fraction of the atoms of uranium disintegrating, and the rate of disintegration of uranium must certainly be greater than $1{\cdot}2 \times 10^{-10}$, but to an, at present, indeterminate extent. This direct value therefore may be unsound, and the error affects also the derived calculations for thorium. As about to be shown, the increase from this cause is not, unfortunately, likely to be very great.

There is also an indirect method of calculating the rate of production of helium by a comparison of the α-rays, for which Boltwood has just recently supplied much more complete data than were before available. It leads to a greater value than the direct method, which we have seen is likely to give too low a value, and is perhaps to be preferred. Boltwood deduces from his most recent determination of the proportionate α-radiation contributed by each of the radioactive bodies in uranium minerals (Am. Journ. Sci., April 1908, p. 296) that the α-activity of radium (free from all products) is 1,300,000 times that of uranium. As the range of the α-particle is the same in each case, the rate of disintegration of uranium by this method comes out at $3{\cdot}48 \times 10^{-4} \div 1{\cdot}3 \times 10^{6} = 2{\cdot}7 \times 10^{-10}$. This is 2·25 times the "direct value," and gives for the rate of production of helium from uranium and thorium $4{\cdot}5 \times 10^{-12}$ (year)$^{-1}$. For pitchblende, containing equilibrium amounts of all products, Boltwood (*loc. cit.*) finds the α-activity to be about 4·7 times that contributed by the uranium. As some of this activity is due to α-rays of much higher velocity than those of uranium, one can deduce in this method of calculation that for pitchblende the rate of production of helium should be about four times that of the uranium it contains. Whereas, of course, on the simple disintegration theory, which recognizes in pitchblende the existence of seven, and indicates eight, α-ray or helium-producing changes, only one of which is contributed by uranium, it is to be expected that pitchblende would produce helium at eight times the rate of the uranium present, which is twice the preceding value. Boltwood himself points out that the discrepancy could be partially accounted for on the assumption that uranium suffers two α-ray changes, which is, according to the preceding view, that the uranium atom gives two helium atoms. Certainly his results are most suggestive. The α-radiation from the radium series is in good agreement with the view that a single α-particle is expelled by radium and by each of its successive α-ray products, the α-radiation from uranium is slightly more than would be the case if it expelled two α-particles, while the whole of the α-ray-changes of the actinium series together only constitute about one-half the effect of a single α-ray change in the radium series. As there are four α-ray changes known in the actinium series, these results indicate that out of eight atoms of uranium disintegrating, seven go to produce radium and one to produce actinium. With these assumptions the direct and indirect values for the rate of disintegration of uranium become consistent and give the same value $2{\cdot}7 \times 10^{-10}$ (year)$^{-1}$. Thus $4{\cdot}5 \times 10^{-12}$ (year)$^{-1}$ may be taken as the more probable value in both cases, while for pitchblende, assuming that all the helium formed comes into evidence as α-rays, the more probable value is four times that of the uranium it contains. The smallest possible quantity of helium that can be detected under present conditions will be shown to be about a millionth of a cubic centimetre, or $1{\cdot}8 \times 10^{-10}$ gram. That is to say, a gram of uranium or thorium should produce a just detectable amount of helium in a period of 40 years, while for a quantity of pitchblende containing a gram of uranium and all its products the same should occur in 10 years. Even with considerable quantities of material the accumulation of results must therefore be necessarily a slow process. So far it has not been practicable to deal with quantities of material containing more than a third of a kilogram of the element, so that on the new data it is to be expected that the minimum period of accumulation to give a positive result with uranium or thorium must be considerably over a month, on the indirect value, or three months on the direct value.

In absence of direct experiments the question has been attacked indirectly, with conflicting conclusions by different observers, from the association of helium with uranium and thorium in minerals. Boltwood (Am. Journ. Sci. 1907, xxiii. p. 77) considers that helium is probably not a product of thorium disintegration, and that, even in thorianite, the helium can be accounted for by the disintegration of the uranium series alone. This would of course involve the abandonment of the view that the α-particle is an atom of helium and of almost all the preceding theoretical calculations. The only datum that would remain would be that from the "direct value" of the rate of disintegration of uranium, namely, that the helium production is $N \times 2.10^{-12}$ (year)$^{-1}$, where N is the number of atoms of helium formed from one atom of uranium, and this would be subject to an increase should branch series, such as actinium, occur. Strutt (compare Proc. Roy. Soc. 1908, 80 A, p. 572), on the other hand, has advocated the other view. He regards the existence of helium in a specimen of fluor from Ivitgut, Greenland, examined by Prof. Julius Thomson, which contains thorium and helium but no radium, as conclusive evidence that helium is a disintegration product of thorium. He finds from a recent examination of a large number of rare, and representative common minerals, that helium in detectable quantity is present in all. In every case but one it can be accounted for by the presence of the uranium-radium series and of thorium. The exception is *Beryl*, which contains noticeable amounts of helium and is scarcely radioactive. The existence of even this one exception would appear to weaken somewhat the argument he draws from the presence of helium in fluor, and shows the necessity for caution in drawing conclusions by the indirect method.

Sufficient has been said to show the deep importance of obtaining if possible a direct experimental determination of the rate of production of helium from the primary radio-elements and from the radioactive minerals. There is little doubt that such results, if they can be obtained, would prove invaluable in settling some of the outstanding problems in radioactivity which radioactive methods from their nature are unable unaided to solve.

Method of Work, and Early Experiments.

The process recently described (Soddy, Proc. Roy. Soc. 1907, 78 A, p. 429) for the detection and measurement of infinitesimal quantities of helium has been exclusively used. It depends on the use of calcium heated to its volatilisation point in a specially constructed vacuum electric furnace. All known gases but those of the argon family are perectly absorbed. The completeness of the absorption under proper conditions is such that the residual gas compressed several thousand times (by filling the absorption vessel after cooling with mercury) into the smallest possible spectrum-tube hardly suffices to conduct the discharge, and, in the absence of argon gases, the spectrum-tube remains on the verge of non-conductance. The sensitiveness of the method as a test for the presence of helium is increased many thousand times by filling the apparatus with mercury, although the labour of the investigations entailed in the continual cutting down and building up of the complex apparatus is of course very great. The general method throughout has been to store the substances under examination in solution in glass flasks placed on water-baths. The air is first as completely as possible removed by boiling the solutions and pumping with a mercury-pump through a U-tube placed in a freezing-mixture. A new mercury-pump filled with new mercury, provided with two large drying-tubes, containing sulphuric acid and phosphorus pentoxide respectively, was erected at the commencement of the work, and has been kept exclusively for these experiments. In making a test for helium, the calcium furnace is first pumped out as completely as possible, the calcium is then heated, and the pumping continued, so that the expelled gas serves to wash out the last traces of air. The pump is then sealed off, and communication made with the flask through the cooled U-tube, and the solution boiled. The calcium furnace is sealed off and, when cold, filled in the dark room with dry mercury. As soon as the spectrum-tube conducts at all, the spectrum is rapidly examined with a Ramsay train of prisms, and if D_3, the characteristic line of the helium, is observed, the tube is generally sealed off and examined with a good spectroscope.

The first and also the second series of experiments with thorium and uranium came to a premature end on account of accidents; but the third series, of which the experiment with thorium was started first, has been more successful, and is still in progress. The main experimental difficulty at first encountered was air. The argon in a few cubic centimetres of air is sufficient to prevent completely the detection of the minute amounts of helium looked for in these experiments. To free a litre or more of solution from every trace of air, and to preserve it for months or years in this condition while making provision for the complete removal of the gas for testing at will, calls for very perfect arrangements, and the method employed in the last series is the outcome of many previous failures. In the first series of experiments, started in August 1905, about a kilogram each of uranium nitrate and thorium nitrate, of ordinary commercial quality, were employed. The exit tube from the flasks was joined to a Y-tube, the vertical limb of which was a barometer dipping into a mercury reservoir which could be raised or lowered, sealing or opening the passage through the upper branches of the Y-tube. The other branch of the Y was provided with a tap, and the pump, &c. could thus be sealed to it without air entering the solution. In this way the air-tightness of the tap was depended upon only during the actual removal of the gases to the testing-furnace, and any air leaking through during the long periods of accumulation could be removed before lowering the mercury seal. This worked well until one night the lubricant of the tap failed, and the next morning air was found to be bubbling through the mercury seal into the flasks. Before this ten tests had been made—six with the uranium and four with the thorium. The whole of six former and the first three of the latter were failures

[illegible] [illegible] on [illegible]

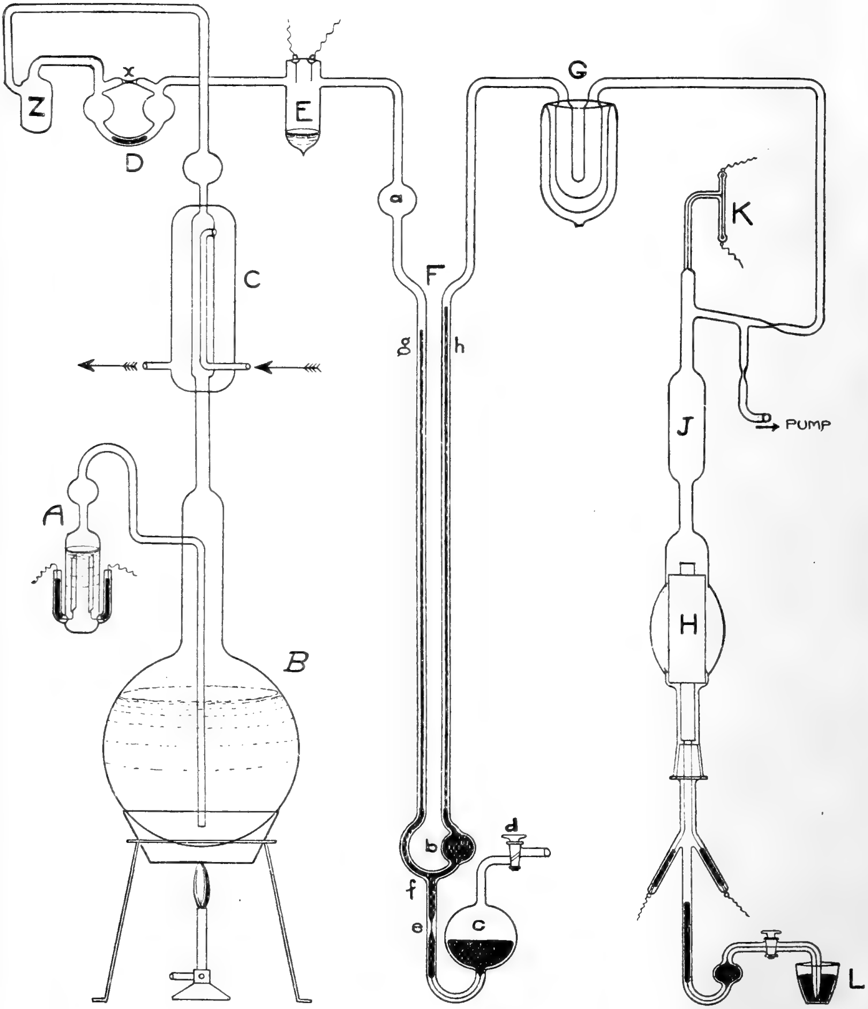
on account of the presence of argon, from air in the solutions. The last test with thorium was completely successful, but it was in the nature of a blank experiment, the period of accumulation of gas in the thorium being only about 22·5 hours. No sign of helium was seen. The minimum quantity detectable under the circumstances—about 2×10^{-9} gram—would have been observed, as the experiment was a very perfect one.

In the second series of experiments, vertical all-glass reflux condensers were sealed to the flasks, and the principle of the mercury seal was pushed to its logical conclusion by making the two upper limbs of the Y-tube the barometric height, so that there could be a vacuum on the one side and the pressure of an atmosphere on the other. The principle was correct, and is being used in the experiments now in progress; but the design was faulty, and the arrangement need not therefore be described in more detail. Four flasks were set up in this series, but only two, with the uranium and thorium preparations before employed, are concerned in this investigation. The first and the only test with the thorium solution failed on account of argon being present. Carbon dioxide was noticed in the gas as it was admitted to the furnace, and, after the absorption, the spectrum was that of pure argon. The first two tests with uranium failed also from the same cause, but the last was a perfect experiment. The solution had been left to accumulate for six days and four hours, and D_3 was present faint and clear on the spark-spectrum of argon. The spectrum-tube was of soda-glass with a volume of 0·3 c.c., a kind that has been subsequently abandoned. With it, a quantity of about 2×10^{-9} gram helium could be detected.

During the experiment, however, a violent bumping of the uranium solution during boiling projected some of it over on to the top of the mercury in the tap, and the strongly acid liquid at once began to attack the mercury with the evolution of oxides of nitrogen. These, of course, did no harm, as the calcium absorbs them, but the flask had to be cut down. In this operation, owing to faulty design of the mercury taps, the whole of the flasks were spoiled, and this series of experiments came to an end. With regard to the single result, it must be borne in mind that the experiment was performed three years ago, before the possible sources of error were as well known as now, and no significance is to be attached to it. In fact, more recent results have failed to confirm it.

In the first experiment of the third series with thorium now in progress, many changes and improvements were introduced. So far as the flask and its attached mercury tap is concerned, the design then adopted has been adhered to with but slight modification in all the later experiments, and has been found to work perfectly, and will therefore be described in detail. But frequent changes have been made from time to time in the method of performing the testing operations. As finality in this direction has perhaps not even yet been reached, the detailed description of this part of the work will be deferred. The apparatus in its present form is shown in the diagram in fig. 1 (p. 522), and the photographs of the actual thorium apparatus, from the front and from the sides, are shown in Plate XX. The earlier failures had shown the difficulty, first of freeing a large quantity of liquid perfectly from dissolved air, and secondly of getting it under these circumstances to boil regularly. The dangerous percussive boiling, which made the earlier experiments so precarious, was reduced, and at the same time the dissolved air was efficiently and rapidly removed by sealing into the flask (B) a tube reaching to the bottom and connected to a voltameter (A) for generating a mixture of hydrogen and oxygen. An all-glass vertical condenser (C) with double circulation of water was sealed to the neck of the flask, and provided at the upper end with a large bulb. This was connected to a trap (D) formed by a single drop of mercury, for the purpose of preventing the expelled gas from diffusing back into the flask. During the preliminary removal of the air the by-pass (x) was open, and then it was sealed as shown. E is a glass chamber for combining the hydrogen and oxygen by means of a discharge from a coil, and for condensing the bulk of the water produced. F is the mercury tap. G is the U-tube to condense water-vapour, which in the later experiments has been immersed in liquid air. H is the calcium furnace, which, after the experiment, is sealed off and filled with mercury from the crucible (L). K is the spectrum-tube described later. J is a subsidiary volume, only used in the more recent tests, the purpose of which is to neutralize the effect of the volume of the U-tube. The device is copied from that employed by Ramsay & Cameron (Journ. Chem. Soc. Trans. 1907, p. 1598, fig. 1). The U-tube G must necessarily have a somewhat large volume to prevent its becoming choked with ice. At the temperature of liquid air its volume is virtually trebled, whereas the volume of the calcium furnace at the high temperature is virtually halved. Hence an inconveniently large fraction of the gas remains in the U-tube when it is sealed off. To avoid this, J is surrounded with a cup of moist filter-paper which is then filled with liquid air. Its volume is equal to or greater than that of the U-tube, and hence the greater part of the gas is obtained for the test.

Fig. 1.



The procedure in removing air is simply to keep the solution boiling and to pass a rapid current of gas from the voltameter, recombining it with occasional sparks in the chamber E. From time to time, the mercury in the tap is lowered and the contents of E removed by the pump. The tap F alone calls for more detailed description. It is worked by connecting the tap *d* to a mechanical air-pump. It is made slow-acting by means of the construction (*e*). Obviously the bulb (*c*) must be below the level of the junction of the limbs (*g*) and (*h*); so that if the tap (*d*) were left open to the air when *h* is also open to the air, the mercury would be blown out of the tap into the flask. This is the sole danger to guard against. If the tap (*d*) is closed in time, even a sudden break anywhere on the *h* side of the mercury tap does no harm. The small bulbs *a* and *b* take up the inertia of the moving mercury, and the slow flow of mercury into *c* increases the pressure of the air there above the atmospheric so that the mercury remains in the tap permanently above the level *f*. The dimensions of the tap are as follows:—

Height over all, 107 cms.
Distance between the bulbs *a* and *b*, 85 cms.
Diameter of bulb *c*, 40 mms.
Diameter of barometer-tubes *g* and *h*, 3 mms.
Diameter of bulbs *a* and *b*, 26 mms.

What is very important is that these dimensions have sufficient margin to allow of the slight excess of pressure required for glass-blowing operations on the *h*-limb of the tap while there is a vacuum in the other. It was the failure to allow for this contingency which caused the accident to the second series of experiments.

The height of the mercury in the limb *g* indicates the pressure of gas in the flask, which is never allowed to exceed a few cms. of mercury. Soon after setting up the thorium and uranium flasks, some of the mercury in the trap D found its way into the solutions during the operations, contaminating them and causing oxides of nitrogen to be present in the removed gases. This does no great harm, but in the later experiments the trap Z has been added to avoid this contingency. It is probable no further modification of this part of the apparatus will be called for.

What may be called the engineering of so unwieldy an apparatus may be seen from the Plate (XX.). On the small wood base supporting the water-bath is fixed a vertical bar of T-iron to which the flask, condenser, voltameter, and mercury tap are fastened. The voltameter is between the flask and mercury tap, and is not seen in the photographs except by reflexion in the circular mirror placed behind it. The apparatus, when sealed off from the furnace, is self-contained, and can if necessary be moved. When not in use, the tube attached to the limb *h* is exhausted and sealed. In reopening it, it is advisable to break the tip under a rubber cap and to admit the air slowly, although each mercury tap, before being used, is tested under working conditions by a sudden break to ensure that it is correctly dimensioned. Recently such a sudden break occurred with the thorium flask, doing no harm.

Spectroscopic Test for the presence of Helium.

Before discussing the results so far obtained, it is necessary to state exactly what is and what is not considered sufficient evidence of the presence of these infinitesimal quantities of helium. The D_3 line is generally the only line visible, and fortunately its position is quite easy to verify with accuracy owing to its proximity to the sodium lines. The D_3 line becomes quite brilliant under all circumstances before any of the other lines in the helium spectrum appear. Now the hydrogen secondary spectrum, which is composed of so many lines in the yellow and green region that it appears more or less continuous, has a line so near D_3 that it cannot be distinguished by visual observation even with a good spectroscope. It is always less brilliant than other lines on the more refrangible side. An ordinary hydrogen tube, filled at not too low pressure, shows this line; and it is useless to attempt to detect the minimum amount of helium in presence of the hydrogen secondary spectrum. It is also useless when argon is at all strong, as there are lines in the spectrum very close to D_3, although there is always more than one, relatively weak, in the small tubes used, compared to the other lines. In the cases mentioned the test would be rejected. What is required is that D_3 should be seen on a black background with no lines in its immediate neighbourhood, except D_1 and D_2 if a soda-glass spectrum is used, and the position of the line must be exactly found both with reference to the sodium line, and by comparison with a helium-tube.

A considerable quantity of helium, say 10 or 20 times the minimum amount, can be detected in presence of a strong argon spectrum, as D_3 under these circumstances is far brighter than the neighbouring argon lines. Very small quantities of argon do not interfere greatly with the observation of D_3; for under these circumstances only the blue or spark spectrum of argon is observed, which has practically no lines in the less refrangible part of the spectrum.

With the infinitesimal quantities of gas dealt with in these experiments, the passage of even a weak discharge causes the spectrum-tube to become non-conducting in a few seconds. All observations must be carried out very quickly, but with experience a single glance is usually sufficient; and one's first judgment, even with the smallest quantities of helium, is rarely reversed by subsequent observations.

One other very important consideration must be mentioned. The fact that the argon from a cubic millimetre of air is sufficient to spoil the test is in reality a very great advantage, and constitutes its main claim to suitability and safety in the present work. If, for example, the method of Sir James Dewar, of absorbing non-helium gases by cold charcoal, were employed, since that method absorbs argon also, there never *could* be any complete certainty, when helium was observed, that it was not derived from atmospheric air which had been left in the solution, or had leaked in. With the method employed the slightest leak of air is fatal in itself, and there is no possibility if helium is observed that it is derived from the air. When first devised, it was thought the method would make the work comparatively easy; but afterwards, when the numerous failures due to residual argon were being experienced, it seemed as though little had been gained. In the work with radium the difficulty had been nitrogen; whereas here exactly the same precautions had to be taken to exclude air as if the calcium had not been able to absorb nitrogen. Its ability to absorb the hydrogen and hydrocarbon gases always normally present in work of this character, is, however, its real advantage.

Calibration Experiments.

Everything depends, if the results are to have any theoretical significance, upon the smallest amount of helium that can be detected by the method described being accurately and definitely known; and this part of the investigation has been carried out with great care. The results have been gratifying in that they have shown that the limit of visibility of the D_3 line constitutes a perfectly sharp and definite quantitative test for helium. Some preliminary experiments on this question were given in the original paper describing the method. Ordinary Plücker tubes were employed and the apparatus was not filled with mercury, but the minimum quantity detectable was arrived at by dividing the total quantity added by the ratio of the total volume to that of the spectrum-tube employed. The present data show that there is an error somewhere in these calculations, owing probably to the limiting partial pressure of helium detectable in an ordinary Plücker tube being less than in a tube of minimum volume. The minimum detectable quantity of helium, even in a tube of the smallest possible volume, is much greater than was formerly deduced by calculation. Thus while the estimates of the amounts of helium to be expected have grown less, the estimates of the capabilities of the spectroscope have also diminished; so that the task is now known to be more difficult, for a double reason, than was at first supposed.

In the present series of tests the processes of sealing off, absorption, and subsequent filling of the apparatus with mercury, were carried out exactly as in actual experiments. Tests were conducted with three different types of spectrum-tubes, all furnished with electrodes of simple platinum wire. Those used in the early work, but now abandoned, had a volume of about 0·3 c.c., and were made of soda-glass. The bore of the capillary was rather too wide for the best results. The kind now used exclusively consist of a very small tube indeed, with hardly any unnecessary space around the electrodes, made of lead-glass with a total volume of only about 0·04 c.c. A third type were exactly similar except that they were made of soda-glass. They all became exhausted under the discharge with great rapidity, but for the present work the advantage of smaller volume, made possible by the use of platinum electrodes, outweighed the advantage of longer life to be derived from using aluminium electrodes.

Several mixtures of pure helium with pure oxygen, containing only a few parts per million of helium, were made up by the principle of successive dilutions, with the greatest care, using the spectrum-tube filler devised by Sir William Ramsay. With the same device, a known fraction of a cubic centim. of the mixture was admitted to the exhausted calcium furnace. The furnace was sealed off, and a correction applied for the part of the gas not used. The absorption of the oxygen and filling of the apparatus with mercury were then carried out in the usual manner.

The general result has been to show that with the lead-glass tube described, a quantity of helium below a "tenth-gram," that is 10^{-10} gram, cannot be detected; while in a perfect experiment two tenth-grams can be detected with certainty. For the tubes of soda-glass otherwise similar, the quantity detectable is about twice this. In the first place the brightness of the neighbouring sodium lines interferes with the test; and, secondly, the glass conducts much more readily than lead-glass; so that the discharge under some circumstances passes, not through the glass at all, the spectrum of which is not observed, but almost wholly along the glass surface, causing it to fluoresce brilliantly and show the sodium lines. Test C VI. of the table was a very instructive one in this respect. On first running the tube the sodium lines were strong and D_3 scarcely visible, but the character of the discharge suddenly changed and D_3 came out more strongly, and continued for some little time quite obvious. The experiments with the old type of tube show the great advantage of reducing the volume; for with these the minimum detectable quantity of helium was about 16 tenth-grams. It was found in actual practice that even when the absorption of the residual gas by the calcium was as perfect as possible, there was no danger of the helium being so pure that it would not conduct the discharge (compare Mackenzie and Soddy, Proc. Roy, Soc. 1908, 80 A, p. 92). In order to avoid all doubt from the fact that the electrodes of spectrum-tubes absorb the rare gases, a new spectrum-tube was always used for the actual tests with the radio-elements, and in doubtful cases in the calibration tests.

In the following Table (p. 528) the calibration experiments have been collected. The first column gives the number of the test (C=calibration). The second column gives the amount of helium added in "tenth-grams" (10^{-10} gram). The third column gives the perfection of the experiment, that is, the degree to which the absorption of the residual gas was complete. If some running of the tube was necessary to clear the spectrum, the test is classed as good, fair, or bad, according to the amount of running required. Any experiments in which the spectrum could not be cleared are not included.

With regard to C XIV, which was a blank test with air purposely introduced, it was found impossible to mistake any of the lines in the argon spectrum for helium.

Lastly, tests have been made to see what multiple of the minimum quantity of helium detectable by means of the D_3 line is required to show the bright red line 6677, and the faint red 7056. In these experiments the calcium furnace was not filled with mercury. The minimum quantity of helium to show D_3 in a small lead-glass spectrum-tube without filling with mercury was found to be about

$$3 \times 10^{-3} \text{ c.c. } (=5{\cdot}4 \times 10^{-7} \text{ gram}).$$

As the ratio of the volume of the whole apparatus to that of the small spectrum-tube was about 1 : 2500, this is in good agreement with the preceding tests. Before any glimpse of the red line 6677 was seen three times this quantity had to be added, while with four times the line, though still faint, was obvious. To bring out the faint red line 7056, at least 20 times the minimum quantity is required; while with 30 times

Number of Test.	Helium in tenth-grms.	Quality of Experiment.	Observation of D_3.	Remarks.
Lead-glass spectrum-tubes, 0·04 c.c. volume.				
C I.........	0·9	Perfect.	Not seen.	Certainly below limit,
C II	1·8	Good.	Seen clearly.	Fairly bright argon also.
C XI	1·64	Perfect.	Ditto.	D_3 less bright than argon lines.
C XII	3·3	Good.	Ditto.	D_3 not much brighter than in last test.
C XIII ...	16·8	Good.	D_3 the brightest line.	Exceptionally strong argon spectrum.
C XIV ...	Blank test.	Perfect.	No line like D_3.	·025 c.c. of air added.
Soda-glass spectrum-tubes, 0·04 c.c. volume.				
C III......	1·4	Good.	Not seen.	Sodium lines strong.
C IV	1·8	Good.	Seen for a moment only.	Sodium lines interfere.
C V	2·2	Fair.	Seen for a short time.	Not enough to be depended upon.
C VI	3·6	Good.	Seen well.	But for some time D_3 was hardly visible.
Soda-glass spectrum-tubes, 0·3 c.c. volume.				
C VII ...	3·6	Bad.	Not seen.	Strong hydrocarbon spectrum at first.
C VIII ...	4·1	Fair.	Not seen.	Certainly below limit.
C IX	8·2	Good.	Not seen.	Ditto.
C X	16·4	Good.	Seen clearly.	About the limit.

this line is still excessively faint. The characteristic colour of the helium glow appeared with about 6 times; and the tube began to conduct easily, the spark-gap falling below 2 cms. with about 150 times the minimum quantity. In these experiments arrangements were made to admit small quantities of water-vapour when the tube became non-conducting. Then, by making the furnace very hot, the hydrogen of the calcium hydride formed exerts an appreciable tension of dissociation so that the discharge will pass. The degree of vacuum and the amount of hydrogen present did not, within the limits tried, have any appreciable effect on the various quantities of helium required to show the different lines. It may be inferred that, so long as a discharge will pass at all, D_3 will be seen if the minimum quantity of helium is present, however little other gas is present.

It is of interest to compare this quantity of two tenth-grams of helium found to be the minimum quantity detectable by the spectroscope, with the minimum quantity of radium, for example, detectable by radioactive methods. Using the emanation of radium for the test, about 10^{-11} gram is about the smallest detectable quantity, though no doubt with some refinements this could be with certainty reduced. The radioactive method in the case of radium is thus about 20 times more sensitive than the spectroscopic in the case of helium, a comparison much more in favour of the older method than might at first have been anticipated.

Results with Thorium.

In addition to the calibration tests already described, in all about 30 tests, involving the filling of the apparatus with mercury have been carried out, but only a few of these have been successful, and the results so far obtained are regarded merely as preliminary. Now, however, with greater experience, comparative certainty and immunity from failure have been secured. In the third series of experiments, which remain to be considered, four flasks have been set up, containing thorium nitrate, uranium nitrate, pitchblende in nitric acid solution, and sodium sulphate. The latter is intended partly as a blank experiment. Only the thorium experiment will be detailed in this paper, as the others have not yet been under observation a sufficient period of time.

The flask contains a solution of ordinary commercial thorium nitrate, several years old, corresponding to about 350 grams of the element thorium. The first test was a failure, and the second was rendered ambiguous owing to a trace of mercury entering the spectrum-tube. The third test was carried out successfully after a period of accumulation of 35 days. The absorption of the gas was only moderately perfect, but no indication of D_3 was observed at any stage of the experiment. The subsidiary volume J before referred to was not used in this experiment, so that only about one half of the gas would have been obtained for the test. The test therefore indicates that the rate of production of helium from thorium is not greater than 10^{-11} $(\text{year})^{-1}$, which is in agreement with the theory given.

In the next test the period of accumulation was 203 days, or about six times the preceding. As before, only about one-half of the total gas, probably, was obtained for the test. The experiment was a very perfect one, and D_3 was seen clearly in a fairly strong blue argon spectrum. It was exactly identified with reference to the sodium lines and with a comparison helium tube, and its quantity was estimated to be about 2 tenth-grams. It corresponded very closely with the calibration test C II. This gives for the rate of production of helium from thorium about 2×10^{-12} per year.

Further experiments must now be waited for. Not until a consistent series of quantitative tests of this character have been carried out, can any reliance be placed upon the results.

Summary.

The present rate of production of helium from uranium and thorium indicated by theory is about 2×10^{-12} per year as a minimum value if it is produced at all, or about $4{\cdot}5 \times 10^{-12}$ per year, calculated by an indirect method on the assumption that the α-particle is an atom of helium. The first of these values is almost eight times less than the value indicated when these experiments were started three years ago.

The minimum quantity of helium detectable by the spectroscope by the special methods employed has been shown to be two tenth-grams (10^{-10} gram), which is somewhat greater than was supposed at the commencement of the work. In consequence, the question has proved more difficult to settle than at first appeared. With the quantities of uranium and thorium employed in these experiments, a period of accumulation of several months is necessary to detect the helium if produced at the theoretical rate.

The experimental difficulties in the way of performing such tests have now been overcome, but only one positive result has so far been obtained. This was with 350 grams of thorium in the form of nitrate. Helium to the extent of about two tenth-grams was detected after a period of accumulation of nearly seven months, which corresponds with a rate of helium production of 2×10^{-12} per year. This result is of course of no significance until it is confirmed. All the other tests so far obtained only indicate that the rate of production of helium from both uranium and thorium is certainly below what was first deduced from the imperfect theory, and is certainly not above the rate indicated by the present theoretical data.

Since this paper was written, by the help of a research grant from the Carnegie Trustees, a new series of experiments have been successfully started with quantities of materials five-fold greater than before attempted.

Physical Chemistry Laboratory,
Glasgow University.

FIG. 2.

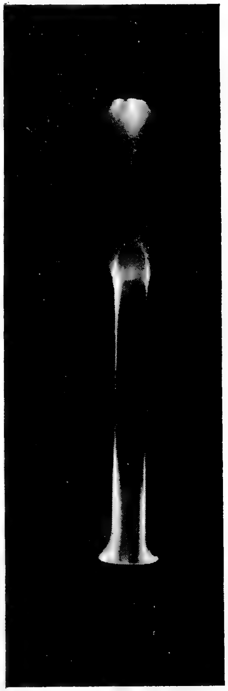


FIG. 3.

FIG. 4.

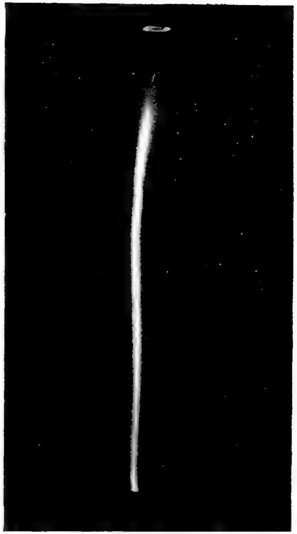


Fig. 5.

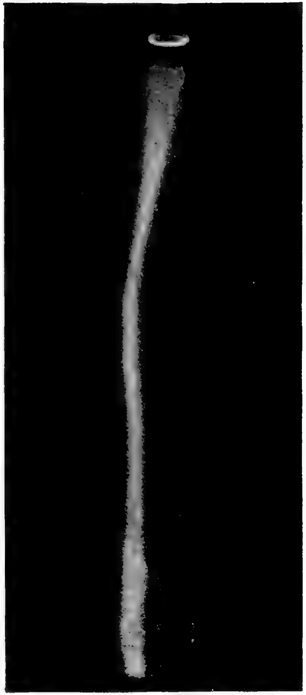
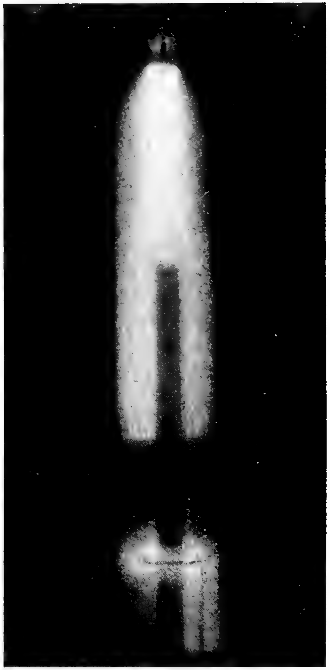


Fig. 6.

Fig. 7.



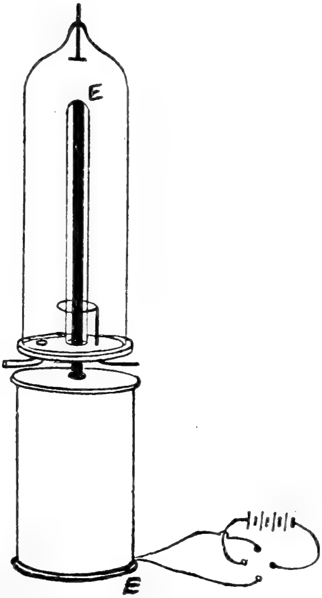
XLVII. *Magnetic Rotation of Electric Discharge.*
By Prof. D. N. MALLIK, *B.A.*, *Sc.D.*, *F.R.S.E.**

[Plate XXI.]

1. THE present paper presents a detailed study of the properties of the electric discharge in De La Rive's apparatus.

The apparatus is of the usual form. The vacuum-tube, however, is in communication with a pump and an ordinary barometric gauge. An aluminium disk and ring of the same material form the electrodes.

Fig. 1.



The electromagnet (E, E) is, as usual, made up of a coil carrying current and a soft iron core projecting from it. The discharge (in most of the experiments) is passed from an induction-coil, the E.M.F. of which is varied by changing the number of cells in the primary circuit.

2. As the pump is worked, it is found that at a certain pressure depending on the number of cells in the primary of the induction-coil, *i.e.* the E.M.F. of the induction-coil, and

---

* Communicated by the Author.

the distance between the electrodes and the nature of the gas, the discharge passes, but this discharge when it becomes continuous is, as a rule (§ 18), in the form of a spray or shower consisting of infinite number of streams or "rays" all round the axis of the tube. This discharge is unaffected when the electromagnet is excited.

Figs. 2, 3 (Pl. XXI.) are photographs* of such a discharge in air. The streams seem to be reflected at the side of the vessel; their shape therefore depends partly at least on the shape and dimensions of the vessel and the electrodes. Fig. 3 shows also a few bright streaks. They were formed temporarily, one after the other, during exposure of the plate, and were the results of the confluence of a certain number of "streams."

3. As the exhaustion proceeds, more and more of the rays aggregate into a band which becomes brighter and thicker as aggregation proceeds. This band is at first unsteady owing evidently to the fact that there is a continuous change in the constituent streams. Fig. 3 shows the initial stage of this process.

4. The bright band gradually becomes steady when the constituents do not any longer change with time. It then extends from a *definite* point on the ring to the nearest point of the disk (cathode), which is partially surrounded by a glow.

In the present apparatus (in which the ring has a gap) this point in the ring is about 180° from this gap. It is apparently the point in the ring at which the electric density is greatest, and the path of the band then meets the anode at the point at which normal electric force is greatest.

Fig. 4 (Pl. XXI.) shows a fully developed "band" dis charge. [The dark space in this is only apparent by contrast.]

5. The pressure at which this band attains steadiness and definite form depends on the E.M.F. of the induction-coil and also on the distance between the electrodes and the nature of the gas.

With the induction-coil I have used in these experiments, and for air, when there were three cells in the primary circuit, this state was attained somewhere about the pressure of 22 millimetres of mercury. With four cells it was about 26 millimetres, and with five cells about 30 millimetres, the distance between the electrodes being 18 cm.

6. It is when the discharge forms a band of definite shape that rotation ensues on the application of the magnetic field.

---

* Kindly taken for me by Mr. Hughes of the Cavendish Laboratory.

With a weak magnetic field the discharge sticks and rotates with a jerk, but gradually the rotation becomes steady as the magnetic field is intensified. As the pressure is further lowered, the "band" gradually broadens and changes in colour (fig. 5, Pl. XXI.).

7. The dark space is now well defined, increasing in size as the pressure becomes less, while the glow surrounding the disk is seen to extend, changing in form from oblate spheroid through spherical to prolate. And the rotation continues *so long as a considerable portion of the discharge passes very nearly through the same point of the ring.*

In air, the rotation at first follows the law investigated later, viz., $p\omega$ = constant, where p is the pressure and ω the corresponding angular velocity (§ 22); but when the pressure is less than a certain amount, depending on E.M.F. of the induction-coil, &c. (§ 5), the angular velocity increases less rapidly than would be consistent with that law. Gradually the ring end of the discharge (ring being the anode) extends over a *finite* arc of the ring (fig. 6, Pl. XXI.). In this case there is only a twist on the application of the magnetic field. The pressure at which this occurs depends on the E.M.F. of the induction-coil &c. (§ 5), as well as on the magnetic field itself. Thus in my experiments with three cells in the primary it was about 3 millimetres; with four cells 4·5 millimetres; and with five cells 5 millimetres (fig. 6).

8. Finally the discharge spreads over a considerable portion of the ring, gradually becomes striatory and whitish in colour, and ultimately fills the whole tube (fig. 7, Pl. XXI.). The only effect of the magnetic field in this case is to produce an apparent lengthening of the negative column, due to the fact that the ions move in spirals on the application of the field (§ 17).

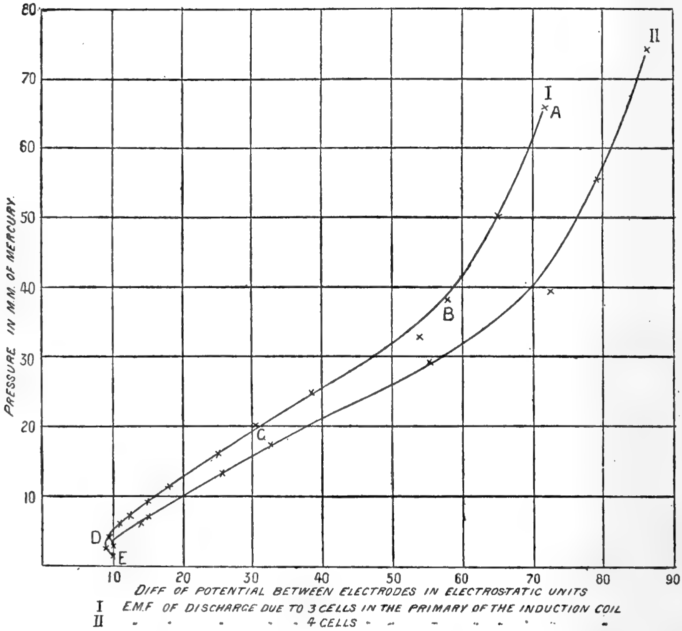
9. It will be thus seen that whenever the discharge consists of a large number of rays going in all directions there is no rotation.

10. Thus rotation is only possible if the bulk of the discharge follows a certain path. This path joins the point of maximum electric density in the anode to the cathode, and is apparently the *least path* from the cathode to this point. Moreover, this is the case when the pressure is between certain limits (depending on the E.M.F. of the induction-coil and other quantities). The "band" discharge thus behaves like a flexible wire carrying current of sufficient intensity to produce rotation under a magnetic field of suitable intensity.

11. Nearly all the salient points with regard to these

discharges in air can be derived from the curves (fig. 8, I. & II.). In these, pressures in millimetres of mercury

Fig. 8.—I. & II.



are ordinates, and the corresponding potential-differences between the electrodes in electrostatic units are abscissæ.

These curves were obtained by measuring the lengths of sparks between two brass spheres of 3 cm. diameter *in parallel* with the discharge tube and deducing the corresponding potential-difference from the table given at p. 461 of J. J. Thomson's 'Conduction of Electricity through Gases,' 2nd ed., by interpolation.

12. It will be seen that we may roughly distinguish four portions in each curve, AB, BC, CD, DE. The first portion (AB), which is very nearly straight, corresponds to the "spray" discharge. As the pressure decreases the character of the discharge changes; it forms into a band by the confluence of most of the discrete streams. This is indicated by the bend in the curve at B.

After this, the relation between pressure and potential-difference is given by a straight line BC. Throughout this stage, the discharge is in the form of a band of light which rotates according to the law $p\omega=$constant. Gradually the curve bends away from the straight line BC, and at this point (somewhere about C) it appears that the above law ceases to hold. Ultimately it bends round, as is also *a priori* evident from the fact that at a very low pressure the resistance to the passage of discharge is very great. With the method of spark distance, it is difficult to trace this portion of the curve; I have accordingly made use of a different method (fig. 8, III., p. 536) for the purpose.

13. If we admit that pressure × spark-length is a linear function of the corresponding potential-difference between the electrodes, the fact that AB, BC are approximately straight indicates that the average length of the path of the discharge is very nearly constant during these stages, and moreover that the path is longer for AB than for BC. That this is actually the case would be evident from an inspection of the figures 2, 3, and 4.

14. Curve I. traces the changes in the case in which there were three cells in the primary circuit of the induction-coil, and Curve II. when there were four. It is evident that the potential-difference for the same pressure is greater in the second case than in the first, and it approximates to equality as the pressure decreases.

15. Again, the pressure at which the band appears is seen to be higher in the second curve than in the first; so also the pressure at which the rotation ceases, the difference being more marked in the first case than in the second.

16. For the same strength of the magnetic field, the rotation is very much less when the ring is the cathode than when the disk is the cathode.

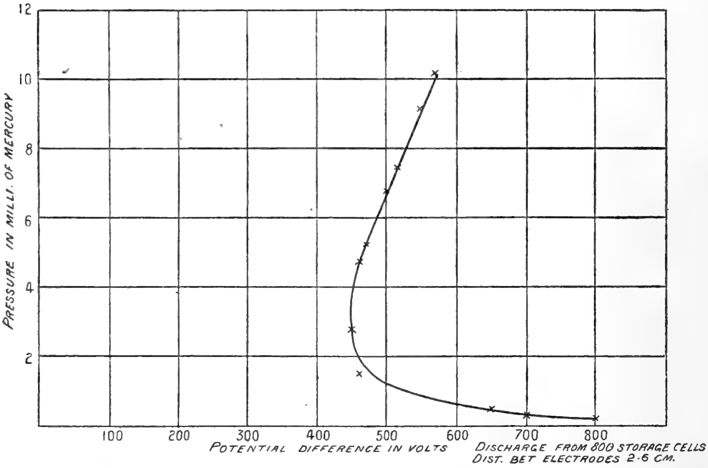
It is found that there is no essential difference in the two cases as regards the variation of electric intensity with pressure. The observed difference is therefore likely to be due to a difference in the number of ions.

17. As the discharge from an induction-coil is intermittent, it is likely that, during the interval in which the discharge is not passing, a certain number of ions recombine. In order to find how far this affects the rotational effect, a steady discharge from 800 storage-cells was passed through a tube, the distance between whose electrodes had now to be much less (2·6 cm.) than in the previous experiments.

It is found that the discharge passes at a pressure of about 12 mm., and it is, as is to be expected, a "band" discharge which rotates as usual. As the pressure decreases the rotation ultimately ceases, the discharge spreading over the whole ring. In this state, on the application of the field a well-marked spiral is seen to mark the path of the ions, the number of convolutions depending on the strength of the field (§ 8).

I have used the discharge from storage-cells to investigate the nature of the curve connecting the potential-difference between the electrodes and pressure when the latter is low, but as the nature of the discharge changes not merely with pressure but also with the current carried by the discharge which it is difficult to keep constant, the measurement of difference of potential between the electrodes in the case of a steady discharge is much more difficult than would appear *a priori*. The following curve (III., fig. 8), however, fairly represents the main features of the relation between pressure and difference of potential between the electrodes, for a current strength of 10 milliamperes: the difference of potential was read off on an electrostatic voltmeter.

Fig. 8.—III.



18. It is not without interest to compare the character of the discharge in this case with that obtained for the same distance between the electrodes when an induction-coil is used. In the latter case, also, the general character of the discharge is of the same form, there being only two stages of the discharge "band" and "glow"; only the range of pressure for which the discharge is in the form of a band is much greater than with storage-cells, being due to the much higher E.M.F. of the induction-coil producing the discharge.

Experimental Determination of the Relation between Pressure and Angular Velocity, &c.

19. If a magnet-pole of strength m acts on a movable and flexible wire carrying current i, the energy of motion of such a wire is $mi\Omega$, where Ω is the solid angle subtended at the pole by the area described by the wire.

Moreover, if ϕ be the angular displacement of the wire

$$\Omega=(\cos\theta_1-\cos\theta_2)\phi,$$

where θ_1 and θ_2 are the angles made by the bounding radii of the wire, to the pole, with the axis of the magnet.

∴ the moment of couple acting on the wire

$$=mi(\cos\theta_1-\cos\theta_2).$$

If, instead of a single pole, we have a distribution of magnetism and ρ is the linear density of magnetism, the moment

$$=i\int\rho\,dx(\cos\theta_1-\cos\theta_2).$$

In the case of an electromagnet as in fig. 1, and a flexible wire extending between the electrodes of the discharge-tube of fig. 1, it is

$$=i\rho\int_0^l dx\left(1+\frac{x}{\sqrt{a^2+x^2}}\right)$$

$$=\tfrac{3}{2}im \text{ nearly,}$$

(a=the radius of the ring, being small), if m is the total magnetic strength and l the length of the iron rod above the ring.

Here ρ has been taken to be constant. This is found to be the case, both as the result of theory and experiment ("Experimental Determination of Magnetic Induction," Phil. Mag. Jan. 1908).

20. Assuming that the "band" discharge can be replaced by such a wire (and experiments justify the assumption), the equation of motion of the discharge will be of the form

$$I\omega=\tfrac{3}{2}mi-\int u(A_1+A_2)rnds,$$

where I is the moment of inertia of the discharge about the axis of rotation;

ω = angular velocity;

u = velocity of an ion, due to rotation at a distance r from the axis;
n = number of ions per unit length of the discharge, positive and negative;
A_1, A_2 = the retardations of + and − ions respectively per unit velocity;
ds = an element of length of discharge.

Again, if

S = electric intensity along the line of discharge,
e = charge on an ion,
K_1, K_2 = the velocities of + and − ions under unit electric intensity;

then K_1S, K_2S will be the velocities of the ions along the line of discharge.

$$\therefore \quad Se = K_1SA_1; \qquad \therefore \quad A_1 = \frac{e}{K_1}.$$

Similarly, $$A_2 = \frac{e}{K_2}$$

∴ the equation of motion becomes

$$I\omega = \frac{3}{2}mi - \omega\, ne\left(\frac{1}{X_1} + \frac{1}{K_2}\right)\int r^2 ds$$

$$= \frac{3}{2}mi - \mu\omega, \quad \text{say.}$$

This gives

$$\omega = \frac{3}{2}\frac{mi}{\mu}\left(1 - e^{-\frac{\mu}{I}t}\right).$$

∴ when the steady state is reached,

$$\omega = \frac{\frac{3}{2}mi}{en\left(\frac{1}{K_1} + \frac{1}{K_2}\right)\int r^2 ds}.$$

Moreover,

$$Se(K_1 + K_2)n = i;$$

$$\therefore \quad \frac{\omega}{\frac{3}{2}m} = \frac{K_1K_2S}{\int r^2 ds}.$$

21. Experiments * were made to obtain the law connecting

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* Similar experiments with a different apparatus have also been made by Prof. H. A. Wilson and Mr. Martyn (Phil. Trans. June 1907).

pressure (p), ω, m, and V (the E.M.F. of the induction-coil) in air in the first instance. It should be noted that this law pertains entirely to the portion AB of the curves, fig. 8.

Experiment I.—Current in the electromagnetic circuit constant (=2·2 amperes). E.M.F. of the induction-coil 3 E, where E is the E.M.F. due to one cell in the primary circuit.

p (in millimetres of mercury).	T (in seconds).	$\frac{P}{T}$.
16·5	1·97	8·4
14·5	1·55	9·3
11·76	1·25	9·3
9·4	1	9·4
	Mean	9·1

Experiment II.—C=2·2 amperes. V=4 E.

p.	T.	$\frac{P}{T}$.
18·85	1·67	11·1
15	1·27	11·3
13·5	1·15	11·8
12	1·07	11·2
10·97	·98	11·1
	Mean	11·4

Experiment III.—C=2·2. V=5 E.

p.	T.	$\frac{p}{T}$.
23	1·605	14·37
19	1·26	15·8
15	·99	15·1
12	·72	16·6
10	·63	15·8
8	·515	15·5
	Mean	15·5

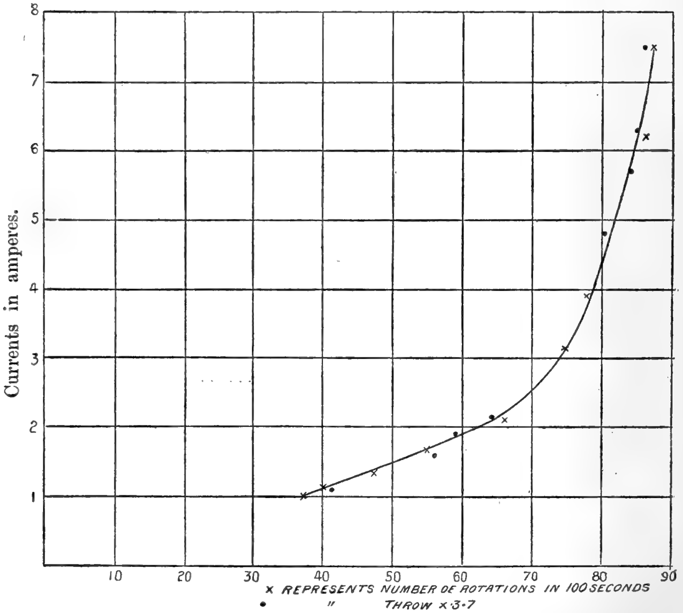
Combining all these results, we see that

V.	$\frac{p}{T}$.	$\frac{p}{TV}$.
3 E	9·1	3
4 E	11·4	2·8
5 E	15·5	3·1

22. And we conclude that $p\omega = \lambda V$, where λ is independent of p, ω, V, but depends on m and the nature of the gas. It also depends on the spark-length.

23. It was *a priori* evident that ω varies as m. In order to verify this and obtain the value of m, in the particular case in which the current in the electromagnet circuit was 2·2 amperes, the following method was adopted :—

Fig. 9.



Experiment IV.—ω was determined for different values of the current in the coil of the electromagnet, and the results were represented by a curve, in which the ordinates represented current (in amperes), and abscissæ number of revolutions in 100 seconds (fig. 9).

Experiment V.—In the next place a small coil ($\frac{1}{4}$ inch thick) containing 36 turns of wire, in circuit with a ballistic galvanometer and an earth inductor (in series) was placed in the same relative position to the soft iron rod, as the ring of the discharge-tube (which was removed for the purpose) and the throws (d) of the galvanometer corresponding to different currents were noted. Then, if μ = strength of pole of an elementary magnet of length dx, $\mu dx = \mathrm{I}dv$, where I is the intensity of magnetization;

or $$\mu = \mathrm{I}ds$$

$$= \frac{\mathrm{B}}{4\pi}ds,$$

or

$$m = \frac{1}{4\pi} \times \text{total magnetic induction.}$$

Hence, $\dfrac{4\pi m \times 36}{\mathrm{P}} = \dfrac{d}{d'}$, where P is the magnetic induction through the earth inductor, and d' the corresponding throw, when the earth inductor is rotated through 180°, about a horizontal axis. Therefore m evidently varies as d. Now when these throws were plotted, as abscissæ on a suitable scale, currents in amperes being ordinates as in Experiment IV., it is seen the curve so obtained virtually coincides with the curve obtained in Experiment IV. This proves that $\omega \propto m$.

In particular, when the current in the magnetizing coil is 2·2 amperes, m is given by

$$\frac{4\pi m \times 36}{8{\cdot}6 \times 10^4} = \frac{17{\cdot}2}{7{\cdot}5}, \text{ since P was known to be } 8{\cdot}6 \times 10^4\,;$$

and we have ultimately

$$\mathrm{K}_1\mathrm{K}_2\mathrm{S}p = \frac{\lambda\mathrm{V}}{\frac{3}{2}m} \cdot \int r^2\,ds,$$

where $$\lambda\mathrm{V} = 2\pi \times 9{\cdot}1 \text{ when } \mathrm{V} = 3\mathrm{E},$$

and $$m = \frac{17{\cdot}2}{7{\cdot}5} \times 8{\cdot}6 \times 10^4.$$

In order to determine $\int r^2\,ds$ and $\int ds$, the band discharge was photographed and the quantities calculated from measurement.

p.	V.	$\int r^2 ds$.	$\int ds$.
14·5	5E	38·16	19·97
17	4E	36·92	19·85
30	5E	37·12	19·92
	Mean ……	37·4	19·91

24. Therefore, finally, we have

$$K_1K_2V'p = 3{\cdot}28 \times 19{\cdot}91,$$

where V′ is the potential-difference corresponding to S at the pressure p.

25. It is not without interest to note that Prof. Wilson and Mr. Martyn's result can be written

$$pV'K_1K_2 = 23{\cdot}4 \times 3{\cdot}1.$$

26. If we take V′ equal to the actual potential-difference between the electrodes, we have the following values of K_1K_2 for different values of p.

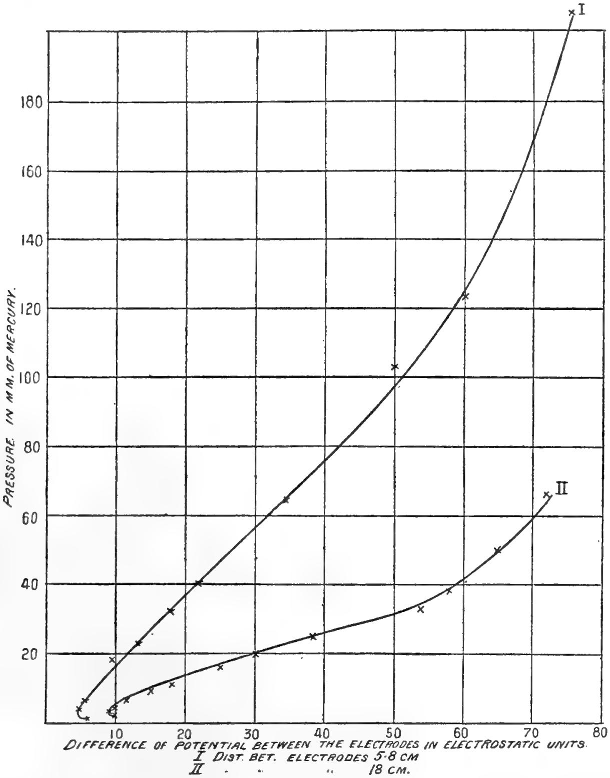
p	V′ in volts.	S in volts per cm.	K_1K_2.
3	1158	58·2	$1{\cdot}878 \times 10^6$
5	2130	107	$6{\cdot}159 \times 10^5$
10	4560	229	$1{\cdot}438 \times 10^5$

27. These results may obviously depend on the special conditions of the experiments, such as the distance between the electrodes besides the E.M.F. used for producing the discharge. I proceeded accordingly to investigate the effects of these quantities.

28. In order to examine the effect of the distance between the electrodes on the discharge, the potential-difference between the electrodes for different pressures was determined as in art. 11, for the case in which the discharge between the electrodes was 5·8 cm. (fig. 10). The curve for this case and that in which the distance was 18 cm. are plotted together (fig. 10) for purposes of comparison.

It will be seen that the first bend in the curve associated with a change in the character of the discharge occurs at higher pressure when the distance between the electrodes is less and is, moreover, less marked. In fact when the distance

Fig. 10.



is small (2·5 or 3 cm.) there is no such bend, the first stage in which the discharge is showery being absent (§ 18).

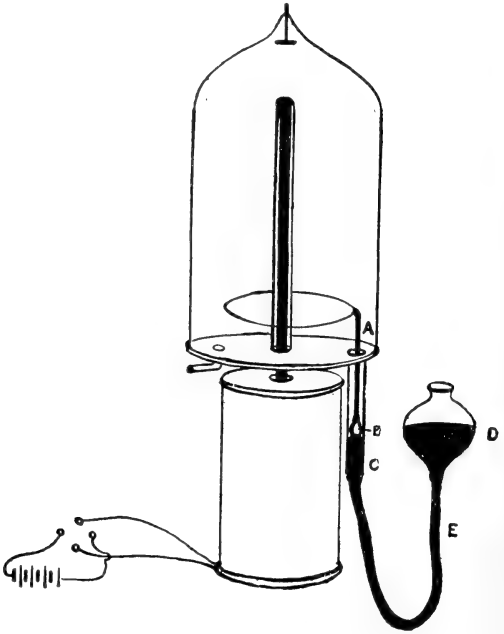
29. In order to determine the effect of the distance between the electrodes on rotation, the apparatus (fig. 11, p. 544) was used.

The ring electrode is joined to a stiff copper wire (A), passing through and moving with a glass float B, which slides in the tube C. Mercury fills a portion of C, the flask D and the indiarubber tube E. The ring can be raised or lowered by the adjustment of the level of mercury in C.

30. In this way experiments were made at different pressures and different distances between the electrodes. The

results are given in the following table and are also exhibited in the curve (fig. 12, p. 545). In these I have taken the amount of induced magnetism proportional to the length of the iron core of the electromagnet above the ring, in accordance with results already established ("Experimental determination of magnetic induction in an elongated spheroid.")

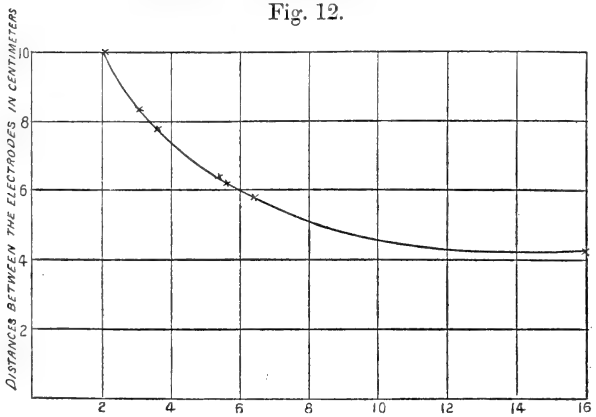
Fig. 11.



Distance between electrodes (l).	$\frac{p}{Tm}$ proportional to	$\frac{pl^2}{Tm}$ proportional to
10	2·1	210
8·35	3	209
7·8	3·6	219
6·4	5·4	237·5
6·3	5·8	230·2
5·8	6·4	215·2
4·2	16	281

i. e., $\frac{p}{Tm}$ varies inversely as the square of the length of the discharge, as a rough approximation.

Fig. 12.



$\frac{p}{Tm}$, where p is in millimetres of mercury, T in seconds, and m taken equal to the length of the rod above the ring.

31. But since we have

$$\frac{2\pi}{Tm}=\frac{\omega}{m}=\frac{\frac{3}{2}K_1K_2S}{\int r^2 ds},$$

we have, corresponding to any pressure, $\frac{K_1K_2S}{\int r^2 ds}$ varying as $\frac{1}{\left(\int ds\right)^2}$ roughly or K_1K_2V' very nearly, independent of the distance between the electrodes. That is, K_1K_2 is practically independent of this distance except in so far as V' depends on this distance.

32. I have also examined the behaviour of different gases and vapours, when the discharge is passed through them at different pressures.

In all the following experiments, the distance between the electrodes was 4·5 cm., the number of storage-cells in the primary of the induction-coil = 3, and the current in the electromagnet circuit 3·4 amperes.

(For purposes of comparison, the results for air obtained with the same apparatus are given below.)

Air.

p (in millimetres of mercury).	T (in seconds).	$\frac{p}{T}$.
58	1·41	41·1
49	1·14	43·3
39·4	·95	41·1
34	·86	40
	Mean	41·35

At lower pressures $\frac{p}{T}$ decreases as p decreases. Thus

p.	T.	$\frac{p}{T}$.
26·5	8	33
19	7	27

Nitrous oxide (N_2O).

The discharge passes at a higher pressure than in air.

The rotation begins above a pressure of 10·4 cm.; the relation between pressure and the corresponding period of rotation is similar to that in air.

p.	T.	$\frac{p}{T}$.
62	2·4	25·8
39	1·6	24·4
33·6	1·37	24·5
23·58	1	23·5
14·82	·6	24·7
	Mean	24·6

Since in air $\frac{p}{T} = 41{\cdot}5,$

$\frac{p}{T}$ varies inversely as the density, very nearly.

The curve connecting pressure and potential-difference between the electrodes is of the same type as that for air, being situated further from the p-axis than the latter.

Carbonic acid (CO_2).

The discharge passes at a very high pressure, the band discharge appearing at a pressure above that of 15 cm.

$p\omega$ is not constant, but increases with pressure as is shown below.

p (in millimetres of mercury).	T (in seconds).	$\frac{p}{T}$.
125·5	1·8	70
102	1·7	60
75	1·4	53·5
42	1·07	40
32	·84	38
23·5	·7	33·5
15	·55	27·3

The relation between p and T is represented by curve I. (fig. 13).

Fig. 13.

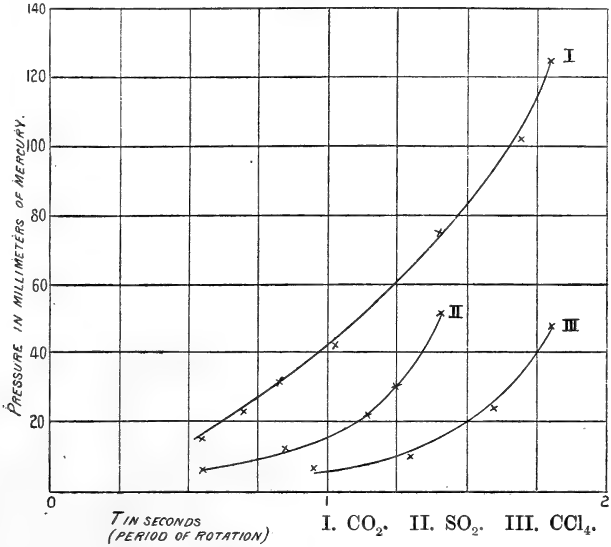
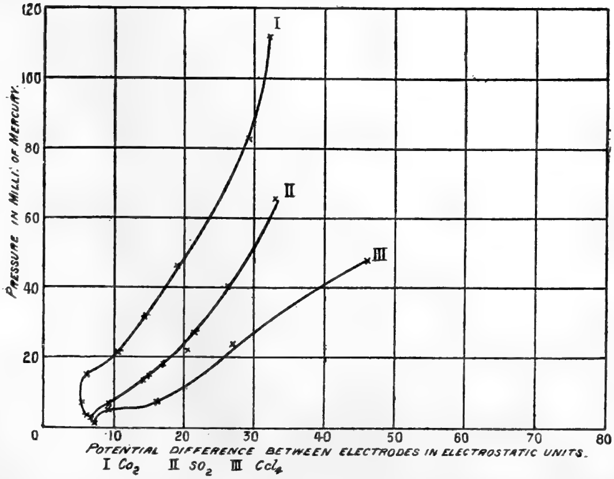


Fig. 14.



The relation between p and potential-difference between the electrodes is represented in curve I. (fig. 14).

In order to get rid as far as possible of the effect of decomposition on the passage of the discharge, the gas was pumped out and fresh gas introduced several times during the experiments.

Carbon tetrachloride (CCl_4).

The "band" discharge appears at about 48 millimetres and the rotation continues up to a pressure of 6·9 millimetres.

The following results indicate the variations of the period of rotation T and pressure :

p.	T.	$\frac{p}{T}$.
6·9	·95	7·2
10	1·3	7·7
24	1·6	15
48	1·8	26·6

It was found to be a rather inconvenient gas to work with ; accordingly, sufficient number of determinations could not be obtained.

The curves of p, T, and p and the potential-difference are given in figs. 13 and 14.

Sulphur dioxide (SO_2).

Rotation was observable between the pressures 46 mm. and 3 mm.

$\frac{p}{T}$ increases with pressure.

p.	T.	$\frac{p}{T}$.
46	1·45	31·7
30	1·25	24
21	1·19	17·6
13	·84	15·5

The curve connecting p and T, and that connecting p and potential-difference are given in figs. 13 and 14.

When discharge was passed through benzene, ammonia and ether, they decomposed so rapidly that no measurements could be obtained.

Further experiments on the subject are in progress, and I am also engaged in working out a theory of these rotations. In the meantime, the following conclusions are justified by the results already obtained.

Conclusions.

1. The discharge in a De La Rive's tube, in general, passes through three stages, "showery," "band," and "glow."

In air, when the distance between the electrodes is small, the first stage is absent.

2. The discharge rotates under the influence of the magnetic field, only when it is in the form of a "band," over a range of pressure, depending on the nature of the gas or vapour in the tube, the E.M.F. producing the discharge, and the distance between the electrodes.

3. Gases can be divided into two groups as regards the law of rotation :

(1) In gases such as Air, H *, N *, N_2O, *i. e.*, probably all elementary gases and those which do not decompose under the electric discharge, for a certain range of pressure (depending on the distance between the electrodes and E.M.F. producing the discharge)

$\frac{p}{T}$ = constant, which varies inversely as the density of the gas, where T is the period of rotation at pressure p. For lower pressures, $\frac{p}{T}$ decreases as pressure decreases.

(2) In other gases (*e. g.*, CO_2, SO_2), which probably tend to decompose when the discharge passes through them, and probably all vapours (*e. g.*, $C\,Cl_4$), $\frac{p}{T}$ increases with pressure and with the density of the gas (fig. 13).

4. In the case of the first group of gases, for pressures at which there is rotation according to the law $\frac{p}{T}$ = constant, the potential-difference between the electrodes is a linear function of the pressure.

For each group the potential-difference between the electrode increases with the density of the gas.

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* Prof. H. A. Wilson and Mr. Martyn have investigated the law relating to these gases.

5. For all substances, the potential-difference increases with pressure (except for very low pressures), with the E.M.F. producing the discharge, and the distance between the electrodes.

6. In air, and probably in all gases, the angular velocity of rotation is proportional to the E.M.F. producing the discharge, and increases as the spark-length decreases.

7. Since
$$\frac{\omega}{m} \propto \frac{K_1K_2S}{\int r^2 ds},$$
$$\frac{1}{T} \propto K_1K_2S\ ;$$

but since S increases with density and T also increases with density, K_1K_2 rapidly decreases as density increases.

8. K_1K_2 is independent of the distance between the electrodes (except in so far as the potential-difference in the discharge depends on it) but varies with the E.M.F. of the discharge.

I have to thank Professor J. J. Thomson for permission to work at the Cavendish Laboratory and for many valuable suggestions.

XLVIII. *Homogeneous Secondary Röntgen Radiations.* By CHARLES G. BARKLA, *M.A., D.Sc., Lecturer in Advanced Electricity, and* CHARLES A. SADLER, *M.Sc., Demonstrator in Physics, University of Liverpool* *.

THOUGH there are many phenomena of Secondary Röntgen Rays still awaiting investigation, it seems desirable in publishing the results of recent experiments—principally on the homogeneous secondary radiations—that a general survey should be made of the whole subject of "Secondary X-Rays emitted by substances subject to X-Rays," and that a more concise statement of the experimental results and the conclusions based on these should be given. This, indeed, appears a necessity not only in order to make intelligible the results of what would otherwise appear isolated experiments of little significance, but to exhibit the observed limitations or the generality of laws

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* Communicated by the Physical Society: read June 12, 1908.
The expenses of this research have been partially covered by a Government Grant through the Royal Society.—C. G. B.

which are continually being tested by further experiments on a variety of substances and under a variety of conditions.

As has been shown in previous papers *, the behaviour of substances subject to X-rays varies enormously with the atomic weight of the substance exposed, and generalizations cannot safely be arrived at except after an extensive series of experiments on a large number of elements.

The results which have so far been found to be perfectly general will be briefly stated †:—

All substances subject to X-rays are a source of secondary X-rays.

The radiation from a given element is independent of the physical state of the substance and of its mixture or even chemical combination with other elements.

The character of the secondary radiation from an element is independent of the intensity of the primary radiation producing it.

The intensity of secondary radiation from an element is proportional to the intensity of the primary radiation of definite character producing it.

The absorption by a thin sheet of any substance of the secondary rays from various elements subject to the same primary beam is a periodic function of the atomic weight of the radiating substance.

There are, however, groups of elements of neighbouring atomic weight into which substances may conveniently be divided; for when a primary beam of ordinary penetrating power is used, the radiations from the various elements in one group are very similar in properties, while those from elements in different groups differ considerably. But it should be understood that this grouping is somewhat

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* As frequent references are made to the following papers, they are denoted by the letters *a–g*:—

Barkla: *a*. Phil. Mag. June 1903, pp. 685–698.
b. Phil. Mag. May 1904, pp. 543–560.
c. Phil. Trans. A, vol. 204, 1905, pp. 467–479.
d. Roy. Soc. Proc. A, vol. 77, 1906, pp. 247–255.
e. Phil. Mag. June 1906, pp. 812–828.
g. Phil. Mag. Feb. 1908, pp. 288–296.
Barkla & Sadler: *f*. Phil. Mag. Sept. 1907, pp. 408–422.

† These results were given in the papers to which reference has already been made; later experiments have not revealed any exceptions. It appears quite possible, however, that under certain conditions exceptions will be found. Crowther, who by careful experiment has further verified some of these results (Phil. Mag. Nov. 1907), finds much less intense radiation from nickel when in combination as nickel carbonyl than we have obtained from the pure element in the solid state. As this cannot be accounted for by variation in the primary beams used, it is perhaps worthy of further investigation.

arbitrary, as elements of intermediate atomic weight emit radiations possessing intermediate properties, and the classification depends to a certain extent on the character of the primary radiation. It is, however, convenient for the purpose of description.

H–S GROUP.

The group of substances of atomic weights from that of hydrogen to that of sulphur appears simplest in behaviour under X-rays of ordinary penetrating power.

Each element, when subject to such a primary beam, emits a secondary radiation which has almost exactly the same penetrating power as the primary producing it. The secondary beam is complex like the primary, and contains the rays of various penetrating powers in approximately the same proportion as the primary (*a* & *b*).

Though it is very difficult, if not impossible, to detect by direct methods a difference in the penetrating powers of primary and secondary beams, when the primary is not more than moderately penetrating, it appears from indirect evidence that the secondary radiation is always slightly more absorbable than the primary (*b*). With more penetrating primary rays the difference is more marked (*b* & *).

The intensity of radiation emitted by these elements is proportional merely to the quantity of matter passed through by a primary beam of definite intensity, if of low to moderate penetrating power: in other words, the intensity of radiation from an atom is proportional to the atomic weight † (*a* & *b*).

The secondary radiation proceeding from one of these substances in a direction perpendicular to that of propagation of the primary is fairly completely polarized, when the rays are of the absorbable type (*d*).

The intensity of secondary radiation from each of these substances varies in different directions perpendicular to that of propagation of a polarized primary beam (*e*).

The amount of polarization in a primary beam, as indicated by the secondary rays, diminishes with an increase in the "hardness" of a given X-ray tube emitting the primary radiation.

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* Beatty, Phil. Mag. Nov. 1907, pp. 604-614.

† It was considered possible that the discrepancy in the case of hydrogen, as found by one of us, might be explained by the mixture of a small quantity of air. Crowther, however, from more recent experiments has concluded that hydrogen and helium in this group are exceptions to this law of intensity.

The secondary radiation from these substances is approximately twice as intense in the direction opposite to that of propagation of the primary rays as the average in directions at right angles, when the primary beam consists of rays of the easily absorbed type (*g*). (Polarization produces variation in different directions at right angles to the primary beam.)

This ratio varies somewhat with a variation in the character of the primary rays, but has not been found to exceed 2 : 1.

The results of all the experiments when an easily absorbed primary was used as the exciting beam, may be explained on the theory as given by Professor J. J. Thomson * shortly after the earliest systematic experiments on light gases. The electric displacement in the primary Röntgen pulses when passing over the electrons produces accelerations in these in the direction of that displacement, and thus causes the emission of secondary pulses of equal thickness. The natural deductions from this theory have all been strikingly verified by experiments on substances of low atomic weight when subject to an easily absorbed primary beam.

Before the phenomena of secondary X-rays from these light atoms may be said to be fully understood, we must explain the effects produced when the primary rays change to those of more penetrating type. In experiments that have been described the secondary rays began to differ in penetrating power from the primary,—they were more easily absorbed ; they gave less evidence of polarization of the primary beam, the variation falling from about 20 per cent. to 6 or 7 per cent. in experiments made while the primary became more penetrating ; the ratio of intensity of secondary radiation in the direction opposite to that of propagation of the primary beam to that in one at right angles dropped considerably; the ratio of ionization in the secondary electroscope to that in one testing the primary beam increased slightly.

These results might be explained qualitatively either by the introduction of a secondary radiation of different type superposed on the almost perfectly scattered, or by the scattering becoming more imperfect by the introduction of forces of considerable magnitude other than those produced directly by the primary pulses during the passage of those primary pulses over the electrons, or by the intro-

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* 'Conduction of Electricity through Gases' (2nd edition) p. 321.

duction of a greater proportion of tertiary rays due to the emergence of the secondary rays from greater depths of the radiating substance, or by a combination of these.

Though the experiments, the results of which are stated above, were not performed concurrently, it was evident that the variation in intensity of secondary radiation exhibiting the polarity of the primary beam changed from about 20 per cent. to only about 6 or 7 per cent. as the X-ray tube became "harder," even before a difference between the penetrating powers of primary and secondary beams could be detected by direct comparison. It was not evident whether this change was actually one in the polarization of the primary beam itself or in the efficiency of the secondary rays in exhibiting a polarization of constant magnitude. The latter appeared the more probable when considered in conjunction with the changes that had been found in the ratio of intensities of secondary rays in a direction almost opposite to that of primary propagation and one at right angles. Further experiments were therefore made to determine if the changes were all attributable to the same cause. It was found, however, that although increasing the hardness of a given X-ray tube produced a decrease in the amount of polarization detected, the more penetrating portion of a primary which was transmitted through a sheet of aluminium did not exhibit less polarity but slightly more, indicating that the effect was due not merely to change in the penetrating power of the radiation but to some change in the polarity of the primary beam itself. This was supported by the fact that the secondary radiation did not become appreciably different in penetrating power from the primary producing it,—indicating a fairly perfect scattering. Finally, later experiments have shown that for a primary radiation proceeding from a tube in the state of hardness which has invariably been found to exhibit a minimum of polarity in the primary, the ratio of intensities of secondary rays in the two directions indicated has been such as would be given by an almost perfectly scattered radiation.

We cannot then attribute the decrease in the amount of polarization of a primary beam exhibited by the secondary rays to the scattered rays being only partially a scattered radiation or to imperfection of scattering, but it is almost certainly a decrease in the polarity actually existing in a primary beam when the tube becomes harder.

These results are possibly due to the more swiftly moving cathode particles in the X-ray tube being productive of more secondary cathode rays in the anti-cathode. As the secondary cathode particles are not directed like the primary cathode rays, they produce radiation which is not polarized. The greater the number of secondary cathode particles produced, the less is the polarity of the complex radiation. As the X-radiation from the secondary cathode particles is probably less penetrating than that due to the primary cathode particles, the more penetrating portion of the complex X-radiation exhibits slightly more polarity than the more easily absorbed.

The small increase observed in the intensity of secondary radiation from air, paper, &c., as measured by the ionization produced in an electroscope, when the primary beam is made more penetrating, is possibly due to the superposition of a homogeneous unscattered radiation, such as is emitted by elements of higher atomic weight. This would account for the complex secondary radiation differing more and more in penetrating power from the primary as the latter became more penetrating; for it has a definite penetrating power characteristic merely of the element emitting it. Though experiments have not yet been made to analyse this secondary radiation set up by the more penetrating radiation, it appears, for reasons discussed later, exceedingly probable that such a radiation does appear when a penetrating primary beam is used.

A point still awaiting investigation is the change in the observed ratio of intensities of secondary radiation in directions approximately opposite and perpendicular to that of primary propagation. Experiments have been made to ascertain the amount by which this ratio is affected by a change in the polarization of the primary beam, by the superposition of tertiary rays in greater proportion, and by the superposition of homogeneous radiation characteristic of the radiating element. In these later experiments, however, the deviation from the theoretical ratio for perfect scattering has through all the changes made in the primary beam been much less than in the first experiments; and it has been found that even a fairly penetrating primary beam—much more penetrating than any used in the experiments referred to in a previous paper (*g*)—sets up secondary rays whose intensity distribution is within a few per cent. of that which would be given by perfect scattering. This matter is being further investigated *.

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* It ought to be remarked, that though an elementary consideration of the production of secondary rays indicates that the intensity of radiation is the same in the forward and backward directions, and that each of these is double that in a direction at right angles, a more complete

Cr–Zn Group.

The radiation proceeding from elements of atomic weight between those of chromium and zinc, when subject to X-rays of ordinary penetrating power, is of a very different type from that discussed, for from no two elements in this group is the penetrating power the same. The absorption by a thin sheet of aluminium ·0104 cm. thick is, between these limits of atomic weight, a decreasing function of the atomic weight, varying from 94 per cent. for the radiation from chromium to 64 per cent. for the radiation from zinc. [One of the primary beams used was absorbed to the extent of about 34 per cent.]

Homogeneity.—One of the most remarkable features about the radiation from any one of these elements is that though the primary rays incident upon the substance are very heterogeneous, that is consist of rays varying considerably in penetrating power, the secondary rays are homogeneous. This point has been briefly referred to in a previous paper (*f*).

To give a particular example :—The ionization produced in a given electroscope by a primary X-ray beam was diminished by 51 per cent. by placing a sheet of aluminium ·0208 cm. in thickness in its path ; after 77 per cent. had been absorbed by aluminium, a similar plate produced a further diminution of this ionization by 27 per cent. ; after 91 per cent. had been absorbed the same plate cut off only 18 per cent., showing that the rays after each transmission became on the average more and more penetrating. This effect has been explained as due to the more absorbable constituents being sifted out.

Although such a primary beam produced in one of this class of substances the secondary radiation experimented upon, it was found that the secondary radiation was of an entirely different type, being equally absorbed after transmission through sheet after sheet of absorbing substance.

The radiation from thick copper was found not to differ appreciably from that from a very thin sheet which was only thick enough to absorb 14 per cent. of the primary rays. Thus the radiations from the deeper layers after transmission

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theory shows that these results can at best be only approximately true. It is only necessary to consider the action of the magnetic field in the primary pulses on the electrons as they begin to move under the action of purely electric forces, to see that dissymmetry must exist. A complete theory must also take into consideration the distribution of the tubes of electric force round each radiating electron.

through the surface layers were of the same character as those from the surface layers. Consequently, in dealing with these secondary rays it is not necessary as in the H—S group to deal with very thin plates in order to determine the character of the radiation as emitted by the atoms themselves.

Using zinc as the radiating substance, the direct ionizing effect of the secondary rays was determined, and afterward the ionization produced by the same beam after transmission through thin sheets of zinc and aluminium placed at a distance of several centimetres from the detecting electroscope in order to avoid complications due to the more easily absorbed corpuscular secondary rays from the metal sheet.

The effect of the radiation from air was determined by separate experiments, and correction was then made for this in each observation, though when a large proportion of the secondary rays was absorbed, the air radiation was quite a considerable fraction of the whole and the possible error was as a consequence greatly increased.

Below are tabulated the percentage absorptions by a plate of zinc ·00131 cm. thick and one of aluminium ·0104 cm. thick of the secondary beam direct from zinc and of this beam after transmission through various thicknesses of aluminium. These results exhibit the striking homogeneity of the radiation from zinc.

TABLE I.

Radiation from Zinc (thick sheet).

I. Percentage Absorption by Al previous to absorption in column II. or III.	II. Percentage Absorption by Zn (·00131 cm.) after absorption in column I.	III. Percentage Absorption by Al (·0104 cm.) after absorption in column I.
0	*36·5*	*67·5*
22	36·2	67
67	35·4	—
0	*35·8*	—
89	35·4	67
97	33·9	66
0	*34·2*	—

Similar experiments were made on the absorption of the radiation from zinc by zinc when that radiation had been passed through various thicknesses of zinc to absorb different proportions of it.

The radiation from copper was examined in the same way.

Table II.

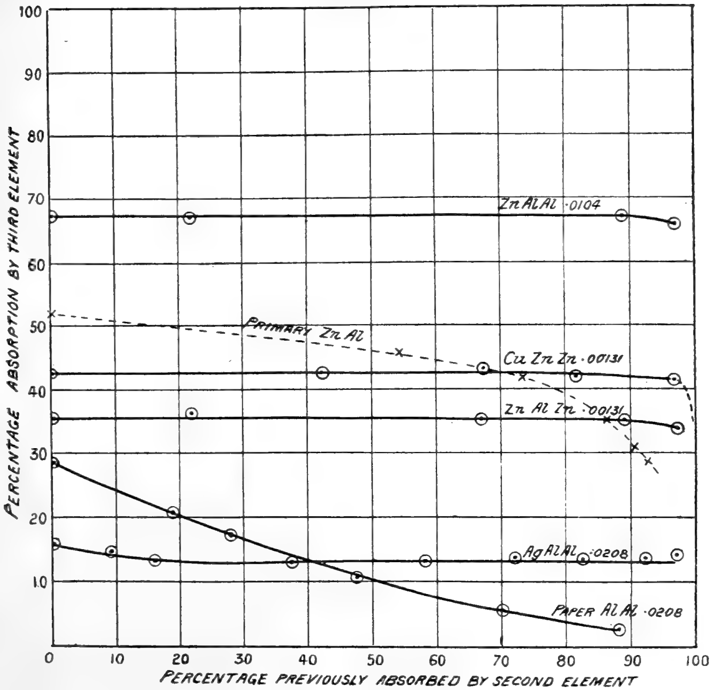
Radiation from Copper (thick sheet).

I. Percentage Absorption by Zn previous to absorption in column II.	II. Percentage Absorption by Zn (·00131 cm.) after absorption in column I.
0	*43*
44	44
0	*41·4*
42·6	42·6
67·5	43·1
81·5	42
96·7	41·8
0	*42·5*

All these experiments show extremely little change in the percentage absorption even after almost complete absorption. The contrast between primary and secondary beams is strikingly shown in fig. 1 (p. 559), in which the absorptions are represented by ordinates and the amount previously absorbed by abscissæ. The corresponding curve for the secondary radiation from paper (in this case subject to penetrating primary rays) is given for comparison (fig. 1).

Independence of Primary Rays.—To exhibit the independence of the penetrating power of the secondary radiation from one of these metals Cu, of that of the primary producing it, we have tabulated below the absorbability of various primary rays and that of the secondary rays produced by these. Though the absorption of the primary by aluminium ·0208 cm. thick varied from 52 to 18 per cent., the absorptions of the corresponding secondary beams from copper by aluminium ·0104 cm. thick were as nearly as observable the same, the experimentally determined values being 58·3 and 58·1 per cent. respectively. This constancy in character makes accurate experiments on these radiations possible.

Fig. 1.



Note.—Cu Zn Zn ·00131 indicates :—Copper radiation after transmission through Zn is absorbed by Zn ·00131 cm. thick to extent shown by ordinates.

Table III.

Radiation from Copper (thick sheet).

I. Percentage Absorption by Al of Primary Radiation previous to incidence on Cu radiator.	II. Percentage Absorption of Primary Rays by Al (·0208 cm.) after absorption given in column I.	III. Percentage Absorption of Secondary Rays by Al (·0104 cm.).
0	. .	58
52	. .	58·6
0	52	58·3
77	27	58·8
0	51	58·4
91	18	58·1
0	51	58·8

Each of these elements therefore emits a characteristic radiation which is independent of the penetrating power of the primary beam setting up this radiation, and being homogeneous, the absorption-coefficient calculated from the relation $I=I_0e^{-\lambda x}$ has a value which is independent of the thickness x of absorbing substance *—a property which appears to be unknown among X-ray beams hitherto experimented upon.

The absorption-coefficients for the radiations from Fe, Co, Ni, Cu, and Zn, when absorbed by Al, Fe, Cu, Zn, Ag, Sn, and Pt have been given in a previous paper (*f*).

Though it has been shown that the secondary radiation from some of the substances in this group (Cr–Zn) is remarkably homogeneous in comparison with the primary which produces it, the test applied is not one of extreme delicacy, and the presence of the scattered radiation similar to that of the first group (H–S) and of intensity given by the law found for that group would be exceedingly difficult to detect, as it would produce only about $\frac{1}{300}$ of the total ionization actually produced by the secondary rays from a very thin sheet of copper. Now we have seen that a radiation after transmission through metals may contain a considerable proportion of the radiation which is characteristic of the metal traversed and which was not in the incident radiation. This acquired radiation may even, if the substance traversed has almost completely absorbed the incident radiation, constitute the bulk of the transmitted radiation. In such a case, experiments on the transmitted beam in order to analyse its constituents would be misleading, the constituents not being present in the original beam.

To eliminate the possibility of this error, we have tested the radiation from copper after transmission through thin sheets of copper by absorbing by further plates of copper. Thus radiation of a fresh type was not introduced.

It was found that after absorbing 98·3 per cent. of the copper radiation by copper, the absorption by copper ·00296 cm. thick had dropped from 74 to 70 per cent. The effect was more pronounced in the case of the radiation from iron, the numerical data for which are given below.

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* After transmission through sheets of absorbing substance, secondary rays are superposed on the transmitted radiation, and the resultant radiation in some cases ceases to be even approximately homogeneous. This effect can, however, be readily distinguished from true heterogeneity by using as absorbers only those substances in which a radiation of different type is not stimulated.

TABLE IV.

Radiation from Copper (thick sheet).

I. Percentage Absorption by Cu previous to absorption by Cu, Zn, or Al.	II. Percentage Absorption by Cu, Zn, and Al after absorption in column I.		
	Cu ·00296 cm.	Zn ·00262 cm.	Al ·0104 cm.
0	74	69·7	72
98·3	70	66	68

Radiation from Iron (thick sheet).

I. Percentage Absorption by Fe previous to absorption by Fe, Cu, or Al.	II. Percentage Absorption by Fe, Cu, and Al after absorption in column I.		
	Fe ·00313 cm.	Cu ·00296 cm.	Al ·0104 cm.
0	80·5	91·5	90
80	79·8	91	89·5
96	76·9	86	83·5

There was thus evidence of a slight heterogeneity even in these radiations.

Scattered Rays.—To test if this heterogeneity could be accounted for by the mixture of a scattered radiation, like that from light atoms, with the homogeneous radiation, a direct comparison was made between the ionization produced by the secondary beams from thin sheets of copper [·00067 cm.] and paper, subject to the same primary radiation. The paper which was used had ten times the mass of the thin copper, yet the ionization produced by the secondary rays from the copper was 19·5 times that produced by the secondary rays from paper even though a greater proportion of the radiation from copper was absorbed by the copper itself than that from the paper in the paper. As sheet after sheet of aluminium was placed in the path of the two secondary beams, the copper radiation was absorbed to a much greater extent than the radiation from paper; thus 34 per cent. of the radiation from paper was transmitted through aluminium ·0416 cm. in thickness, while only ·7 per cent. of the copper radiation got through. The ratio of the ionization due to the copper radiation to that due to the rays scattered from paper, after transmission through ·0416 cm. Al had dropped to ·401 : 1. After transmission through ·0782 cm. of Al the two radiations appeared approximately equal in penetrating power, the last ·26 per cent. of the copper radiation being much more penetrating than the homogeneous radiation which had been practically all absorbed. When the two transmitted radiations were approximately of the same character, the ratio of their ionizing effects was about ·18 : 1 ; or from equal masses of copper and paper—disregarding all internal absorptions the intensities of the penetrating rays were in the ratio 1·8 : 1.

TABLE V.

I. Thickness of Al in path of Secondary beams.	II. Percentage of Cu radiation absorbed.	III. Percentage of Paper radiation absorbed.	IV. Ratio of ionizations due to Secondary beams from equal masses of Cu and Paper.
0	0	0	195·5 : 1
·0208	94·5	51·8	22·1 : 1
·0416	99·3	66	4·01 : 1
·0574	99·6	71	1·94 : 1
·0782	99·74	78	1·88 : 1
·0990	99·8	83	1·83 : 1

Allowing for the small extra absorption of the penetrating portion of the copper radiation in the copper plate itself above that of the corresponding rays in the paper—quantities which were determined by separate experiments—the radiation from copper must have contained approximately twice as much of the penetrating radiation as the radiation from paper.

By using a thicker copper plate as radiator the intensity of secondary radiation was increased, but the correction for absorption in the metal itself was also increased so that the result could not be regarded as more accurate, this correction not being obtainable with great accuracy. The conclusion was however practically identical with the above. We thus see that mixed with the homogeneous radiation from copper is a more penetrating radiation. The most penetrating portion of this is about twice as intense as the corresponding radiation from substances of the H–S group.

The radiations from other elements of the Cr–Zn group have not been examined so minutely as that from copper, but it has been seen that these also contain a small quantity of a more penetrating radiation which is probably scattered radiation. This more penetrating radiation was more evident in the radiation from thick iron, probably because the homogeneous iron radiation being very absorbable emerges from a thinner surface layer, while a scattered radiation emerges from greater depths than in the metals of higher atomic weight owing to the greater transparency of iron than substances of higher atomic weight. Consequently the scattered rays—if we may assume them to be such—are in reality from a much greater mass of iron than the homogeneous rays, and produce more than their appropriate portion of the total ionization.

It may be objected that in this case the radiation was transmitted through a second substance Al, and may have contained a considerable quantity of secondary radiation from Al of a kind not existent in the original radiation from copper. The production of a secondary radiation more penetrating than the primary producing it is, however, contrary to all experience.

Energy.—The ionization produced by the secondary rays from one of the elements of this group has been shown to be enormous in comparison with that produced by the secondary scattered rays from an equal mass of an element of low atomic weight. From a sheet of copper ·00067 cm. thick, absorbing 14 per cent. of the primary radiation, the secondary radiation produced an ionization in the detecting electroscope 200 times as great as that from an equal mass of paper. Correcting for absorption of primary and secondary rays, the ratio of ionization produced by the rays from equal masses of copper and paper was approximately 300 : 1. This is considerably greater than would have been found if all the radiation absorbed had been simply scattered as an untransformed radiation. This, however, by no means gives us a measure of the energy of the secondary rays, for these are of much more absorbable type than the primary. The percentage absorption by a thin sheet of aluminium is about five times as great for these secondary rays as for the primary. If we assumed the same ratio for the ionizations produced in air by the two radiations if of equal intensity, we should be led to conclude that the energy of this homogeneous radiation is about 45 times that of the scattered radiation from an equal mass of paper, and about $\frac{1}{3}$ the total energy absorbed in the copper *.

Though it is impossible by such experiments to determine the energy with accuracy, we may safely conclude that the energy of the homogeneous radiation is many times greater than the energy of secondary radiation scattered from an equal mass of one of the light elements.

Comparisons of the ionizations produced by the rays from other elements of this group have been made. They are all of the same order of magnitude.

Distribution.—It has been shown by one of us that the secondary radiation from thick copper, when this is subject to a primary beam of ordinary penetrating power, is approximately equally intense in a direction almost opposite to that of propagation of the primary and in a direction at right angles. As probably 98 per cent. of the ionization produced by the secondary radiation from thick copper is due to the homogeneous rays, this may be said to be the result for the homogeneous rays alone.

From thick iron, however, the radiation varied in intensity by an amount represented by the ratio 1·1 : 1 in these two directions. But as we have shown, the heterogeneity of the radiation from thick sheets of iron is more marked, and this can be accounted for by the fact that from iron the homogeneous rays are very easily absorbed, consequently scattered rays emerge from a much thicker layer and appear in more than their normal proportion. The ratio 1·1 : 1 verifies this by showing the presence of a radiation which is controlled by the electric field in the primary pulses.

The result is of the order of magnitude that would be given by a mixture of scattered rays of about the same intensity as found in the radiation from copper with the characteristic radiation uniformly distributed.

Polarization Experiments.—Though very careful experiments have been made with iron, copper, and zinc as secondary radiators placed in a partially polarized primary beam of Röntgen radiation, the secondary rays from these have not been found to give evidence of any polarity. Thus the intensity of secondary radiation in a given direction is independent of the position of the plane of polarization of the primary beam producing the radiation ; in other words,

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* The homogeneous radiation has been assumed to be distributed uniformly in all directions and the scattered radiation to be proportional to $\sin^2 \theta$, where θ is the angle between the direction of radiation considered and that of acceleration of the radiating electron.

the intensity of secondary radiation from members of this group is independent of the direction of electric force in the primary radiation. Again, this result may be taken as applicable to the homogeneous rays, as these constitute the bulk of the radiation from these metals.

Efficiency of Primary Rays as Secondary Ray Producers.—Although in addition to the relatively small amount of scattered radiation, rays of only one penetrating power were emitted by an elementary substance upon which a heterogeneous primary beam fell, it was still possible that only one constituent (rays of one penetrating power) in each heterogeneous primary beam was producing this radiation. It was therefore important to determine to what extent each constituent of the primary beam was effective in producing these secondary rays.

To do this, a portion of the primary beam direct from the X-ray tube was sent through one electroscope while another portion was incident on a secondary radiator, some of the rays from which passed through a second electroscope. The method was then simply to place absorbing plates in the primary beam before falling on the radiator, and to observe the extent by which the primary and the secondary radiations were reduced. It is obvious that the more penetrating constituents of the primary beam penetrate to greater depths than the absorbable constituents, and so are really transmitted through a greater mass than these. Hence, if two homogeneous constituents of primary radiation in passing through equal masses of radiating substance were equally efficient as secondary-ray producers, the radiation emitted by a thick plate would be produced principally by the more penetrating constituents; consequently an absorbing plate placed in the position indicated, would, by cutting off the more easily absorbed constituents, produce less diminution of the ionization in electroscope E_2 than of that in E_1. It was therefore necessary to use as the radiator a sheet of metal which would absorb very little of the primary radiation, so that even the deepest layers would transmit different constituents in proportions approximately the same as those transmitted through the first surface-layer.

It was found that a sheet of Cu ·00067 cm. in thickness when placed in the primary beam produced an absorption of only 14·5 per cent., as measured by the ionization produced in an electroscope. This was considered sufficiently thin for use as a radiator. The deflexions of the electroscopes were first observed when no absorbing plate was used. Aluminium plates of thickness shown in column I of Table VI. were placed in the primary beam, and the deflexions of the primary and secondary electroscopes were diminished by the amount given in columns III and IV.

TABLE VI.

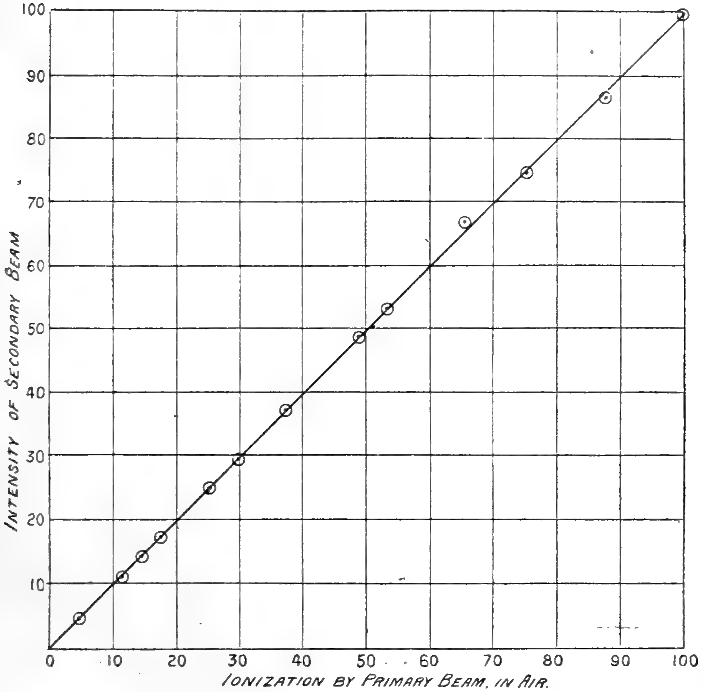
Radiation from Copper (thin sheet absorbing 14·5 per cent. of primary rays.)

I. Thickness of Al in Primary beam in centimetres.	II. Absorption of Primary by Cu (·00293 cm.) after passing through Al in column I.	III. Percentage of Primary absorbed by Al in column I.	IV. Percentage diminution of Secondary by Al in column I. absorbing Primary.	V. Ratio of Ionizations in Secondary and Primary electroscopes (relative).
0	84	0	0	1
·0032	82·8	12·2	13·6	·98
·0064	81·4	24·9	25·5	·99
·0104	80·3	34·2	33·1	1·01
·0168	77·5	46·7	46·6	1·00
·0208	75·9	51·1	51·4	·99
·0312	72·3	62·9	62·9	1·00
·0416	69·6	70·2	70·5	·99
·0520	65·2	74·6	75·0	·98
·0728	60·4	82·4	82·3	1·00
·0936	57 0	85·8	85·8	1·00
·124	51·2	88·6	88·9	·97
·248	41·7	95·4	95·3	1·02

In fig. 2 the ionization produced by the primary beam in air is indicated by abscissæ and that produced by the corresponding secondary beam from a thin sheet of copper as ordinates, when different portions of the primary beam have been absorbed.

As the secondary beam is practically homogeneous we have exhibited the relation between the ionization produced by a primary beam in the air, and its power of producing secondary rays in copper. We are thus led to the conclusion that the intensity of this homogeneous secondary radiation set up in a thin sheet of copper is proportional to the number of ions the primary beam would produce in a thin layer of air. Thus if two beams of Röntgen rays, which in passing through a thin film of air would produce equal ionizations in that air, be sent through a thin sheet of copper, the intensity of secondary radiation produced on that sheet by one beam will equal that produced by the other, even though one is three or four times as penetrating to copper as the other one. As for such ranges of penetrating power as are possessed by the constituents of such a primary beam, the relative ionizations produced by those constituents in different substances are usually fairly constant, it is highly probable that the intensity of the homogeneous rays from copper is through wide ranges of penetrating power of the primary proportional to the ionization which takes place in the copper, and is independent of the character of the primary producing it.

Fig. 2.



It does not necessarily follow from this that the process of ionization produces the radiation, but it seems to indicate that the energy of the homogeneous secondary radiation is, for such ranges in penetrating power, proportional to the energy of the primary beam spent in the process of ionization.

When the primary radiation was transmitted through copper or iron before falling on the copper radiator, the ratio of intensity of secondary radiation to ionization produced by the primary beam dropped slightly, showing that the radiation transmitted through these substances was less efficient as a secondary-ray producer in comparison with its power of producing ionization in air. This may have been due to the fact that in transmission through these plates, a gradually increasing quantity of secondary radiation from the plates was superposed on the primary. This being in one case of the same penetrating power as the secondary emitted by the radiator, and in the other more easily absorbed than it, would not afterwards produce secondary rays in the copper (see later). When the radiation was absorbed by zinc, the ratio remained fairly constant. This result would, on the corresponding theory, be due to the fact that the radiation from zinc is slightly more penetrating than that from copper, consequently the zinc radiation acquired in the primary beam would be capable of stimulating a feeble secondary in copper. (See Table VII.)

Table VII.

Radiation from Copper (thin sheet absorbing 14·5 per cent. of primary rays).

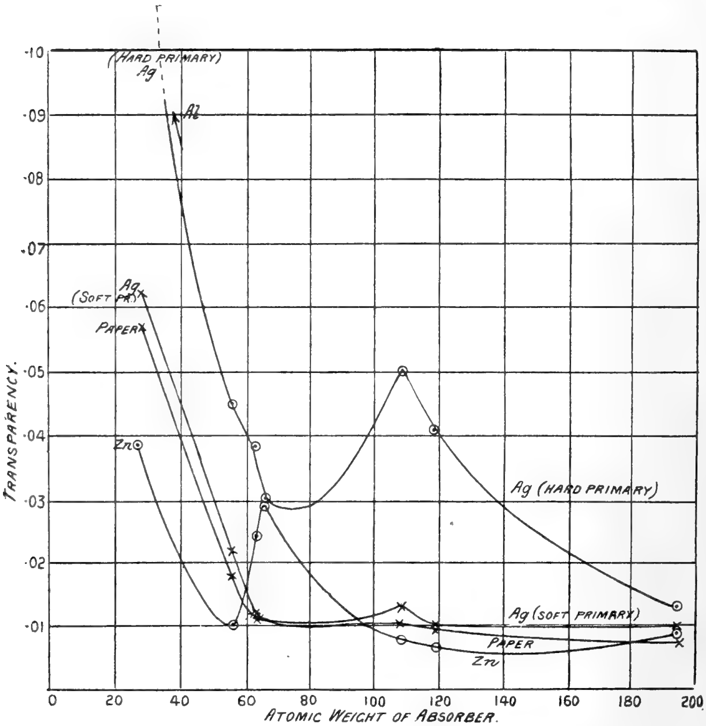
I. Thickness of plate in Primary beam.	II. Percentage of Primary absorbed by Zn in column 1.	III. Percentage diminution of Secondary by Zn in column 1 absorbing Primary.	IV. Ratio of Ionizations in Secondary and Primary electroscopes.
Zn ·00131 cm.	59·4	59·6	·99
·00262 ,,	77·5	77·6	·99
·00393 ,,	84·8	84·8	1·00
·00524 ,,	89·1	90·1	·91
·00786 ,,	93·5	93·6	·98
·01179 ,,	97·2	96·3	1·32
Cu ·00067 cm.	43·5	45·1	·97
·00134 ,,	65·0	66·5	·95
·00296 ,,	82	84·8	·84
·00592 ,,	90	91·6	·84
·01184 ,,	97	98	·66
Fe ·00315 cm.	77·2	80·8	·84
·00630 ,,	89·0	91·4	·78
·00945 ,,	93·0	95	·71

Whatever may be the true explanation, these results show that the proportionality exhibited after absorption by aluminium is not general even when copper is the radiating substance. This result may be contrasted with the corresponding phenomena exhibited by the homogeneous radiation from silver. In these experiments the homogeneous rays disappeared when the primary beam was made more absorbable and more efficient as an ionizer of air. The difference is almost certainly due to the fact that in the latter case the primary radiation passes from one more penetrating to one more easily absorbed than the secondary radiation characteristic of the element exposed to the primary rays. It seems highly probable therefore, that with sufficiently absorbable primary rays no such relation as that shown by fig. 2 would be obtained, but that the secondary would disappear while the primary still produced considerable ionization in air. It will be interesting to learn if a primary which ceases to stimulate the homogeneous radiation ceases also to produce ionization in the radiating substance. We, of course, know that elements of the H–S group are ionized, but do not emit a homogeneous radiation which can be detected. This appears to indicate no necessary connexion between ionization and radiation, but is not conclusive for various reasons.

Special Penetrating Power.—In studying the absorption of these homogeneous radiations by a number of elements, it was found that the relation between the absorption by a given substance of the various homogeneous radiations from elementary substances and the atomic weight of those radiating substances was similar for all absorbing substances, except in the case of the radiating and absorbing elements being identical or possessing neighbouring atomic weights. Each substance appeared to be especially transparent to its own radiation, and to a less extent to that from elements of neighbouring atomic weight.

The transparency of various elements to an ordinary heterogeneous beam of X-rays has been investigated by Benoist, who studied the phosphorescence produced by the beam after passing through absorbing substances. He compared the transparencies by finding the mass of a prism of absorbing substance of definite cross-section, which when placed in the path of the beam absorbed it by a definite amount. The relation between the transparency so defined and measured, and the atomic weight of the absorbing substance was shown by a curve similar to that for paper given in fig. 3. It shows a rapid decline of transparency, with increase in atomic weight for low atomic weights, the rapidity of the fall of transparency diminishing with an increase of atomic weight. In the case of very soft rays this decline becomes a slight incline.

Fig. 3.



By using thin plates of absorbing elements and testing by the ionization method the percentage diminution of intensity of the secondary beams by transmission through these plates, it was easy to calculate the thickness and hence the mass per unit cross-section necessary to absorb a given proportion —in this case 75 per cent. Some of these results we have given in a previous paper (*f*)*. They show that in place of the usual relation between transparency and atomic weight there is a strongly marked deviation in each case in the neighbourhood of the atomic weight of the radiator, the rays from an element being especially penetrating to that element

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* In the paper referred to the numbers given in Table II. represent mass in grammes, not thickness in centimetres as stated.

and to a less extent to elements of neighbouring atomic weight.

That this special penetrating power is not due to the constituent easily absorbed by the radiating substance having been sifted out before emergence through the surface layer might be inferred from the fact of its homogeneous character, unless of all the constituents in the radiation as emitted from the atom itself this was the only one transmitted through even fairly thin layers of the substance. But we find other secondary rays transmitted with almost the same facility. We may conclude, therefore, that it is not merely from the surface of relatively thick sheets that the radiation emerges in a homogeneous state, but that it is so emitted by the atoms themselves. The special power of penetration is thus a specific property of the secondary rays and does not appear to be due to previous selective absorption.

Tertiary Rays.—Some of the most interesting phenomena in connexion with these homogeneous rays were those shown by experiments made in order to investigate the special penetrating power of these rays.

When the characteristic homogeneous radiation from iron was passed through a thin sheet of copper—a substance whose characteristic radiation is of more penetrating type—it was partially absorbed, and the transmitted radiation appeared unchanged in character.

When, however, the radiation from copper was passed through iron there was superposed on the copper radiation a considerable quantity of iron radiation; when the thickness of the absorbing plate of iron was sufficient to produce almost complete absorption, the bulk of the transmitted radiation was iron radiation.

Similar experiments were made on copper and zinc. The radiation from the former, which is more absorbable than that from the latter, when passed through zinc was transmitted without admixture of other radiations, but when the radiation from zinc was transmitted through copper it became more like the copper radiation. The effect was not so well marked as in the case of the transmission of copper radiation through iron.

Thus a characteristic homogeneous radiation was emitted by a metal when the primary beam to which the metal was exposed was of more penetrating type than the characteristic radiation. When the primary was of a more absorbable type, this characteristic secondary radiation was not emitted*.

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* Details of these experiments will be given later.

Ag–I GROUP.

When subject to primary beams of moderate penetrating power such as those used in these experiments, the elements of atomic weights from that of silver to that of iodine are exceedingly susceptible to small changes in the penetrating power of that primary radiation, both as regards the character and the intensity of the secondary rays that they emit. This is indeed the most remarkable feature of this group of elements.

Silver and tin are the only elements of this group which have been examined in any detail, but they appear from superficial observation to be typical of the whole group. In previous papers it has been shown that the radiation from these two when subject to a primary beam of only moderate penetrating power, is not a scattered radiation like that which proceeds from elements of the H–S group, for it differs much more in penetrating power from the primary producing it than the radiation from the elements of that group, though not so much as the radiation from Cr, Fe, Cu, &c. The radiation does not exhibit the polarity of a primary beam where such exists, and it is not distributed in the manner of the radiation from substances of low atomic weight, the intensity in a direction almost opposite to that of primary propagation being approximately equal to that in a direction at right angles. It was not possible, however, to perform this experiment with anything like the degree of accuracy with which it was done in the case of the radiation from Fe, Cu, &c., because the ionization produced by the secondary beams from Ag and Sn was much less intense.

Secondary Scattered Rays.—Experiments with the softest rays procurable from an X-ray tube of ordinary type, however, considerably simplified the secondary radiation, for it was found that the secondary rays from silver then differed very little in penetrating power from the soft primary. When the intensity of secondary radiation set up by a powerfully polarized primary was examined in the two principal directions at right angles, it was found that it varied by approximately the same amount as that from elements of the H–S group, thus exhibiting the same perfection of scattering. When tin was examined in the same way, the variation in intensity was found to be about half that exhibited by the rays from paper and from silver. Thus by using a very soft primary radiation, an almost purely scattered secondary radiation was emitted by silver, and a radiation consisting of a large proportion of scattered rays was emitted from Sn.

To compare the intensity of this scattered radiation from silver with that from elements in the H–S group, the ionization produced by the secondary radiation from a thin sheet of silver ·00064 cm. thick was compared with that produced by the radiation from paper. The masses of silver and paper emitting the secondary rays were ·2695 gr. and 2·72 gr. respectively. The relative ionizations produced by the secondary rays from these were 148 and 280. From other experiments on the absorption of the primary beam by sheets of silver and paper of different thicknesses, it was estimated that about 60 per cent. of the silver radiation and 75 per cent. of the paper radiation was transmitted through the surface layer. The intensities of radiation from these masses were, therefore, in the ratio 37 : 56 approximately. From equal masses this was 37 : 5·6, or 6·5 : 1 approximately.

As the primary radiation incident on silver became more penetrating, the ionization produced by the secondary rays increased enormously, the variation of intensity in the two principal directions at right angles to that of propagation of the primary rays gradually decreased from its original amount—about 14 per cent.—until it was inappreciable, though with the same primary the variation in the intensity of radiation from carbon had only dropped to about 6·5 per cent. The evidence of polarity of the primary given by the secondary rays from silver thus disappeared, while that given by the rays from carbon simply decreased from 14 per cent. to 6·5 per cent. It should, however, be noticed that the ionizing effect of the secondary rays from silver increased considerably, and when the evidence of polarity disappeared the total secondary ionization had increased about tenfold, so that such an effect would have been produced by the superposition of the homogeneous radiation, like that emitted by Cu, Fe, Zn, &c.; for such a radiation gives no evidence of polarity in a primary beam, being uniformly distributed around that beam*.

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* An early experiment by one of us on the radiation from tin (*e*) indicated that the scattered radiation was not emitted in even the intensity that could be given by an element of the H–S group. The experiment was performed by comparing a very penetrating portion of the radiation from tin with that from paper. There are possibilities which make such an experiment inconclusive, and we feel that it requires verification. If the numerical values for the polarization given in Table VIII. could be taken as strictly accurate throughout, we should be led to conclude that the evidence of polarity disappeared more rapidly than could be accounted for by mere superposition of the homogeneous radiation, but the measurements in the final stages were too uncertain for such a conclusion to be based on them. We have, therefore, no conclusive evidence of a disappearance of the scattered radiation.

The evidence of polarity of the primary given by the radiation from tin disappears for even softer primary rays than in the case of silver. This must be connected with the fact that the characteristic homogeneous radiation from tin is less penetrating than that from silver, and is set up by a less penetrating primary radiation. It thus appears earlier in the process of hardening the primary and swamps the effect of the scattered radiation sooner.

Table VIII.

I. Absorption of Primary by ·01 Al.	II. Ratio of Ionizations in Secondary and Primary electroscopes.		III. Percentage Variation of intensity of Secondary radiation exhibiting polarity of Primary beam.	
	C radiator.	Ag radiator.	C radiator.	Ag radiator.
35·5	·303	·180	14	11·5
32·6	·340	·359	10·95	4·45
32·3	·318	·305	12·9	6·2
32·0	·315	·369	12·9	4·5
30	·349	·821	9·9	2·8
29·4	·353	·844	9·6	2·45
28·6	·364	1·12	9·15	·9
28·9	·380	1·35	7·5	·75
27·3	·405	1·62	7	·45
25·6	·425	1·82	6·5	0

Homogeneous Rays.—An analysis of the radiation from silver similar to that made of the radiation from elements of the Cr–Zn group shows that when the primary radiation is moderately penetrating, such a homogeneous secondary radiation constitutes the bulk of the rays emitted. Absorption by thin sheets of aluminium showed slight heterogeneity at first, such as would be evident if the scattered radiation were superposed on the more penetrating homogeneous radiation. After the absorption of this more easily absorbed scattered radiation the remainder appeared perfectly homogeneous.

The contrast between the constitution of the copper and silver radiations is shown by the curves given in fig. 1. In the copper radiation the homogeneous rays are more easily absorbed than the scattered rays, so the curve is initially horizontal and finally slopes downwards. In the silver radiation the scattered rays are on the average more easily absorbed than the homogeneous rays, consequently the curve dips initially and finally becomes horizontal. The absorptions at successive states are shown in the following tables. With these results may also be contrasted those obtained for the scattered radiation from paper.

TABLE IX.
Radiation from Silver (thick).

Thickness of Al placed in Secondary beam from Ag.	Percentage diminution of Ionization produced by Secondary rays by transmission through Al in column 1.	Percentage diminution of Ionization by Secondary rays due to absorption by further sheet of Al (·0208 cm.).
0	0	15·9
·0104 cm.	9·2	14·8
·0208 ,,	16	13·8
·0574 ,,	37·7	13·1
·124 ,,	58	13·5
·182 ,,	72	14
·263 ,,	82·5	13·6
·387 ,,	92	13·8
·526 ,,	97	14·2
0	0	16

TABLE X.
Radiation from Paper.

Thickness of Al placed in Secondary beam from Paper.	Percentage diminution of Ionization produced by Secondary rays by transmission through Al in column 1.	Percentage diminution of Ionization by Secondary rays due to absorption by further sheet of Al (·0208 cm.).
0	0	28·1
·0104 cm.	18·7	20·9
·0208 ,,	28	17·4
·0574 ,,	47·5	10·9
·182 ,,	70	5·8
·584 ,,	88	2·5
0	0	27·4

W–Bi GROUP.

The radiations from the elements with atomic weights from that of tungsten to that of bismuth have not been examined minutely. They, however, appear to be very similar to the rays from Cu, Zn, &c. The ionization produced by these rays is of the order of magnitude of that produced by the rays from elements of the Cr–Zn group; but there appears slightly more variation in the character due to changes in the primary rays.

Though accurate observations have not been made, it appears probable that the radiation is a mixture of the scattered with the homogeneous rays, the proportional effect of the scattered being greater than in the radiation from Cu, Zn, &c.

Conclusions.

Secondary Röntgen rays of two distinct types are emitted by substances subject to a beam of X-rays. One, a scattered radiation produced by the motion of electrons controlled by the electric force in the primary Röntgen pulses, has been dealt with in previous papers by one of us, and has been further discussed in this paper with the H–S group of elements. The other, a homogeneous radiation characteristic of the element emitting it, and produced by the motion of electrons uncontrolled by the electric force in the primary pulses, has been but briefly mentioned.

All the phenomena of secondary X-rays so far observed by us may be explained by means of these two.

The experimental results of these investigations, both on the scattered radiation and the homogeneous radiation, are summarized below. In order to make the summary more complete, we have introduced several results which have been previously published. The references for these are given.

Experimental Results.—Scattered X-rays—those produced by the motion of electrons controlled by the primary pulses—constitute the bulk of the secondary radiation from elements of the H–S group when these are subject to a primary beam of low to moderate penetrating power.

Scattered X-rays are also emitted by many elements of higher atomic weight—probably by all—when subject to such a primary beam; but unless the primary is very soft they are accompanied by homogeneous secondary X-rays (characteristic of the radiating element) which produce much greater ionizations.

The law of intensity of these scattered rays which holds for elements of the H–S group—that the intensity of radiation from an atom is proportional to its atomic weight—cannot be extended to include the elements of higher atomic weight. From some elements at least the intensity is greater than would be given by this law.

The scattered radiation from some elements whose characteristic homogeneous radiation is of comparatively penetrating type has been obtained free from admixture with this homogeneous radiation by the use of a primary beam consisting of less penetrating rays than the characteristic secondary.

Those scattered radiations not thus isolated have been accompanied by a homogeneous radiation more easily absorbed than the primary radiation producing them.

We have obtained no conclusive evidence that the relative intensity of secondary scattered and primary radiations changes with the penetrating power of the primary rays.

All elements of atomic weight greater than that of sulphur which have been examined emit a homogeneous secondary radiation when subject to a primary beam of X-rays of ordinary penetrating power. Cr, Fe, Co, Ni, Cu, Zn, Ag, have been examined. All other elements whose secondary radiations have been examined less minutely appear similar in this respect.

The penetrating power of this radiation from each element examined has been found independent of the intensity or the penetrating power of the primary radiation producing it; it is characteristic of the element emitting it.

The penetrating power of this radiation is a periodic function of the atomic weight of the radiating element (*e*).

The ionizing power of this radiation and almost certainly its energy is usually very much greater than that of the scattered radiation.

The homogeneous radiation has invariably been found more easily absorbed than the primary radiation producing it.

In all cases, when a primary was used which was softer than the characteristic homogeneous radiation, this radiation was not emitted. Also there is reason (from the curve connecting absorbability of a secondary radiation and the atomic weight of a radiator) for believing that those elements H–S which do not under ordinary circumstances emit such radiation, possess a characteristic radiation which is more penetrating than any primary beam used.

The intensity of this homogeneous radiation from copper is for a considerable range in the penetrating power of the primary merely proportional to the ionization produced by that primary in a thin film of air and is otherwise independent of the penetrating power of the primary. This is not general, as in many cases—probably all—the homogeneous radiation disappears when the primary radiation becomes more absorbable.

The intensity of the homogeneous rays in a given direction does not depend appreciably on the position of the plane of polarization of primary beam producing them.

The intensity of this radiation in a direction approximately opposite to that of propagation of the primary beam producing it, is within the small errors of experiment equal to that in a direction at right angles (*g*).

This radiation is specially penetrating to the element which emits it and to a less extent to elements of neighbouring atomic weight (*f*).

The fraction of the homogeneous rays from one element—copper—scattered by air, is the same as that for X-rays proceeding direct from an X-ray tube (within experimental errors) (*b*).

The absorbability of the secondary rays from copper which are scattered by air—tertiary rays—is the same as that for the direct secondary (*b*).

Theory.

The theory of the scattered X-rays has been dealt with in various papers, and the experimental evidence in support of that theory—briefly referred to in this paper—is so overwhelming that it need not be further discussed here.

It is important, however, to consider the evidence we have regarding the nature and origin of the homogeneous rays, which are characteristic of the elements emitting them.

The fact that the homogeneous secondary rays from copper are scattered by air in approximately the same proportion as the primary rays proceeding direct from an X-ray tube, and that the absorbability of these scattered rays is the same as that of the direct secondary rays, is strong evidence that they are of the nature of X-rays, for neither the observed intensity, nor the scattering without degradation, would have been expected on any corpuscular theory, whereas they are in perfect harmony with the æther pulse theory.

The relation between the absorption of a mixture of the homogeneous rays from a number of elements by various elements and the atomic weight of those absorbing elements is also very different from that found for any material radiation, while it is very similar to that obtained by experiments on a beam of Röntgen rays[*].

The special powers of penetrating certain substances are such as have not been observed and are difficult to conceive of on any corpuscular theory.

Neither electrostatic nor magnetic deflexion of these rays has been observed.

Finally, the fact that the homogeneous rays are invariably produced by primary rays of more penetrating type, yet not necessarily more than just on the more penetrating side, appears some of the strongest evidence in favour of similarity in type between the primary and secondary rays. If the natures were different, the penetrating powers would represent totally different physical facts, and such connexion between them would be inconceivable. We can only conclude from consideration of this evidence that the nature of the homogeneous rays is similar to that of the primary X-rays.

As the homogeneous rays are of the nature of Röntgen rays, we must conclude that the radiation is set up by disturbance of electrons produced directly or indirectly by the passage of the primary pulses. That this motion of electrons is not controlled by the electric forces in the primary pulses, is proved by the equality of the intensities of radiation in a direction approximately opposite to that of primary propagation and one at right angles, by the absence of evidence from the secondary rays of polarization of a primary beam in which such polarization exists, and by the absence of dependence of the penetrating power of the secondary beam on that of the primary.

The forces called into play which produce the accelerations resulting in radiation cannot then be directly due to the electric displacement in the primary pulses, but must be those called into play in the atom itself. The two possibilities that suggest themselves are that the radiations result from a disturbance of the atom, which quickly recovers its normal configuration, or that it is produced when the equilibrium of an atomic system is destroyed and forces of unusual magnitude are called into play.

The homogeneity of the radiation and its independence of the primary rays suggest a regularity in the motion which is characteristic simply of the atom; and although the relation between intensity of secondary radiation from copper and ionization produced by the primary in air is striking, it does not follow that the radiation is due to ionization in the

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[*] Details of these experiments have not been given.

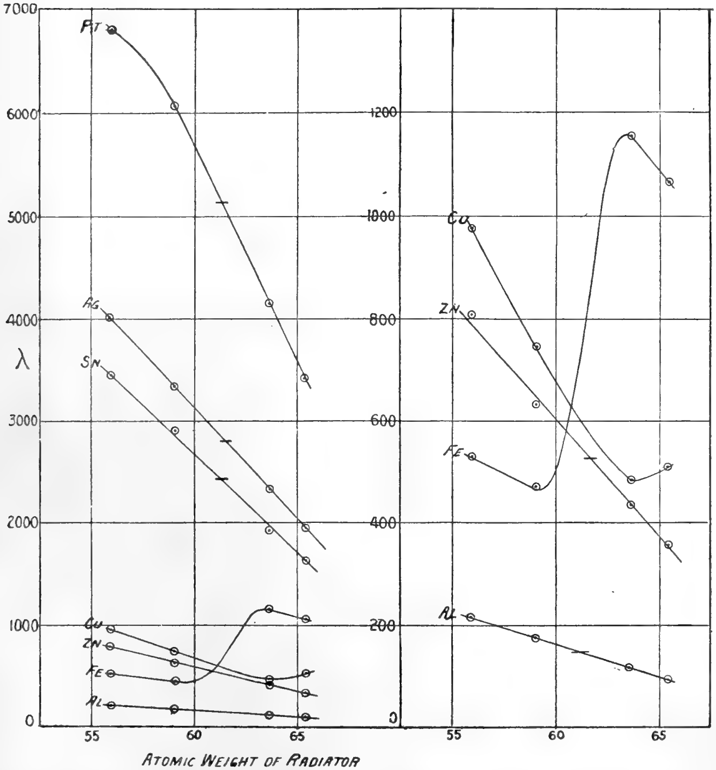
radiating substance. Indeed, this appears highly improbable, for the homogeneous radiation disappears when the primary radiation is made "soft" and appears in great intensity when the primary is "hard."

If, then, the radiation were emitted simply during the process of ionization and were proportional to it, a soft primary radiation would produce little or no ionization and a more penetrating radiation—(that is one more penetrating to most substances)—would produce an ionization at least hundreds of times as great. Though experiments have not been made on the ionizations produced in these substances investigated, such variations in ionization are of a higher order of magnitude than any observed. Again, ionization is undoubtedly produced in substances of the H–S group of elements when homogeneous rays are not emitted in appreciable intensity. We, however, do not know anything of the homogeneous rays from these substances except that they are probably of penetrating type.

The relation between the absorption of a primary radiation and the intensity of secondary radiation emitted by the absorbing substance, also shows that the emission of homogeneous radiation necessitates a special absorption of the primary beam. Also, as far as we can estimate from experiments made, the energy of the homogeneous radiation is more than accounted for by the special absorption necessary to the production of that radiation.

Thus in fig. 4 we have plotted the coefficients of absorption of rays from Fe, Co, Ni, Cu, and Zn by Al, Zn, Ag, Sn, Pt In each case the radiations absorbed are not—if we generalize from results given—capable of stimulating a homogeneous radiation characteristic of the absorbing substance, because these are of more penetrating type. The curves are similar. But when iron is used as the absorbing substance, cobalt radiation, which is just more penetrating, is unable to produce more than a feeble secondary in the iron, so the decline of the line for Fe is not quite so great as would have been expected, because of the little extra absorption necessary to set up this slight radiation from iron. The copper radiation, which is much more penetrating, is able to stimulate an intense radiation in iron and at the same time is enormously absorbed. This is exhibited by the sudden rise in the Fe curve. Beyond copper, the absorption appears to fall again according to the usual law, the absorption of the zinc radiation being a little less than that of the copper radiation. The stage is thus reached when the change in the penetrating power of the primary radiation produces no difference in the relative amounts of secondary homogeneous radiation and ionization by the primary beam, as shown by fig. 2 for the copper radiation. A study of the curves (fig. 3), exhibiting the transparency of various metals to homogeneous rays, shows the same thing. Thus, dealing with the radiation from zinc, aluminium, in which a Zn radiation does not stimulate, a homogeneous

Fig. 4.



secondary radiation is fairly transparent. Iron, in which an intense radiation is set up—the characteristic radiation from iron being considerably softer than that from zinc—is very opaque. Copper is much more transparent, as the zinc radiation being only a little more penetrating, is only able to set up a feeble radiation ; while zinc, in which zinc radiation is unable to set up any further radiation, is more transparent still. The substances Ag, Sn, and Pt appear relatively more transparent to this radiation than to a more penetrating beam*.

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* Also Phil. Mag. Sept. 1907, p. 416, fig. 5.

The zinc radiation is unable to set up radiations in these elements, as they are of more penetrating type. The absorptions are, however, not sufficiently abnormal to speak of with certainty. The effect is more clearly shown by the curve obtained from the homogeneous radiation from silver (fig. 3).

These results show that a substance whose characteristic radiation is equally or more penetrating than the radiation incident upon it, does not absorb that radiation so much as when the incident is of more penetrating type and able to stimulate a secondary radiation in that substance. As the penetrating power of the incident radiation (as measured by most substances) increases, the absorption increases up to a certain point. A definite portion of the absorption thus appears to be connected with the secondary radiation, and may be proportional to it. But this does not conclusively show that ionization, or some kind of disruption in the atom is not the cause of the radiation, for the absorption of a certain amount of energy of the primary beam might be required to produce the instability which liberates more energy.

The facts that the homogeneous rays have invariably been found more easily absorbed than the primary rays producing them, and, in the cases investigated, that the homogeneous rays disappear when the primary becomes more easily absorbed, indicate a relation between primary and secondary which would be difficult to explain if this radiation were directly due to a disruption of any kind taking place in the atom. It appears rather that the radiation is due to what may be regarded as quite a normal behaviour of an atom after it has been passed over by Röntgen pulses, such as a free vibration of electrons.

Let us consider the passage of an electromagnetic pulse, in which the electric field is undirectional, over an electron with a free period of vibration much longer than double the time taken for the pulse to pass over it. (In this case the Röntgen pulse is thinner and more penetrating than the half-wave produced by the free vibration of the electron.) The electron receives an impulse and is left with kinetic energy after the pulse has passed. Consequently it is then acted upon by forces called into play in the atom itself. These produce a motion which is characteristic of the atom of which the electron forms a part, and this results in radiation—probably the homogeneous radiation discussed in this paper.

When the thickness of the primary pulse approaches the half-wave length characteristic of the vibratory motion of the electron in the atom, the restoring force in the atom is brought into play before the primary pulse has passed and the absorption of energy and energy of subsequent radiation are diminished. This explains the diminished radiation when the penetrating power of the primary decreases and approximates to that of the radiation characteristic of the radiating substance. When the primary pulse is thicker than the half-wave characteristic of the motion of the electron, the electron is displaced a short distance and is gradually brought back by the restoring force against a gradually weakening electric force in the primary pulse, so that when this has passed, the electron is near its position of equilibrium again and the motion and radiation produced in the other cases are now absent. It is impossible to give an exact solution without some knowledge of the distribution of electric force in the primary pulses, of the forces binding the disturbed electron to the rest of the atomic system, and of the structure of that system; but we may consider this to be an approximation to the behaviour of each electron directly concerned with the phenomena discussed. The number of such electrons may not exceed one in each atom of radiating substance.

According to this theory, energy is taken from the primary beam and part, at least, appears as secondary homogeneous radiation, the rest being transformed into heat.

As the energy of this radiation is quite a considerable fraction of the total energy absorbed, we should expect that the difference between absorptions of primary rays more or less penetrating than the radiation characteristic of the absorbing element would be evident from a study of the absorption of the various homogeneous beams. But we have seen that there is a large absorption of a homogeneous radiation by an element which emits a much more easily absorbed radiation, because much of the energy is given to the electrons; that for other elements which emit a radiation only slightly softer, the absorption is much diminished because only a feeble disturbance and consequent secondary radiation is set up in the absorber; and when the radiation characteristic of the absorbing substance is more penetrating than the absorbed radiation, the absorption is small and no homogeneous secondary radiation is produced. Thus what we have previously referred to as the special penetrating power of the homogeneous radiations may be explained by the small displacement produced in an atom by a radiation more easily absorbed, equally absorbed, or slightly more penetrating than the radiation characteristic of that atom, for reasons indicated.

Though according to such a theory, if the displaced electrons were merely held by a body of much greater mass, we should expect the emission of wave-trains instead of pulses, yet if the atomic system consisted of a number of interacting electrons, the energy of vibration would be rapidly communicated to other parts of the system and the motion of the displaced electron would be little more than half a complete vibration. The resultant radiation would in that case behave much as a number of isolated pulses.

An explanation on the disruption theory would be similar in many respects, but the displacement of electrons would on such a theory be sufficient to destroy the equilibrium of the atomic system and produce some change in its structure. The evidence against this is perhaps not conclusive, but there is no indication from the energy of secondary X-radiation of such a phenomenon, and the relation between the primary and secondary radiations points rather to the latter being due to the motion of the atomic system in regaining its normal configuration.

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University of Liverpool,
30th May, 1908.

XLIX. *The Amount of Radium Emanation in the Atmosphere. By* JOHN SATTERLY, *A.R.C.Sc., B.Sc., B.A., St. John's College, Cambridge*[*].

IN 1900 Elster and Geitel[†] found that when a negatively electrified wire was exposed to the atmosphere for some time a radioactive deposit was formed on it whose properties agreed very closely with the properties of the active deposit from radium. Blanc[‡] and others have shown that a thorium deposit accompanies the radium deposit, the relative amounts of the two deposits being dependent on the time of exposure of the wire. Eve[§] compared the amount of the active deposit obtained from a known volume of air with the active deposit obtained from the emanation generated by a solution of radium bromide of known strength, and in this way formed an estimate of the amount of radium necessary to keep up the supply of emanation. Strutt[||], Eve[¶], Joly[**]

[*] Communicated by Prof. J. J. Thomson, F.R.S.

[†] Elster and Geitel, *Phys. Zeit.* ii. 1901.

[‡] Blanc, Phil. Mag. Mar. 1907. Also Dadourian, *Le Radium,* April 1908.

[§] Eve, Phil. Mag. July 1905.

[||] Strutt, Proc. Roy. Soc. May 1905, May and Aug. 1906.

[¶] Eve and MacIntosh, Phil. Mag. Aug. 1907.

[**] Joly, Phil. Mag. Mar. 1908.

and others have detected radium and measured its amount in rocks, waters, &c., so that there are many agencies by which radium emanation can be supplied to the atmosphere. It is of importance to find the amount of radium emanation in the atmosphere in order to calculate how far the natural ionization of the air is due to changes going on in the air and how far due to radiation from the earth or from sources exterior to the earth and its atmosphere, and also to find how the amount of emanation in the atmosphere varies with weather conditions.

This paper contains an account of an attempt made by two methods to measure the amount of radium emanation in the portion of the atmosphere near the earth. The amount of emanation in a given volume of air is expressed in terms of the mass of radium which would be sufficient to keep up the supply of emanation, the radium and its emanation being supposed to be in radioactive equilibrium. This necessitated the use of a known quantity of radium; and Professor Rutherford was good enough to give me a solution of radium bromide containing $3\cdot14\times10^{-9}$ gram of radium*. In essence, the principle of the experiment is first to measure, by some means or other, the emanation in a known volume of air, and then to measure by the same means the emanation given off from the solution in a known time. A direct comparison of the two figures enables one to calculate the amount of radium which is capable of supplying the emanation in a known volume of air, the assumption being made that the emanation in the air is in radioactive equilibrium with the radium that gives rise to it.

Two methods of experiment were tried:—

(1) Absorption by Charcoal,

(2) Condensation by Liquid Air;

and an electrical method of testing was used throughout, the amount of emanation being expressed in terms of the increased electrical conductivity it imparted to a known volume of air.

Method (1) will be described first.

(1) *The Charcoal Method.*

In a letter to 'Nature' in Oct. 1906, Prof. Rutherford announced that he had found that when a stream of air containing radium emanation was slowly passed at ordinary temperatures through charcoal made from the shells of coconuts,

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* The solution was acidified with hydrochloric acid. This prevents partial precipitation of the radium by the carbonic acid of the air which is bubbled through the solution.

the emanation was almost completely abstracted from the air, being absorbed in some way or other by the charcoal *. He also discovered that the emanation while absorbed by the charcoal decayed at the usual rate (half value in 3·71 days), and also that when the charcoal was heated to just below a red heat the emanation was released, and could be swept out by a current of air.

In the summer of 1907 I started to adapt this method to the measurement of the emanation in the atmosphere; but except for getting the apparatus together and obtaining practice in the method of work, little progress in actually measuring the amount was made till the beginning of this year when I obtained the radium solution.

Meanwhile a paper had appeared in the Philosophical Magazine of Dec. 1907 by Mr. A. S. Eve, of Montreal, who had measured the amount of emanation in the air at Montreal by the charcoal method. As, however, each one of his experiments lasted between two and three days, whereas I found that I could get a measurable amount in two or three hours, I decided to continue my experiments.

Details of the Apparatus.

(1) *The Testing Vessel and Electrometer.*—The testing vessel was a brass cylinder 40 cms. high and 10 cms. diameter. It was fitted with two side tubes, one of which communicated with a U-tube mercury manometer, the other served as an inlet and outlet tube, and communicated with a calcium chloride drying-tube. The neck of the can was closed by an indiarubber stopper which supported the insulated wire electrode. As it was necessary to exhaust the vessel, sulphur could not be used as an insulating agent. Amber was used instead, a straight amber mouthpiece of a tobacco-pipe proving very convenient for the purpose. The wire electrode was threaded through the amber and fixed in position with sealing-wax ; the amber was similarly fixed in a guard-tube, which was afterwards earthed, and the guard-tube fitted tightly into the indiarubber stopper. Within the vessel the wire reached nearly to the bottom; outside the vessel it was bent round and passing through an earthed shield-tube dipped into a calcium chloride cup supported by one of the terminals of a quadrant electrometer. Communication

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* See also a paper by E. Henriot, "Sur la Condensation des émanations radioactives," in *Le Radium*, Feb. 1908. Using a statical method, he found that the emanation is completely absorbed by coconut charcoal at ordinary temperatures (18° C.), and is completely got rid of by heating the charcoal to dull redness.

with the calcium chloride cup was obtained by a rod which passed through a hole in the side of the shield-tube. This rod was connected with a potentiometer-circuit consisting of a 2-volt cell and a resistance-box; by these means the cup, and therefore one pair of quadrants, could be charged, earthed, or insulated at will.

The quadrant electrometer used was of the Dolezalek pattern, the insulation of the quadrants and terminals being amber and the suspension-fibre a long phosphor-bronze strip. The case of the electrometer and one pair of quadrants were earthed. The needle was kept at a potential of +80 volts by being connected to a battery of small cells, the negative ends of the battery being earthed. For a potential-difference of one volt between the quadrants a deflexion of 90 cms. on a scale two metres distant was obtained.

The testing vessel could be earthed or charged by connexion to a battery of small cells, the other end of the cells being earthed. Usually a potential of −280 volts was applied to the vessel. This was sufficient to produce saturation for all the leaks that I had occasion to measure. Water resistances were inserted between the vessel and these cells, as also between the electrometer-needle and its cells, to lessen any dangers that might have occurred in short-circuiting.

During the experiments it was found that if the air in the testing vessel was left to itself, the air leak gradually increased for some days; but that fairly steady air leaks could be obtained if the vessel was exhausted every day. The usual value of the air leak was about 1·0 cm. per minute on the scale described above. This is equivalent to a production of about 28 ions per c.c. per sec.

Sometimes complications were introduced by the calcium chloride in the drying-tube next the testing vessel. If the vessel was exhausted and then filled quickly through the drying-tube, an abnormally large leak was often obtained directly afterwards, although great care was taken to prevent any dust entering the vessel with the stream of air. This leak gradually decayed to the value of the normal leak in about 8 minutes, the curve of decay being very nearly exponential and the time of half value being about a minute. This abnormal leak was, however, not always obtained; it seemed to depend on the condition of the calcium chloride, and whenever anything peculiar was observed in the ionization-current obtained directly after filling the can, a check experiment was performed as soon after as possible by taking another leak after a quick filling of the vessel.

The various insulations behaved fairly well during the experiments. The insulation leak was often tested. When it became serious enough to gradually slow down the motion of the spot of light when taking the normal air leak the insulation was attended to and put right. In taking the air leak and other leaks of about the same order I observed that the leaks for successive minutes often differed largely from each other, while leaks for longer periods, say five minutes, agreed very closely. From this it seems that small ionizations are rather irregular, the irregularities, however, smoothing out if the leaks are taken over sufficiently long periods. When the leak is large the values for successive minutes agree much more closely than when the leak is small.

Throughout the experiments air was never passed through the testing vessel. The method of renewing the air was always that of exhaustion and refilling through the lower of the two side tubes. The exhaustions were performed by means of a hand Fleuss pump. This pump exhausted down to within about 9 mms. of *vacuo*. Exhaustion took a very long time if a calcium chloride tube was inserted between the vessel and the pump, so that usually the vessel was exhausted without the intermediary of a drying-tube, and the drying-tube exhausted separately and then connected to the vessel.

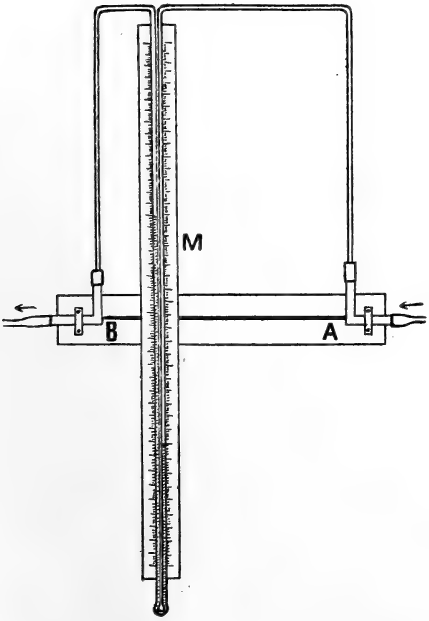
(2) *The Charcoal Tubes.*—Preliminary experiments were made with charcoal in glass combustion-tubes and iron tubes; but the glass tubes did not stand heating and the iron tubes took too long to get hot. Finally, porcelain tubes were tried. Three tubes were obtained about 50 cms. long and 1·6 cm. in internal diameter. The coconut charcoal was made by strongly heating fragments of coconut shells under sand in a fire-clay crucible. The fragments were then ground fine by means of a pestle and mortar. The central 12 inches of the tubes was filled with the charcoal, the column of charcoal being kept in position by wads of asbestos fibre. The ends of the tube were closed by indiarubber stoppers provided with glass tubes and indiarubber caps. Thirty-nine grams of charcoal were placed in each tube. The three tubes made were denoted by A, B, and C for purposes of identification. The furnace used was made of two 6-inch sections of a Fletcher's tube-furnace, and was supplied with twelve burners, and the tubes were always placed on the furnace so that the 12 inches of charcoal got to a bright red heat.

(3) *The Aspirators.*—Two aspirators were made up to collect the gases drawn through the heated charcoal. Each aspirator consisted of two large glass bottles of slightly larger volume than the testing vessel. When collecting the gas

I could run the water out of the collector down to a certain mark, and make sure that when I exhausted the testing vessel and connected the vessel with the collector all the gas collected would pass into the vessel. Tap-water could not be used in the aspirators as Cambridge tap-water gives off quite an appreciable quantity of radium emanation. Distilled water was therefore used. The aspirators were denoted by (*a*) and (*b*) for purposes of reference.

(4) *The Manometers for Measuring the Air-Current.*—During an experiment it is necessary to draw the air-current through the charcoal tubes at a steady rate for some time. A convenient form of manometer by which the air-current could be fairly accurately measured is shown in fig. 1.

Fig. 1.



It consists of a piece, AB, of 1 mm.-bore brass tubing 20 cms. long soldered into two right-angled pieces of brass tubing of much larger bore. The parts of the larger tubing in the straight line of AB were used to carry the air-current; the other parts were connected by indiarubber joints to a glass U-tube manometer containing water and affixed to a paper scale. Calibration of the gauge was effected by connecting it to a large aspirator containing water. This water was run out as a steady stream and collected in a litre flask. The time taken for 1 litre was taken two or three times and the reading of the gauge noted. This was repeated at various speeds, and a curve drawn showing the relation between the air-current in litres per minute and the gauge-reading.

Three such gauges, denoted by A, B, and C, were set up. B was used for some time, but for some reason or other proved untrustworthy. It was then rejected and A and C only were used. These were calibrated separately, and also occasionally compared by putting them in series. They were always in good agreement.

(5) *The Suction-pump.*—When performing the experiments air was drawn through the tubes by a filter-pump fitted to a tap connected with a large cistern in the tower of the laboratory. With the constant head of water thus provided the pump worked very steadily. To damp out small oscillations, which were sometimes produced by water accumulating in the bends of the composition-tube joining the gauges to the pump, a large bottle, which I have called a "collecting-bottle," was inserted next to the gauges. All three gauges connected with this bottle, as did also an extra tube which served as a by-pass. Screw clips were provided to all the tubes communicating with the collecting-bottle, so that the air-currents through these tubes could be readily altered and adjusted.

(6) *The Drying-Tubes.*—Charcoal does not absorb well the emanation from the air if the air is damp. Also on heating the charcoal any water given off condenses in the cold parts of the porcelain tube, and if great care is not taken the tubes crack when taken from the furnace. Calcium chloride was used as a dehydrating agent, the tubes used being about 40 cms. long and 1·5 cm. in diameter. Eve uses sulphuric acid, but I had started using calcium chloride, and continued to use it. It is more convenient to use, and has the advantage that one can see when it has been used sufficiently. The choice of a dehydrating agent is, however, an important one, as besides abstracting the water it might abstract the emanation as well. More on this point will be given below.

Method of conducting an Experiment.

(*a*) *Measurement of the Emanation in the Air.*—The air was drawn from outside by a glass tube passing through a hole in the window. It passed in succession through a glass tube filled with cotton-wool to free it from dust (this was fixed permanently on to the air-tube, it was not always required but was rarely disconnected), a tube filled with calcium chloride, a charcoal tube, a gauge, and to the pump. When the pump was started the stream of air began, and gradually increased up to a steady value which was adjusted, by clipping the indiarubber connecting tubes, to about half a litre per minute. The current was kept passing at this rate for a given period. Meanwhile the testing vessel was exhausted and filled with dry air several times and the air leak taken at intervals. The insulation leak was also tested and the sensitiveness of the electrometer measured. When the period for passing the air had elapsed the charcoal tube was taken and laid on the furnace. One end was connected with an auxiliary glass tube containing coconut charcoal (whose function was to purify the air drawn from outside from any emanation it might contain), the connecting tube between them being at first tightly clipped, and the other end was connected to an aspirator, say aspirator *a*. The two taps of the aspirator were opened and water allowed to run out. The stream quickly stopped as the other end of the charcoal tube was closed. The burners were then lighted and the tube heated to a red heat. When the temperature had sufficiently risen, the clip joining the two charcoal tubes was unscrewed and the aspirator then drew emanation-free air into the heated charcoal tube, and this sweeping out the emanation in the heated tube was collected in the aspirator. When sufficient gas had been collected in one aspirator the taps were turned and the aspirator removed. The other aspirator, aspirator *b*, was then placed in position and filled in the same way. Then the charcoal tube was allowed to cool. Nearly all the emanation was collected in the first aspirator. Sometimes there was some in the second, often there was none. The amounts collected were then tested. It is more convenient to test the gas collected in the second aspirator first. The steady value of the air leak in the testing vessel having been found, it was exhausted by the pump and the inlet-tube then clipped. The drying-tube attached to it was then exhausted and also clipped. This tube was then connected to the upper tap of the aspirator, and then all the taps being opened the water rose in the aspirator, driving the contained air and emanation into the testing vessel. The pressure in the testing vessel usually just got up to atmospheric pressure when all the gas collected had been passed in.

The leak was then taken. Mr. Eve states that he rarely took initial leaks, they being small; but he waited for three hours when the leak had increased to a maximum. This increase is due to the growth of the radioactive deposit (Radium A, B, and C) on the walls of the vessel. Sometimes I took initial leaks and also leaks three hours afterwards; but usually time could not be spared, and after taking the initial leak the air was pumped out before the emanation had time to deposit any active matter*. Usually the air leak was repeated again to test this point. The first aspirator-full was then passed into the vessel and the leak again read. From the two sets of readings the total leak due to the emanation given off by the charcoal tubes could be calculated by deducting the air leaks†. Now this emanation is not all due to the air. I found that when a charcoal tube is left to itself it gradually accumulates radium. The amount accumulated in different times I measured at odd intervals by heating, collecting, and testing as above. From the mean of these auxiliary measurements I calculated for each experiment the amount of emanation accumulated by the charcoal itself between the last heating and the present one. By subtraction the leak due to the emanation in the air passed through the tubes during the run was found.

If the emanation absorbed during an experiment was not measured till a day or two after absorption, the amount of the emanation when first absorbed was calculated from the decay curve of radium emanation (fig. 2).

(*b*) *Measurement of the Emanation from the Solution.*—The solution given me by Prof. Rutherford was placed in a bottle furnished with a stopper and delivery-tubes. Air was bubbled ‡ through the solution, thus removing the emanation. If the solution had been allowed to stand for some time the emanation would have been accumulated in the solution and the first volume of air drawn through would be very strongly radioactive. It is essential, therefore, to pass air through the solution for some time before beginning the

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* Soddy and Mackenzie (Phil. Mag. Aug. 1907) recommend that the leak be taken 8 minutes after filling the vessel with emanation. A temporary maximum occurs about that time, and the leak is comparatively constant for about 15 minutes. This was what I usually did, for my readings, though often commenced directly after filling the vessel—which itself took some time—lasted about 20 minutes.

† There will be a quantity of carbon dioxide in the gas collected in the aspirators. This, however, had no effect on the air leak. The point was tested many times.

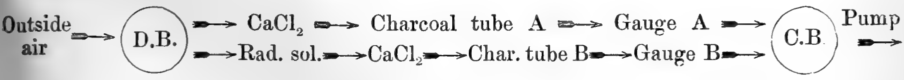
‡ Several experimenters have urged the boiling of the solution to get rid of all the emanation, but it seems to me that bubbling through the cold solution will put the solution in a steady state which is all that is required during the experiment. I tried boiling once, but a long condenser would be required to remove the excessive amount of water-vapour carried on by the air-current; and as bubbling seemed to me quite sufficient, I contented myself with it.

experiment proper. I usually ran an air-current through the solution for three or four hours, and hoped that the solution would have then got into a steady state. The solution was then connected up as follows:—

Outside air → Dust tube → Radium solution → Calcium chloride tube → Charcoal tube → Gauge → Pump.

Air was drawn through the solution for a known time and at the same rate as in the air experiment. The tube was then heated and the emanation collected in the two aspirators and the leaks due to it measured. The result gives the leak due to the sum of the emanation due to the known volume of air drawn through, and the emanation generated by the solution in the given time.

Since the amount of emanation in the air may be subject to considerable variation, it was thought well to carry out the two experiments at the same time, so that the emanation due to the air would be the same in both tubes. To do this the tube from the outside air was connected to a bottle which I shall call a "distributing" bottle, from which two tubes led, and the two tubes from the two gauges led, as before mentioned, into one bottle, a "collecting" bottle, from which one tube led to the pump thus:—



If the same volume of air goes along each path, then by subtraction we can get the value of

$$\frac{\text{emanation in a known volume of air}}{\text{emanation generated in the solution in a known time}}.$$

The method being a comparative one, gives true results only if all the emanation is absorbed, or if the amounts absorbed are the same fractions of the total amounts whatever be those total amounts. Experiments made to test this proportionality with solutions giving about the same amounts of emanation as those obtained in the experiments gave fairly satisfactory results.

CALCULATIONS.

The factors that are required—

(1) To correct for the decay of emanation if the emanation is not measured till some time after it is absorbed;

(2) To correct for the accumulation of emanation in the charcoal;

(3) To calculate the amount of emanation generated in a given time by the solution *;

are all obtained from the decay curve of radium emanation, and its inverse, the production curve.

Taking the time of half value of radium emanation to be 3·71 days, we have, using the nomenclature of Rutherford,

$$T = 3{\cdot}71 \times 24 \times 3600 \text{ seconds.}$$

Now if λ = the radioactive constant of the emanation,

$$\lambda T = \log_e 2 = {\cdot}693;$$

$$\therefore \quad \lambda = 2{\cdot}16 \times 10^{-6}.$$

The equation of the "decay" curve of radium emanation is

$$I_t = I_0 e^{-\lambda t},$$

where I_0 is the initial amount of emanation and I_t the amount in existence at time t.

If a radium solution is completely exhausted of its emanation at a time $t=0$ and then left to itself, the emanation will gradually accumulate, the equation of the "production" curve being

$$I_t' = I_0(1 - e^{-\lambda t}),$$

where I_t' is the amount in existence at time t, and I_0 the amount in existence after an infinite time.

Taking I_0 equal to 50, the numbers in Table I. have been calculated. They give the corresponding values of t and I_t, t and I_t', t in the tables being expressed for convenience' sake in days.

TABLE I.

t.	0.	½.	1.	2.	3.	4.	5.	6.	7.	∞.
I_t......	50	45	41	34	28	23	19	16	13	0
I_t'. ..	0	5	9	16	22	27	31	34	37	50

From this table the curves A B, C D of fig. 2 have been

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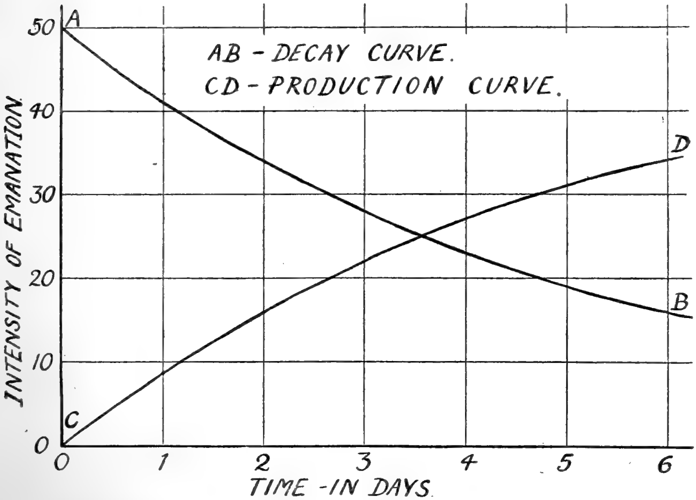
* Eve (Phil. Mag. Dec. 1907) neglected altogether the time element of his solution.

plotted. It will be noted that for all times the ordinates of the curves for the same value of t add up to a constant amount (*i. e.* $I_t + I_t' = I_0$).

Fig. 2.



If, for instance, the emanation is measured when it is one day old, its measured amount must be multiplied by $\frac{50}{41}$ or 1·22 in order to find what the amount would have been if it had been measured when collected. The factors for 2 and 3 days are 1·47 and 1·78 respectively.

Again, if a radium compound is cleared of all emanation and then left to itself for two days, the amount of emanation accumulated is only $\frac{16}{50}$ of the amount of emanation that would be *generated and in existence* were the radium left until it was in radioactive equilibrium with its emanation.

The "production" curve C D, drawn to the scale of fig. 2, will not give us accurate values of I_t' for small values of t. It must be expanded in its initial stages. The equation of the production curve may be written as

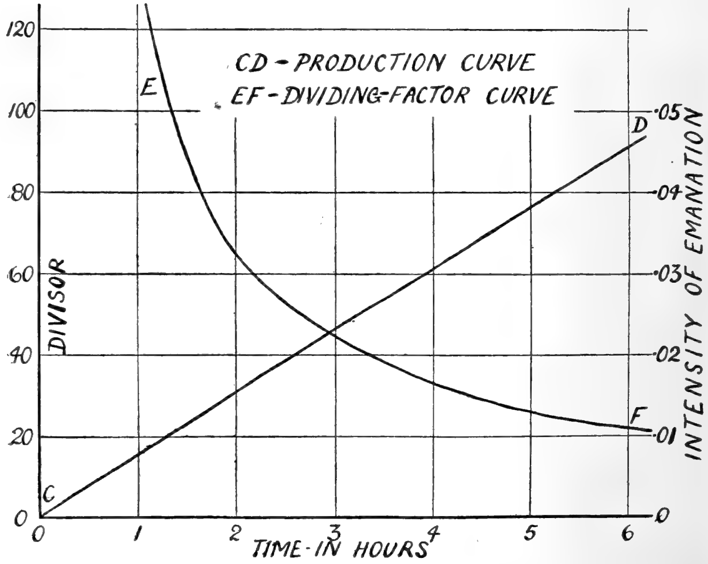
$$\frac{I_t'}{I_t} = 1 - e^{-\lambda t},$$

and the numbers in Table II. give values of $\frac{I_t'}{I_0}$, and its reciprocal, $\frac{I_0}{I_t'}$, for values of t from 1 to 7 hours.

TABLE II.

t in hours.	1.	2.	3.	4.	5.	6,	7.
$\frac{I_t'}{I_0}$ ……	·0077	·0154	·0231	·0306	·0381	·0456	·0530
$\frac{I_0}{I_t'}$ ……	135	65	45	33	26	22	19

Fig. 3.



From this table the curves C D, E F of fig. 3 have been plotted. I have called $\frac{I_0}{I_t'}$ the "dividing factor."

It will be noted from the curve C D (fig. 3) that the amount of emanation in existence increases very nearly proportional to the time when the time is small, but that there is a slight falling off due to the decay of the first portions produced.

We see from Table II. and fig. 3 that in 2 hours the amount of emanation that can be got from a solution is only $\frac{1}{65}$ the amount that could be got

(1) From a solution in radioactive equilibrium, could all the emanation present be removed at once; or
(2) From a solution were the removal carried on for an infinite time and the emanation given off collected in some absorbing agent.

As an example of the method by which the radium-content of the air is calculated, the mean values of the results of Table IV. may be taken. It is there shown that 70 litres of atmospheric air contain, on an average, an amount of emanation represented, say, by 0·3, while my solution containing $3{\cdot}14 \times 10^{-9}$ grm. of radium gives in 2 hours an amount of emanation represented on the same scale by 2·5. From these numbers it follows that 1 cubic metre of atmospheric air contains an amount of emanation that would be generated by

$$\frac{1000}{70} \times \frac{\cdot 3}{2{\cdot}5} \times 3{\cdot}14 \times 10^{-9} \text{ grm. of radium in 2 hours,}$$

i. e. an amount that would exist in radioactive equilibrium with

$$\frac{1000}{70} \times \frac{\cdot 3}{2{\cdot}5} \times \frac{3{\cdot}14 \times 10^{-9}}{65}, \text{ or } 80 \times 10^{-12} \text{ grm. of radium.}$$

Record of the Tests of the Amount of Radium Emanation accumulated in the Charcoal Tubes when left to themselves.

In Table III. are given, 1st the date of testing, 2nd the tube, 3rd the time the tube had been resting since the last testing, 4th the amount of emanation accumulated measured by the leak per minute it caused when passed into the testing vessel, 5th the amount of emanation accumulated per day. The amounts in this column are calculated from the amounts in the last column by means of the production curve of radium emanation (fig. 2).

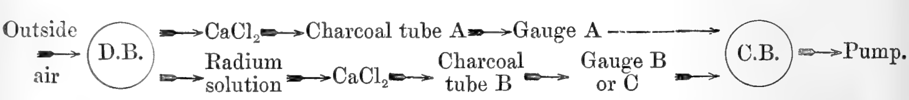
From this table I find that on the average the accumulations of A and B per day are ·19 and ·23 respectively. The results agree with the mean of the combined accumulations given in the last two rows of the table. C was so high that it was not used in the following experiments.

TABLE III.

Date of testing.	Charcoal Tube.	Period of Rest in days.	Amount accumulated: expressed in divs. per min.	Amount accumulated per day: expressed in divs. per min.
Wed. Jan. 5	A	26	1·1	·20
Mon. „ 20	B	31	2·0	·36
Thurs. Feb. 13	A	6	·8	·20
„ „ „	B	6	·75	·20
Tues. „ 18	C	25	2·6	·47
Wed. „ 19	A	5	·6	·18
„ „ „	B	5	·65	·19
Wed. „ 25	A	7	·55	·13
„ „ „	B	7	·90	·24
Thurs. Mar. 4	A	6	·67	·19
„ „ „	B	6	·5	·13
Tues. „ 10	A	4	·56	·19
„ „ „	B	4	·8	·26
„ Apr. 7	A+B	4	1·0	·33
Wed. May 6	A+B	27	3·2	·57

First Set of Experiments with the Charcoal Tubes.

During this set two tubes were connected in parallel as shown in the diagram below:—



So that the air absorbed in tube B should contain volume for volume the same amount of emanation as the air absorbed in tube A. Once or twice tubes A and B were interchanged in order to detect any differences in the absorbing powers of the charcoal, but none was found. Sometimes the run was made one day and the tubes heated the next; corrections in all cases were made for accumulation and decay. The results are indicated in Table IV. In the last column I have tabulated the relative amount of emanation absorbed from the solution per two hours' run. The amount is not quite constant, but very nearly so, if the run of Jan. 27 is omitted. The approximate constancy is a test of the accuracy of the method.

TABLE IV.—First Set of Charcoal Readings.

Date.	Weather and Barometer.	Speed of Air Current. Litres per minute.	Time of passing Air Current. P.M.	Volume of Air drawn through. Litres.	When tested.	Leak due to Emanation from the Air tube.	Accumulation in Air tube.	Leak due to Emanation from the absorbed Air.			Leak due to Emanation from Air and Solution tube.	Accumulation in Air and Solution tube.	Leak due to the Emanation from Air and the Solution in the given time.		Leak due to Emanation from Solution alone	
								When tested.	When collected.	When collected. Per 70 litres.			When tested.	When collected.	in the given time of the experiment.	in two hours.
JAN. Mon. 27	Dry; 757, falling.	·54, air. ·49, air & solution.	4–6 =120 min.	65, air. 60, air & solution.	Next day.	1·2	·2	1·0	1·2	1·3	6·1	·2	5·9	7·1	5·9	5·9
Fri. 31.	Dry; 758, rising.	”	2–3.30 =90 min.	49, air. 45, air & solution.	Same day.	·5	·2	·3	·3	·4	3·0	·2	2·8	2·8	2·5	3·3
FEB. Tues. 4.	Dry; 778, rising.	”	2.20–4.20 =120 min.	65, air. 60, air & solution.	Next day.	·48	·34	·14	·17	·2	2·5	·4	2·1	2·5	2·3	2·3
Thurs. 6.	Dry; 780, steady.	”	2.40–5.40 =180 min.	97, air. 88, air & solution.	Next day.	·72	·34	·38	·46	·4	4·1	·4	3·7	4·4	3·9	2·6
Fri. 14.	Dry; 769, falling.	”	2–3.45 =105 min.	52, air. 46, air & solution.	Same day.	·61	·2	·4	·4	·5	2·6	·2	2·4	2·4	2·0	2·3
Thurs. 27.	Wet; 753, falling.	·5, air. ·5, air & solution.	1.45–6.15 =270 min.	135, air. 135, air & solution.	Next day.	·54	·34	·2	·24	·1	4·8	·4	4·4	5·3	5·0	2·2
MAR. Fri. 6.	Damp; 743, steady.	·41, air. ·2, air & solution.	10.45–3.15 =270 min.	111, air. 55, air & solution.	Same day.	·75	·19	·56	·56	·3	7·0	·2	6·8	6·8	6·5	2·9
Wed. 11.	Fine; 760, rising.	·5, air. ·5, air & solution.	10.45–5.20 =395 min.	202, air. 199, air & solution.	Next day.	·77	·35	·42	·50	·2	5·5	·4	5·1	6·1	5·6	1·8
						Mean (omitting the first)......				·3	Mean (omitting the first)......					2·5

From the numbers in the last table the following results were calculated. The time factors of the radium solution were obtained from the curves of fig. 3.

TABLE V.

Date.	Weather and Barometer.	Amount of Radium required per cub. metre of Air to keep up the quantity of Emanation to the observed amount.
Jan. 27	Dry ; 757, falling.	150×10^{-12} grm.
,, 31	,, 758, falling.	85×10^{-12} ,,
Feb. 4	,, 771, rising.	50×10^{-12} ,,
,, 6	,, 780, steady.	85×10^{-12} ,,
,, 14	,, 769, falling.	160×10^{-12} ,,
,, 27	Wet ; 753, falling.	35×10^{-12} ,,
Mar. 6	Damp ; 743, steady.	75×10^{-12} ,,
,, 11	Fine ; 760, rising.	67×10^{-12} ,,
		Mean... 88×10^{-12} grm.

Some more measurements made in April and May agreed very nearly with these. The mean of the three results given by Eve in his paper (the mistake in his calculations makes all his results too large ; I have corrected them according to the rules stated above) is 26×10^{-12} gm. so that it would seem that there was much more emanation in the air of Cambridge than in the air of Montreal. Now Professor Thomson * found that Cambridge tap-water contained a large quantity of radium emanation, and therefore it is not surprising that the air of Cambridge should contain more than the normal amount of emanation.

Although the correlation is not very definite the results above seem to indicate that with a falling barometer the amount of emanation in the atmosphere increases, unless this fall is accompanied by wet weather. A rising barometer seems to give about the same amount of emanation as a steady barometer at high or low.

In this connexion it is interesting to note that Campbell and Wood † found that weather conditions were entirely without effect on the spontaneous ionizations of air in closed vessels.

Nearly all the runs given in the table above are short runs ($1\frac{1}{2}$ hrs. to $4\frac{1}{2}$ hrs.) taken in the afternoon. Later on, I made some long runs, during the night and day. For the night runs the air-current was started at about 6 or 8 o'clock in the evening, and left on till about 7 or 9 or 12 o'clock in the

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* Phil. Mag. Sept. 1902.

† Phil. Mag. Feb. 1907.

morning. For the day runs the air-current was started at about 6 or 9 in the morning and left on till about 5 or 7 in the evening. The average current was about ·5 litre per minute. The results are stated below:—

TABLE VI.

Date.	Night or Day.	Weather and Barometer.	Volume of Air drawn through, in litres.	Emanation expressed in leak in div. per min.	Emanation per 400 litres of air.
Apr. 7–8 ...	Night	Fine; 770, falling.	550	·8	·6
" 8–9 ...	"	Fine; 766, falling.	521	2·1	1·6
May 6–7 ...	"	Wet; 748, rising.	414	·9	·9
" 7–8 ...	"	Fine; 760, steady.	378	·4	·4
" 12 ...	Day	Wet to fine; 760, falling.	315	1·8	2·4
" 12–13 ...	Night	Fine; 758.	378	1·1	1·2

There is unfortunately only one day run amongst these, but its result, 2·4 per 400 litres, is considerably higher than the highest result for the night runs and more than twice as high as the average night run. Hence, from these results we should conclude that on the average there is more emanation in the air during the day than during the night.

Later on, however, I made two long runs, using sulphuric acid as the dehydrator with the following results:—

TABLE VII.

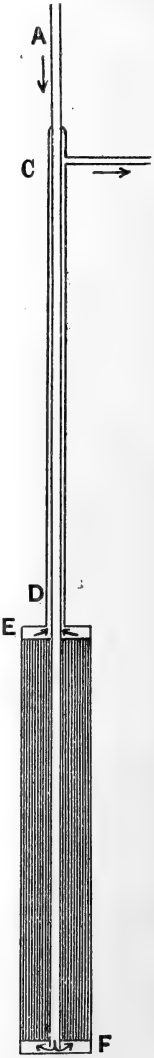
Date.	Run.	Weather and Barometer.	Volume of air drawn through.	Emanation in the given volume of air expressed in terms of the leak.	Emanation per 400 litres of air.
May 13–14...	Night	Fine; 755.	329 lit.	5 1	6·2
May 14	Day	Fine; 755.	302 "	4·6	6·1

So that in this case the amount of emanation was very nearly the same in the night as in the day following. The barometer was very steady all the time.

II. *The Condensation Method.*

Another method of measuring the emanation now suggested itself to me, viz. that of freezing or rather condensing the emanation out of the air by the help of liquid air. At normal pressures liquid air boils at about −182° C. Rutherford and Soddy[*] found that radium emanation condensed at a temperature of about −150° C. They also found that with a flow of 2 cc. per sec. through their tube (which meant a velocity along the tube of 50 cms. per sec.) there was no escape of emanation at −154° C. (they could read to $\frac{1}{1000}$ part). At −152° C. one-half per cent. came off and at −150° C, 50 per cent. came off. No doubt all would come off if given a time long enough. They concluded that the condensed emanation exerts a true vapour-pressure and commences to volatilise slowly 2° C. below its volatilising point.

Fig. 4.



From these results it seemed that if I could pass air through a long tube immersed in liquid air so that the air was a long time in the neighbourhood of metal surfaces at −182° C. I had a very good chance of condensing out all the emanation.

My first thought was to imitate Rutherford and Soddy and use a long spiral of fine-bored copper tubing. If air passed through a spiral of tubing of 1 mm. bore at the rate of half a litre per minute (my usual current), the velocity of the air would be 1000 cms. per second, and even if I used 500 cms. of such tube the air would take only half a second to pass through the spiral. This was not thought long enough. The next plan was to put a large number of fine tubes in parallel so that the apparatus could be made more compact, the magnitude of the current increased, and also the length of time during which the air was subjected to the action of the liquid air increased. The form finally adopted is shown in the figure (fig. 4). The apparatus is made of brass. Although brass is heavy and the apparatus therefore has a large capacity for heat, yet it was

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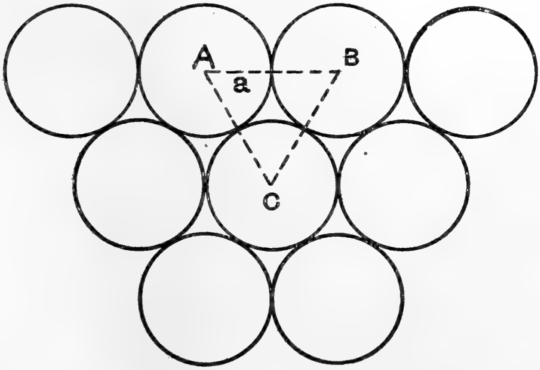
[*] Phil. Mag. May 1903.

thought that the good conducting qualities of the metal compared with those of glass would more than counterbalance the large capacity of heat and the consequent large consumption of liquid air. AB (fig. 4) is a straight thin brass tube about 42 cms. long and ·43 cm. in external diameter. It fits centrally through a thin tube CD, 20 cms. long and ·69 cm. in external diameter so that 5 cms. are outside at the higher end and 17 cms. at the lower end. CD supports a much wider brass tube EF 17 cms. long, 2·75 cms. in external diameter, and 2·62 cms. in internal diameter, and closed at both ends except where attached to CD. The space between AB and EF is packed tightly full with straight brass wires 16 cms. long and ·185 cm. in diameter. 154 such wires were got into the annular space. These wires leave spaces ·5 cm. deep at the top and bottom of EF so that AB can deliver air to the bottom of the apparatus; this air can pass up between the wires, collect at the top of EF, and pass out along CD and the side tube attached to the upper end of CD.

Calculations relating to the Condenser.

It is of interest now to calculate the approximate sum of the cross-sections of the tubular spaces thus formed. Fig. 5 represents a number of rods in close contact (I cannot conclude that my rods were packed so closely as is here shown but no doubt patches of them were).

Fig. 5.



Let the radius of cross-section of the wires = a cm.

Then area of the triangle ABC formed by joining three centres = $a^2 \sqrt{3}$ sq. cm.

The area of the three portions of the circle enclosed in this triangle = half the area of cross-section of a wire = $\pi a^2/2$.

$\therefore$ area of cross-section of one tube

$$= a^2(\sqrt{3}-\pi/2) = \cdot 161a^2.$$

$\therefore$ fraction of whole cross-section which is tubular

$$= \frac{\cdot 161}{1\cdot 732}.$$

Now area of cross-section of the annular space occupied by the tubes

$$= \frac{\pi}{4}\{2\cdot 62^2 - \cdot 43^2\} = 5\cdot 25 \text{ sq. cms.}$$

$\therefore$ Total cross-section of the tubes

$$= \frac{\cdot 161}{1\cdot 732} \times 5\cdot 25 = \cdot 48 \text{ sq. cm.}$$

To calculate the number of wires required on the assumption that they are as closely packed as possible we note that with each wire there is associated two tubes, and since total cross-section required per wire and two tubes $= 2a^2\sqrt{3}$ the number of wires

$$= \frac{5\cdot 25}{2 \times \left(\frac{\cdot 185}{2}\right)^2 \times 1\cdot 73} = 177.$$

As a matter of fact no more than 154 tubes could be placed inside so that the appproximate total cross-section of the tubes is greater than ·48 sq. cm. For the total cross-section of 154 wires

$$= 154 \times \frac{\pi}{4} \times (\cdot 185)^2$$

$$= 4\cdot 14 \text{ sq. cms.}$$

$\therefore$ total cross-section of the tubes

$$= 5\cdot 25 - 4\cdot 14 = 1\cdot 1 \text{ sq. cms.}$$

Taking, then, 1·0 sq. cms. as the total area of cross-section of the tubes and half a litre a minute or 8·3 c.c. per sec. as the usual rate of flow of air during the experiments the velocity of the air through the tubes is 8 cms. per sec., and since the length of the tubes of the condenser is 16 cms. the air spends two seconds in going through the tubes of the condenser, and to this may be added a little more, due to the stem of the condenser. So that the condenser has two seconds in which to reduce the temperature of the air from 15° C., say, to $-150°$ C. If we assume that the tubes are as closely packed as possible the greatest distance a particle of air could be from the cold metal $= \cdot 185/\sqrt{3}$ cm. or 1 mm. Of course if the packing is irregular there will be some tubes much larger than the others, and most of the air will go through these large tubes.

The mass of the condenser was 713 grms., of which, say 700 grms. fell to the temperature of liquid air. To cool it from ordinary temperature to the temperature of liquid air $700 \times \cdot 095 \times 200$ calories of heat must be abstracted. The latent heat of vaporisation of air is 55 calories per grm. Hence $\frac{700 \times \cdot 095 \times 200}{55}$ or 245 grms. of liquid air are used up in reducing it to the temperature of liquid air. The air passing through the condenser also gives out heat. The amount of liquid air boiled away by a stream of air flowing at the rate of $\frac{1}{2}$ litre per minute for two hours,

$$= \frac{60 \times 1 \cdot 3 \times \cdot 238 \times 200}{55} = 68 \text{ grms.}$$

It was also calculated that 130 grms. would be required to supply the heat conducted down the stem of the condenser in two hours. This gives a total of 450 grms. of liquid air required for a 2 hours' experiment. As a matter of fact I usually required $\frac{3}{4}$ litre for a 3 hours' experiment.

Method of conducting an Experiment.

The apparatus used was the same as before except, of course, that no charcoal tubes, furnace, or aspirators were required.

The stem of the condenser was covered with cotton-wool and supported by a clamp so that the condenser could be placed well into the interior of a cylindrical Dewar's tube about 4 cms. in internal diameter and 28 cms. deep internally.

In beginning an experiment the Dewar tube was about two-thirds filled with liquid air and the condenser gradually lowered into it. When lowered into position, which was as near the bottom of the tube as possible, more liquid air was poured in until the condenser was quite cold and the liquid air came to within 1 cm. of the top of the tube. The inlet tube, AB fig. 5, was then connected by a length of india-rubber tubing to the drying-tube (either a calcium chloride tube or a sulphuric acid bottle or a cold spiral (see below) which was connected to the dust tube and the open air. Since the gauges were calibrated with air at ordinary temperatures and the air leaving the condenser would be very cold and therefore less viscous, it was deemed necessary to pass this air through a long copper spiral so that it might attain a normal temperature before reaching the gauge. The outlet tube CD was therefore connected by a length of india-rubber tubing to such a spiral containing 230 cms. of tubing of one centimetre bore, the other end of the spiral being connected to one of the gauges.

The connexions being made, air was sucked through the condenser by the pump at the steady rate of half a litre per minute for a period usually of from 2 hours to 4 hours. In about 40–60 minutes the liquid air in the Dewar tube sank to just above the top of the condenser and required replenishment. Meanwhile the air in the testing-vessel was repeatedly exhausted and renewed and the steady value of the air leak determined. When the time of running the air-current was nearly up, the testing-vessel was exhausted and also its attached drying-tube. Clips on the tubes connecting to the condenser were then closed and the air-current stopped. The clip on the inlet tube AB still being closed, the outlet tube CD was put in open connexion with the drying-tube and the testing-vessel. The liquid air was now removed from the condenser and the condenser warmed by a Bunsen burner until its temperature rose above 0° C. The clip on AB was now opened and the air admitted slowly. It swept through the condenser and carried all the emanation therein to the testing-vessel. The leak in the vessel was now taken. Usually the vessel and its contents were left to stand for three hours in order to see how the leak varied with time. When this last leak was taken the vessel was twice exhausted and refilled and then allowed to stand till the next experiment.

Blank experiments were made to see whether warming the condenser or rushing the air through it gave any increased conductivity to the air, but the results were negative.

As the method of drying the air may be open to criticism (see Method I.) I tried various methods of drying.

Since 60 litres of air at 15° C. and of dew-point 10° C. contain only ·5 grm. of water it was thought that if the air were allowed to pass through the condenser undried it would not choke it. I therefore tried one experiment in which no drying-tube was used at all, but in half an hour the air-current began to decrease, and before the hour was up the condenser was quite choked and the experiment came to an end.

Another plan was to pass the air through a long spiral of composition tubing 500 cms. long immersed in a freezing-mixture of salt and ice (at $-18°$ C.), but even with this arrangement the condenser very nearly choked. A subsequent examination of the spiral showed that very little, if any, water had been condensed by it out of the current of air.

Still another plan was to use strong sulphuric acid as a dehydrator. Two bottles were three parts filled with acid (400 c.c. were used) and fitted with delivery-tubes so that air bubbled through a total length of about 20 cm. of acid. This worked quite satisfactorily. The results are given below. Just as in the case of the $CaCl_2$ tubes I never used a tube for the air that I had already used for the radium solution, so in this case any batch of acid used for the solution was put away and a fresh batch used for the next air reading.

It would have been better if two condensers had been used just as in Method I. two charcoal tubes were used. Simultaneous runs of air and air plus solution could then have been taken, but the large quantity of liquid air required precluded this. Only on one occasion (May 16) did I do two liquid air experiments on the same day.

The following tables contain the experimental results obtained with the condenser. None of the experiments made are omitted. Details of the weather, the height of the barometer, and the time of day of the experiment are inserted in order that any effect on the amount of emanation caused by the weather or time of day could be detected. The leaks are given in scale-divisions per minute. It will be noticed that the air leak is subject to considerable variations. These variations were sometimes caused by the proximity of radium (in sealed tubes) used by other experimenters.

TABLE VIII.

First Set of Results with the Condenser.
Drying Agent Calcium Chloride.

Date.	Weather and Barometer.	Source of Emanation.	Time of passing the Air Stream.	Volume of air passed.	Total immediate leak.	Air Leak.	Leak due to the Emanation	
							Immediately	3 hrs. afterwards.
March.			P.M.	litres.				
Mon. 23 ...	Fine; 762, steady.	Air.	3.8–5.45 157 m.	78	1·8	1·7	·1	·3
Tues. 24 ...	,, ,, ,,	Air +Sol.	3.45–5.45 120 m.	56	4·5	1·2	3·3	5·0
Wed. 25...	Wet; 763, rising.							
Thurs. 26 .	,, 765, steady.	Air.	3.11–5.45 184 m.	77	2·8	1·1	1·7	2·3
Sun. 29 ...	Rained.							
Mon. 30 ...	Windy, Fine; 760, falling.	Air.	2.47–5.32 165 m.	82	2·2	1·0	1·1	1·6
Tues. 31...	Windy; fine, 756, steady.	Air *.	2.32–5.32 180 m.	88	1·8	1·0	·8	...
April.								
Thurs. 2 .	Fine; 762, falling.	Air +Sol.*	2.41–5.14 153 m.	67	7·7	1·5	6·2	...
Fri. 3	Windy, hail, rain; 758, steady.	Air +Sol.*	2.39–5.11 153 m.	70	6·2	1·2	5·0	...
Sat. 4	Cold, hail; 760, rising.	Air.	9.30 A.M.–12.4 154 m.	77	4·0–1·9†	1·2	1·8–·7	·2†
Tues. 7 ...	Cloudless, windy; 773, steady.	Air.	12.43–5.11 268 m.	133	7·0–2·0†	1·4	5·6–·6	·3†
Wed. 8 ...	Cloudless; 769, falling.	Air +Sol.	1.11–5.11 240 m.	120	8·8	1·6	7·2	10·9
Thurs. 9...	Fine; 766, falling.	Air.	12.55–5.7 252 m.	109	1·9	1·7	·2	·3

* Denotes that charcoal experiments were made at the same time.

† These results are curious. The initial leak due to the emanation was high, as shown by the number first given. It rapidly decreased and remained approximately steady about 30 minutes afterwards at the last number given. Three hours after it was small. Evidently the main part of the initial leak was not due to radium emanation. The decay was not exponential, and I have not yet fathomed its cause. It could not be due to any thorium emanation condensed at the same time as the radium emanation was condensed, for this would have long since decayed to an indefinitely small quantity.

This set of readings was taken before the Easter Vacation. Summarising the above we get Table IX. in which are tabulated the leaks, due to the emanation (1) from 70 litres of air, and (2) from 70 litres of air and 2½ hours of the solution at the dates given.

TABLE IX.

Date.	Air, 70 litres.	Air + Solution. 70 litres and $2\frac{1}{2}$ hrs.
March 23	·1	......
„ 24	......	4·1
„ 26	1·5	......
„ 30	·9	......
„ 31	·6	......
April 2	......	6·2
„ 3	......	5·0
„ 4	·7†	......
„ 7	·3†	......
„ 8	......	4·5
„ 9	·2	......
Means	·7	5·0

† See footnote † p. 608.

The air results vary very much among themselves, much more can be accounted for by errors of experiment. This shows that there are large actual changes in the amount of emanation in the air. In taking the mean the anomalous results of April 4 and 7 were neglected.

The results of the air and solution also vary largely, but the agreement is better than in the case of the air alone.

Method II. as well as Method I. is comparative, and the calculations only hold provided that the same proportion of the amount of emanation sent through is condensed in each case.

Assuming that such is the case we have, therefore, that 70 litres of air contain an amount of emanation represented by ·7 and $2\frac{1}{2}$ hours of the solution and 70 litres of air give an amount represented on the same scale by 5·0. By subtraction we find that on the same scale $2\frac{1}{2}$ hours of the solution gives us an amount represented by 4·3.

We can now calculate the mean emanation content of the air, and we find that 1 cub. metre of the air contains the emanation (when in radioactive equilibrium) from

$$\frac{1000}{70} \times \frac{\cdot 7}{4\cdot 3} \times \frac{3\cdot 14 \times 10^{-9}}{51} \quad \text{or} \quad \underline{\underline{140 \times 10^{-12} \text{ grm. Radium.}}}$$

TABLE X.—*Second Set of Results with the Condenser. Drying Agent Calcium Chloride.*

Date.	Weather and Barometer.	Source of Emanation.	Time of passing the Air Stream.	Volume of air passed.	Total immediate Leak.	Air Leak.	Leak due to Emanation.	
							Immediately	3 hrs. afterwards.
April. Wed. 29...	Change to fine; 765, rising.	Air.	P.M. 1.37–5.3 206 m.	litres. 103	2·2–1·1	1·1	1·1–0†	0
Thurs. 30.	Wet; 768, steady.	Air +Sol.	2.32–5.2 150 m.	75	7·3	1·1	6·2	6 8
May. Fri. 1......	Wet; 767.	Air.	......	No drying-tube used.		Condenser choked.		
Mon. 4 ...	Dry, hot, heavy; 756, falling.	Air.	1.57–5.15 198 m.	99	1·6	1·0	·6	·7
Tues. 5 ...	Warm, showery; 751, falling.	Air.	1.9–5.5 236 m.	117	1·7	1·0	·7	·8
Wed. 6 ...	Wet; 748, steady.							
Thurs. 7	Fine; 759, steady.	Air *.	1.9–5.9 240 m.	85	1·6	1·0	·6	·8
Fri. 8 ...	Fine; 759, steady.	Air +Sol.	2–5 180 m.	90	5·9	1·1	4·8	6·8
Thurs. 14.	Showery; 753, steady.	Air +Sol.	12.45–4.45 240 m.	88	8·9	1·4	7·5	not taken.

* See footnote * p. 608.
† „ „ † p. 608.

Summarising Table X. in the same way as before we get Table XI.

TABLE XI.

Date.	Air, 75 litres.	Air 75 litres, and $2\frac{1}{2}$ hours of Solution.
April 30	...	6·2
May 4	·45	...
„ 5	·45	...
„ 7	·52	...
„ 8	...	4·8
„ 14	...	4·7
Means	·5	5·2

The air results agree better this time but are less than before. As in the former table there is a solitary high result for the air and solution together. Still there was only one reason why it should be omitted, namely, that during the three-hour wait it only increased in the ratio 1 to 1·1 whereas the most usual ratio was 1 to 1·4 or 1·5. From the mean results of this table the amount of radium necessary to supply one cub. m. with emanation would be

$$\frac{1000}{75}\times\frac{\cdot5}{4\cdot7}\times\frac{3\cdot14\times10^{-9}}{51}\quad\text{or}\quad\underline{90\times10^{-12}\text{ grm. of Radium.}}$$

In the case of the results with the condenser I have not been able to find any correlation between the amount of emanation in the air and the barometric and weather changes.

Third Set of Runs with the Condenser.

In this third set calcium chloride was not used as a dehydrator. In the first experiment the spiral of composition tubing immersed in ice and salt was used, in the others sulphuric acid was used as the dehydrator. The results vary much among themselves. The result obtained with the "compo" tube is very high, and I thought at first it must be due to emanation given off by the lead. Mr. N. R. Campbell informs me, however, that lead gives off no emanation. If the spiral had been used before in radioactive work it may have got contaminated. It, however, appeared quite new

Table XII.

Date.	Weather and Barometer.	Source of Emanation.	Time of passing the Air Stream.	Volume of Air passed.	Total immediate Leak.	Air Leak.	Leak due to Emanation.	
							Immediately	3 hrs. afterwards.
May.			P.M.	litres.				
Tues. 12 .	Fine; 759, falling.	Air.	1.49–4.13 144 m.	57	5·0	1·4	3·6	5·4
Wed. 13 .	Thundery; 756, falling.	Air.	1.1–3.57 176 m.	89	4·1	1·2	2·9	3·7
Fri. 15 ...	Wet; 755, rising.	Air +Sol.	12.57–4.57 240 m.	126	12·5	1·2	11·3	...
Sat. 16 ...	Fine; 768, rising.	Air.	2.45–5.15 150 m.	75	1·8	1·1	·7	...
Sat. 16 ...	Fine; 768, rising.	Air +Sol.	7.0–9.15 115 m.	67	5·7	1·0	4·7	...

and unused, but the workshop mechanic could not guarantee its virginity. Therefore, either (1) there was an excessive amount of emanation in the air that day, (2) lead does give off an emanation, or (3) the tube was contaminated with radium. I have not tested the last two points.

Expressing the results as before we get Table XIII.

TABLE XIII.

Date.	75 litres of Air.	75 litres Air and $2\frac{1}{2}$ hours of Solution.
May 12	4·7	...
„ 13	2·4	...
„ 15	...	7·1
„ 16	·7	5·2

Little can be done with the huge result of May 12. The result of May 13 is also very high, but if we assume that as the barometer remained fairly steady all the time the emanation in the air would remain the same over to May 15, we get, on subtracting 2·4 from 7·1, an amount 4·7 for $2\frac{1}{2}$ hours of the solution, a result which very nearly agrees with the former results. It will be noted that on May 14th the air and solution gave with calcium chloride an amount 4·7, which is much below 7·1, showing that if the supply was the same, either the chloride absorbed some emanation or the acid gave off some. To test this point the experiments of May 16 were done using fresh acid. On this date, owing to a plentiful supply of liquid air, I was able to do two experiments on the same day so that the amount of emanation in the air had scarcely time to change. The results were

75 litres of air give ·7 *.

$2\frac{1}{2}$ hours of the solution give 4·5.

These results are in agreement with those of the first two sets and show that the amount of radium required to supply the emanation per cub. m. of air

$$=\frac{1000}{75}\times\frac{\cdot 7}{4\cdot 5}\times\frac{3\cdot 14\times 10^{-9}}{51}\quad\text{or}\quad\underline{130\times 10^{-12}\text{ grm.}}$$

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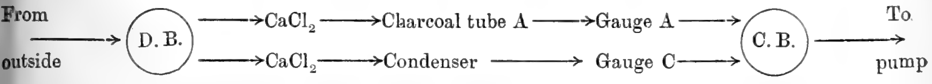
* From this result it is evident that the acid is not responsible for any emanation.

Comparison of the Efficiencies of the Charcoal and Condensation Methods.

It is quite possible that in neither method is the whole of the emanation taken out of the air; it is, however, hoped with each method the same fraction of the emanation in the air and the emanation from the solution will be absorbed so that the comparisons made are correct. To test the relative values of these fractions I did two experiments in which the charcoal tube and the condenser were put in parallel thus:—



The results reduced to the same volume of air are shown in Table XIV.

TABLE XIV.

Date.	Leak from emanation absorbed by Charcoal Tube from 70 litres of air.	Leak from emanation abstracted by Condenser from 70 litres of air.
March 31	·29	·62
May 7	·34	·66

so that

$$\frac{\text{amount absorbed from the air by charcoal}}{\text{amount abstracted from the air by condenser}} = \frac{\cdot 31}{\cdot 64} = \frac{1}{2} \text{ roughly.}$$

Now dealing with the amount of emanation given off in the solution in two hours we get (See Tables IV., IX., XI.)

$$\frac{\text{amount absorbed by charcoal}}{\text{amount abstracted by condenser}} = \frac{2\cdot 5}{3\cdot 6} = \frac{1\cdot 4}{2} \text{ roughly,}$$

so that in each case the condenser takes out about twice as much as the charcoal, the charcoal, however, becoming more efficient as the amount of emanation in the air-current increases. Both methods, therefore, give about the same result for the amount of emanation in the air, but the method of the condenser is quicker and more accurate than the charcoal method. The chief disadvantages of the charcoal method are the accumulation of emanation by the charcoal and the tediousness of the heating and collecting processes. On the other hand, the condenser method consumes a large quantity of liquid air and could only be used in laboratories where there is a good supply of this valuable commodity.

How much of the Natural Ionization of the Atmosphere is due to the Radium Emanation present?

Rutherford* states that the total number of α-particles projected per second by one gram of radium and its disintegration products in radioactive equilibrium is $2{\cdot}5\times10^{11}$. Radium, radium emanation, radium, A and radium C are equally responsible for this output of α-particles, hence it follows that the amounts of emanation, radium A, and radium C in radioactive equilibrium with one gram of radium project $1{\cdot}9\times10^{11}$ α-particles per sec.

It is now necessary to find the number of ions produced in a gas by these α-particles. An α-particle from radium itself produces 86000 ions in a gas before it is absorbed†. On the assumption ‡ that the number of ions produced by an α-particle from any product is proportional to the energy lost by that particle before it reaches its critical velocity § it follows that α-particles from radium emanation, radium A, and radium C produce 106,000, 110,000, and 172,000 ions respectively before they are absorbed, or an average of 130,000.

In comparison with the ionization produced by the α particles, the ionization produced by the β particles and γ rays from the three products considered may be neglected.

The number of ions produced per sec. per cub. metre of air by the emanation, radium A, and radium C in radioactive equilibrium with 100×10^{-12} grm. of radium is therefore

$$(100\times10^{-12})\times(1{\cdot}9\times10^{11})\times(1{\cdot}3\times10^{5})\text{ or }2{\cdot}5\times10^{6},$$

or about three per c.c. per sec.

The number of ions actually produced in the air per c.c. per sec. is subject to great variation. Rutherford ‖ states the number in the open air to be 30; Schuster ¶ found it to

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* Rutherford, 'Radioactivity,' 2nd edition, p. 155.

† *Ibid.* p. 433.

‡ *Ibid.* p. 549.

§ *Ibid.* p. 547; and Phil. Mag. Jan. 1907.

‖ Rutherford, 'Radioactivity,' 2nd edition, p. 526.

¶ Schuster, Proc. Manchester Phil. Soc. 1904.

lie between 12 and 38 near Manchester; Eve [*] calculated values between 1 and 5 for the air over the Atlantic Ocean.

Eve [†] concluded that the radium emanation in the atmosphere near the earth fully accounted for the rate of production of ions observed in it, but the results above show that although the proportion of the natural ionization of the air due to the radium emanation and its products is rather uncertain, it does not seem likely that the radium emanation and its products are responsible for anything like all the natural ionization.

Summary.

The amount of radium emanation in the atmosphere near the earth's surface at Cambridge has been measured by two methods :—

(1) Absorption by charcoal,
(2) Condensation by liquid air,

and the amounts compared with those given off by a radium solution of known strength. The two methods give results fairly close agreement. They show that the amount of emanation in a cubic metre of air is subjected to considerable variation, and is, on the average, equal to that amount which would be in radioactive equilibrium with about 100×10^{-12} grm. of radium. No very definite correlation could be established between the changes in the amount of emanation in the atmosphere and changes in the weather and barometer during the period through which the experiments were performed. I intend to attack this part of the problem again.

The above quantity of radium emanation, together with its disintegration products, would produce about 3 ions per c.c. per sec. As the number of ions actually produced per c.c. per sec. is about ten times this, it follows that only a small proportion of the natural ionization of the air is due to the presence of the radium emanation and its products.

In conclusion, I thank Professor J. J. Thomson for permission to carry out this research in the Cavendish Laboratory and for many helpful suggestions.

May 21, 1908.

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[*] Eve, Phil. Mag. Feb. 1907.

[†] Eve, Phil. Mag. July, 1905.

L. *On Periodic Nongenerating Force of High Frequency.* *By* ANDREW STEPHENSON *.

1. THE influence of periodic nongenerating force of high frequency has been investigated in the two cases when the force is simple oscillatory † and impulsive ‡ respectively. We now take up the general problem of determining the effective spring of a system about a position of equilibrium when acted on by any rapid periodic disturbance of the above type.

In the first place we deal with the case in which the disturbance-time graph has an axis of symmetry: the spring is then made up of a series of simple elements which are in zero phase simultaneously. The equation of motion under such disturbance is

$$\ddot{x}+(\lambda+2n^2\sum_1^\infty \alpha_r\cos rnt)\,x=0,$$

where n is the frequency of the force per 2π units of time. The complete solution is given by

$$x=\sum_{-\infty}^{\infty}\mathrm{A}_r\sin\{(c-rn)\,t+\epsilon\},$$

where ϵ is arbitrary, and

$$\mathrm{A}_r\{\lambda-(c-rn)^2\}+n^2\sum_{s=1}^{s=\infty}\alpha_s(\mathrm{A}_{r-s}+\mathrm{A}_{r+s})=0. \quad . \quad (r)$$

We limit our enquiry to the case when the α's are small, and the applied frequency so large that λ is negligible compared with n^2. Under these conditions it will be observed that a sound approximation is given by

$$\mathrm{A}_r=\mathrm{A}_{-r}=\frac{\alpha_r}{r^2}\mathrm{A}_0,$$

when products of the α's are neglected. Thus A_0 is large compared with $\sum_1^\infty(\mathrm{A}_r+\mathrm{A}_{-r})$, and the mean motion is therefore approximately simple oscillatory

$$x=\mathrm{A}_0\sin(ct+\epsilon).$$

On substituting for the A's in (0) we find

$$c^2=\lambda+2n^2\sum_1^\infty\left(\frac{\alpha_s}{s}\right)^2,$$

an equation determining the effective spring of the motion.

For any given disturbance the coefficients α can be found

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* Communicated by the Author.

† "On Induced Stability," Phil. Mag. February 1908.

‡ "On a New Type of Dynamical Stability," Manchester Memoirs, vol. lii. 1908, no. 8.

by Fourier's theorem, and hence c obtained; but there is a much simpler method of procedure applicable alike to general and numerical cases.

If Λ denotes the variable part of the spring about the mean value, λ, then

$$\int_0 \Lambda\, dt = 2n^2 \sum_1^\infty \int_0 \alpha_r \cos rnt\, dt$$

$$= 2n \sum_1^\infty \frac{\alpha_r}{r} \sin rnt$$

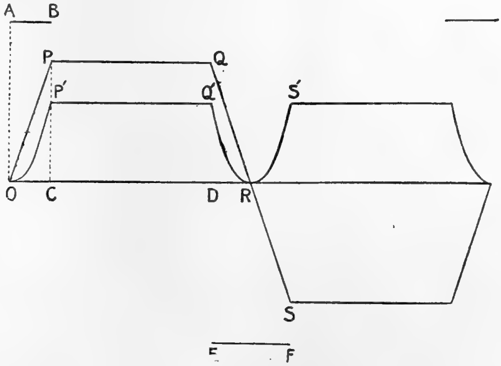
Hence
$$\left\{\int_0 \Lambda\, dt\right\}^2 = 2n^2 \sum_1^\infty \left(\frac{\alpha_r}{r}\right)^2 + 4n^2 \sum_1^\infty \gamma_r \cos rnt.$$

Thus $2n^2 \sum_1^\infty \left(\frac{a_r}{r}\right)^2$ is the mean value of the square of the time integral, from $t=0$, of the spring variation Λ.

If, therefore, the spring of a system is an even function of the time, of high frequency, and if the ratio of the amplitude of each elementary variation to the square of the frequency is small, then the mean motion is the same as if the spring were constant and equal to the mean spring λ, together with the mean value of the square of the time integral of spring variation about λ, the range of integration being a period so chosen that the values of the spring at equal intervals from its limits are equal.

2. As an illustration let us take the extreme case of impulsive disturbance which has already been examined by a different method *.

If the variation of spring is made up of equal and opposite constant changes acting alternately for equal times and following at equal intervals, its graph over a period is



ABCDEF . . . as shown in the diagram, the period being chosen in accordance with the preceding rule.

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* In the latter of the papers referred to above.

The graphs of the required integral and its square are OPQRS ... and OP′Q′RS′ ... respectively; CP=OA . OC, and CP′= CP². The limiting case of impulsive disturbance is reached by keeping OA . OC constant, $=\frac{1}{2}\mu$, say, and continually diminishing OC towards zero. The mean value of the squared integral is then $CP'=\frac{1}{4}\mu^2$; and therefore

$$c^2=\lambda+\tfrac{1}{4}\mu^2.$$

Thus a spring disturbance made up of equal and opposite impulses of magnitude μ, following at equal intervals, increases the effective spring by $\mu^2/4$, provided the frequency of the disturbance is large compared with that of the system.

If λ is zero we have $c=\mu/2$. This case is realised mechanically by pivoting a body so that it is free to rotate horizontally and driving the pivot to and fro in a small horizontal path with constant speed, V say. The amplitude of the imposed motion being small, the action at the pivot is confined to the impulsive forces at the ends of the path. Let h be the distance of the mass centre from the pivot, and k the radius of gyration about the vertical axis through the mass centre. If the angular displacement from the position of relative equilibrium is θ when the pivot is at the remote end of the path, and if ω and ω_1 are the angular velocities before and after the reversing impulse, then since the angular momentum about the pivot is unchanged by the action,

$$(k^2+h^2)\omega_1-\mathrm{V}h\theta=(k^2+h^2)\omega+\mathrm{V}h\theta,$$

i. e.
$$\omega_1-\omega+\frac{2\mathrm{V}h}{k^2+h^2}\theta=0.$$

Simil~~arly,~~ if θ_1 is the angular displacement on reaching the other end, and ω_2 the angular velocity after the impulse there,

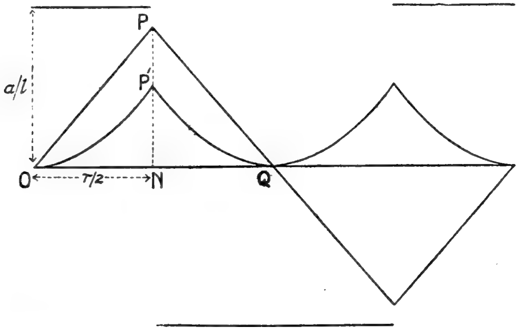
$$\omega_2-\omega_1-\frac{2\mathrm{V}h}{k^2+h^2}\theta_1=0.$$

Thus the spring is made up of equal and opposite impulses of magnitude $2\mathrm{V}h/(k^2+h^2)$ following at equal intervals, and therefore by the preceding the mean motion is a simple oscillation

$$\theta=\alpha\sin\left(\frac{\mathrm{V}h}{k^2+h^2}t+\epsilon\right).$$

If a is the length of the pivot path $c/n=\mu/2n=ah/\pi(k^2+h^2)$, which is small, and the conditions necessary for the approximation are therefore satisfied.

3. As a second example we shall determine the period of a pendulum the point of suspension of which is moved to and fro vertically in a small period 2τ, with constant acceleration a in one half of the path and equal and opposite acceleration in the other. Let l be the length of the simple equivalent pendulum ; then the spring is $(g+a)/l$ and $(g-a)/l$ alternately for equal intervals τ. The spring variation about the mean, the required time integral, and its square, are shown graphically :—



The graph of the squared integral is made up of parabolic arcs OP′, P′Q, . . .

Now

$$NP' = NP^2 = \left(\frac{a\tau}{2l}\right)^2.$$

Hence the mean height of OP′Q is $\frac{1}{12}\left(\frac{a\tau}{l}\right)^2$; therefore

$$c^2 = \frac{1}{l}\left\{g + \frac{1}{12}\frac{(a\tau)^2}{l}\right\}$$

and the period of the pendulum is

$$2\pi\sqrt{l\Big/\left\{g + \frac{1}{12}\frac{(a\tau)^2}{l}\right\}}.$$

It must be remembered that τ is small compared with $\sqrt{l/g}$, but $a\tau$ may be comparable with $\sqrt{lg}$.

4. In the investigation of § 1 the problem is limited to the case when the disturbance is made up of a series of simple elements which are all in zero phase at the same instant. Removing this restriction, we now examine the motion when the spring has any rapid periodic variation $2f(t)$ about its mean value λ.

$2f(t)$ can be split up into the even function $f(t)+f(-t)$, and the odd function $f(t)-f(-t)$; and these are expressible in cosine and sine series respectively. Hence the equation of motion is

$$\ddot{x}+\{\lambda+2n^2\sum_{1}^{\infty}(\alpha_r\cos rnt+\beta_r\sin rnt)\}x=0,$$

where n is the frequency of variation per 2π units of time. The solution is

$$x=\sum_{-\infty}^{\infty}\{A_r\sin(c-rn)t+B_r\cos(c-rn)t\},$$

where

$$\left.\begin{aligned}A_r\{\lambda-(c-rn)^2\}+n^2\sum_{s=1}^{s=\infty}\{\alpha_s(A_{r-s}+A_{r+s})-\beta_s(B_{r-s}-B_{r+s})\}=0\\ B_r\{\lambda-(c-rn)^2\}+n^2\sum_{s=1}^{s=\infty}\{\alpha_s(B_{r-s}+B_{r+s})+\beta_s(A_{r-s}-A_{r+s})\}=0\end{aligned}\right\}. \quad (r)'$$

These equations determine the A's and B's in terms of A_0 and B_0, and the eliminant gives c. Under the same conditions as before

$$A_r=\frac{1}{r^2}(\alpha_rA_0-\beta_rB_0),$$

$$A_{-r}=\frac{1}{r^2}(\alpha_rA_0+\beta_rB_0),$$

$$B_r=\frac{1}{r^2}(\alpha_rB_0+\beta_rA_0),$$

$$B_{-r}=\frac{1}{r^2}(\alpha_rB_0-\beta_rA_0),$$

when terms above the first degree in the α's and β's are neglected.

Hence

$$A_r+A_{-r}=2\frac{\alpha_r}{r^2}A_0,$$

$$B_r-B_{-r}=2\frac{\beta_r}{r^2}A_0,$$

$$A_r-A_{-r}=-2\frac{\beta_r}{r^2}B_0,$$

$$B_r+B_{-r}=2\frac{\alpha_r}{r^2}B_0.$$

Each of the equations $(0)'$ therefore gives

$$\lambda - c^2 + 2n^2 \sum_1^\infty \frac{\alpha_s^2 + \beta_s^2}{s^2} = 0,$$

i. e.
$$c^2 = \lambda + 2n^2 \sum_1^\infty \left(\frac{\alpha_s}{s}\right)^2 + 2n^2 \sum_1^\infty \left(\frac{\beta_s}{s}\right)^2.$$

Now
$$\int_0 \{f(t) + f(-t)\} dt = 2n^2 \sum_1^\infty \int_0 \alpha_r \cos rnt \, dt$$
$$= 2n \sum_1^\infty \frac{\alpha_r}{r} \sin rnt,$$

so that $2n^2 \sum_1^\infty \left(\frac{\alpha}{r}\right)^2$ is the mean value of the function $\left[\int_0 \{f(t) + f(-t)\} dt\right]^2$.

Again,
$$\int_0 \{f(t) - f(-t)\} dt = 2n^2 \sum_1^\infty \int_0 \beta_r \sin rnt \, dt$$
$$= 2n \sum_1^\infty \frac{\beta_r}{r} (1 - \cos rnt).$$

Therefore if M denotes the mean value of the integral over a period

$$2n \sum_1^\infty \frac{\beta_r}{r} \cos rnt = \mathrm{M} - \int_0 \{f(t) - f(-t)\} dt;$$

whence it follows that $2n^2 \sum_1^\infty \left(\frac{\beta_r}{r}\right)^2$ is the mean value of $\left[\mathrm{M} - \int_0 \{f(t) - f(-t)\} dt\right]^2$.

Thus if the spring of an oscillation consists of any periodic variation $2f(t)$ about a mean value, λ, which is small in comparison with n^2, the square of the variation frequency, and if, furthermore, the ratio $f(t)/n^2$ is always small, then the resulting mean motion is simple oscillatory of spring equal to λ together with the sum of the mean values of the periodic functions

$$\left[\int_0 \{f(t) + f(-t)\} dt\right]^2$$

and
$$\left[\mathrm{M} - \int_0 \{f(t) - f(-t)\} dt\right]^2,$$

where M is the mean value of $\int_0 \{f(t) - f(-t)\} dt$.

Manchester,
April, 1908.

LI. *On the Amount of Radium Emanation in the Atmosphere near the Earth's Surface.* *By* A. S. Eve, *D.Sc., Associate Professor of Mathematics, McGill University, Montreal*[*].

IN a previous paper published in this Magazine (December 1907) a preliminary account was given of determinations of the amount of radium emanation present in the atmosphere. In the present communication the results are given of experiments, continued at intervals throughout a year, which not only determine the amount with greater accuracy, but also throw some light on the effect of meteorological conditions in causing variations in that amount.

In order to save reference a brief summary of the previous paper is here given. The experiments were made at Montreal, in the Chemistry Building of McGill University, in a room about fifty feet above the ground. The air, drawn from outside through cotton-wool, was passed through three glass tubes containing charcoal prepared from the shells of coconuts. The air-current was continued for 2·7 days, at a speed of 6·7 cm.^{3}/sec., so that 1·56 m.^{3} of air passed through the tubes, two of which were in parallel[†] and the third in series with them. The tubes were then successively heated over two Bunsen flames, so that the gases absorbed by the charcoal were expelled, and these were collected over water and introduced into a silvered glass electroscope, which had previously been partially exhausted by a filter pump. The movements of the leaf of the electroscope were measured in the usual way with a microscope.

A solution of radium bromide, containing $1·57 \times 10^{-9}$ gram of pure radium, taken from a standard solution prepared by Boltwood[‡], Levin, and the writer, was then introduced into a flask. Air was bubbled through this solution, dried by passing through two flasks of concentrated sulphuric acid, and passed at the same rate for the same time and through the same charcoal as before. The tubes were heated, and the freed gases were collected and tested for radium emanation. It was found that, at the above-named speed, about twenty per cent. of the emanation given off by the solution was in this manner introduced into the electroscope. This percentage was found to be a function of the speed of the air-current, but within wide limits it appeared to be inde-

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[*] Communicated by the Author.

[†] It is better not to place tubes in parallel as the resistances to the air-current are often unequal and inconstant.

[‡] American Journal of Science, vol. xxii. July 1906.

pendent of the total strength of the solution employed, ranging from $1{\cdot}57 \times 10^{-7}$ to 10^{-10} gram of radium.

Thus the emanation from 1·56 m.^{3} of air gave an electroscope reading of 0·125 division a minute, and that from $1{\cdot}57 \times 10^{-9}$ grm. of radium gave 0·98. Hence it was reasoned that one cubic metre of air contained the emanation which would be in equilibrium with $\frac{0{\cdot}125}{1{\cdot}56} \times \frac{1{\cdot}57 \times 10^{-9}}{0{\cdot}98}$ or 127×10^{-12} gram of radium.

The quantities of charcoal employed were varied and experiments were made at intervals during several weeks. The lowest value found was stated to be 24×10^{-12}, and the highest 127×10^{-12}, with a probable average value of 80×10^{-12} gram.

There is, however, a somewhat subtle error in the above method of reasoning. If the speed of the air-current through the tubes is varied, the percentage amount of emanation absorbed by the charcoal is a function of the speed. The exact relations between these quantities have not, however, as yet been determined in the case of radium emanation. When air is drawn for a given time from the atmosphere through the tubes, it is clear that, on varying the speed, the greater the amount of air, the greater is the amount of emanation passing to the charcoal. But when using the standard solution of radium, the amount of emanation passing therefrom to the charcoal *in a given time* is entirely independent of the speed of the air-current, although the percentage amount absorbed is dependent on the speed in both cases. It will be seen then that the method of calculation given above is not quite correct, and it should be replaced by the following :—

I. Let 1 grm. of radium produce m grms. of emanation per second, and let M gms. of emanation be in equilibrium with 1 grm. of radium, so that

$$M = \int_0^\infty m e^{-\lambda t}\, dt = \frac{m}{\lambda}.$$

II. Let the amount of radium in the standard solution be R′, and suppose that initially any accumulation of emanation has been removed by boiling or by an air-current. The amount of emanation given off is $m\mathrm{R}'$ grm. per second, so that if at the end of the experiment, after absorption, heating, and collection, Y′ is the maximum electroscope reading, in divisions per minute, due to the emanation from the solution, we have

$$Y' = \int_0^T km\mathrm{R}'\, e^{-\lambda t}\, dt = km\mathrm{R}' \frac{1-e^{-\lambda T}}{\lambda}. \quad . \quad . \quad (1)$$

Here T is the time during which the air-current passes through the charcoal, and k is a constant depending on the electroscope calibration and on the percentage absorption of the charcoal.

III. In the case of air drawn from outside through the charcoal, let X equal the average number of grams of emanation present in one cubic metre of the atmosphere during the experiment, and let v be the volume, in cubic metres, of air passing to the charcoal every second. If Y is the maximum reading of the electroscope in divisions per minute, after collection, heating, and introduction in the electroscope, we find

$$\mathrm{Y}=\int_0^{\mathrm{T}} kv\mathrm{X}\, e^{-\lambda t}\, dt$$

$$=kv\mathrm{X}\frac{1-e^{-\lambda\mathrm{T}}}{\lambda}=k\mathrm{VX}\left(\frac{1-e^{-\lambda\mathrm{T}}}{\lambda\mathrm{T}}\right), \quad . \quad . \quad . \quad (2)$$

where k is the same constant as before, and $v\mathrm{T}=\mathrm{V}$ is the total number of cubic metres of air passing to the charcoal in time T.

But $\mathrm{X}=\mathrm{RM}=\mathrm{R}\frac{m}{\lambda}$, *where* R *is the amount of pure radium which would be in equilibrium with the emanation actually present in each cubic metre of the atmosphere at the time and place of the experiment.*

So that

$$\mathrm{Y}=k\mathrm{V}\frac{\mathrm{R}m}{\lambda\mathrm{T}}\,\frac{1-e^{-\lambda\mathrm{T}}}{\lambda}.$$

Comparing (1) and (2)

$$\mathrm{Y}'/\mathrm{Y}=\mathrm{R}'\lambda\mathrm{T}/\mathrm{RV},$$

and finally we have

$$\mathrm{R}=\mathrm{R}'\frac{\mathrm{Y}}{\mathrm{Y}'}\,\frac{\lambda\mathrm{T}}{\mathrm{V}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This formula will first be applied to the experiments given in the previously published paper (Dec. 1907).

Case 1.—Eight cubic metres of air were passed in 3·7 days through three iron tubes in parallel, each containing 220 grams of coconut charcoal. From the three tubes 15 litres of gas were driven off by heat, collected and then passed very slowly through three small glass tubes in series, each containing 7 grams of charcoal. In turn these were heated, and the gases driven off were collected over water and inserted in the electroscope.

A standard solution, containing 10^{-9} grm. of radium, was then placed in a flask, the accumulated emanation was removed, and air was passed through the solution to the three iron tubes containing charcoal, and the experiment was in all other respects repeated as before.

Then $$R' = 10^{-9} \text{ grm.}$$
$$Y = 0{\cdot}40, \quad Y' = 1{\cdot}45 \text{ D}/m.$$
$$V = 8 \text{ m}^3.$$
$$T = 3{\cdot}7 \text{ days} = 3{\cdot}19 \times 10^5 \text{ secs.}$$
$$\lambda = 2{\cdot}16 \times 10^{-6} \text{ and } \lambda T = 0{\cdot}69.$$

and hence $$R = 10^{-9} . \frac{0{\cdot}40}{1{\cdot}45} . \frac{0{\cdot}69}{8} = 23{\cdot}9 \times 10^{-12}.$$

This replaces the value 35×10^{-12} given in the previous paper.

Case 2.—The mean of seven observations, made in July and August 1907 gave $Y = 0{\cdot}112$, $Y' = 0{\cdot}98$ D/m, $R' = 1{\cdot}57 \times 10^{-9}$ gm., $V = 1{\cdot}56$ m^3, $T = 2{\cdot}7$ days $= 2{\cdot}32 \times 10^5$ secs.

Hence $R = 57{\cdot}4 \times 10^{-12}$, in place of 127×10^{-12} grm. as given in the previous paper.

Case 3.—A typical example is given for a result subsequent to 11th Nov. 1907, namely, that of 26th Dec. 1907.

$$R' = 1{\cdot}57 \times 10^{-9} \text{ grm.}$$
$$Y = 0{\cdot}39, \quad Y' = 2{\cdot}70 \text{ D}/m.$$
$$V = 1{\cdot}35 \text{ m}^3.$$
$$T = 2{\cdot}32 \times 10^5 \text{ secs.}$$
$$\lambda T = 0{\cdot}50.$$

Hence $R = 84{\cdot}2 \times 10^{-12}$ grm. In every case the value of Y' is given after deducting that due to the emanation in the air passing to the charcoal.

It is unnecessary to give further examples of the method of calculation.

The experiments were continued for almost a year in order to ascertain the relation existing between the amount of emanation in the air and the meteorological conditions existing during the time of the experiment. As the air was passed through the charcoal for a little more than two and a half days, it is clear that the amount of emanation measured is not dependent on merely local conditions. The radium emanation decays to half value in about 3·8 days. With a wind velocity of 20 miles an hour, the emanation collected at the end of an experiment may have travelled 1300 miles since the experiment began; and some of the emanation may have left the radium in the ground, or sea, any time during about a month previous, although the greater proportion must have been of much more recent origin. It is therefore possible to connect only the most strongly marked differences, in excess or defect, of the amount of emanation present, with very clearly defined weather conditions. Moreover, the amount of emanation collected is so small that the effect even in a good electroscope is less than the natural leak, so that too much importance must not be attached to any one reading.

The results obtained are given in the Table which follows (pp. 628–9) and they may be divided into two series, separated by a double line. For, on the 12th November, 1907, there was an abrupt breakdown in the electroscope due to a thin deposit of black dust on the sulphur bead insulation, possibly due to smoke or very fine dust from the charcoal. The whole apparatus was reconstructed of fresh material after this accident, and the natural leak and calibration of the electroscope were therefore altered. The two series give results in satisfactory agreement. In the second column of the table is given the sum of the three readings obtained after testing the emanation expelled by heat from the charcoal in each of the three glass tubes. The figures in the third column are obtained by subtracting from those in the second column the average electroscope reading deduced from a number of "rest" experiments. A "rest" experiment consisted of testing the gases from the three tubes after 2·7 days' rest, during which no air was drawn through the contained charcoal. Before November 12th the "rest" experiments gave, in divisions a minute, ·251, ·221, ·243, ·233, ·276, ·243, ·277, with a mean value ·250. This is larger than three times the natural leak of the electroscope, which was 3 × ·065, or ·195. I have never found the glass tubes, containing the charcoal, entirely free from emanation, some of which probably entered the tubes during cooling from the previous heating, and some was perhaps due to minute traces of radium in the glass or the charcoal. The amount was fairly constant, and too small to interfere with the main issue under investigation. A very slow current of air through the tubes gave rise to about the same electroscope readings as a "rest" experiment.

After November 12th the "rest" experiments gave ·435, ·456, ·432, ·449, with a mean of ·450 divisions a minute, whilst three times the natural leak was 3 × ·123 divisions a minute.

The third column in the table gives the *amount of radium which would be required to supply the emanation to one cubic metre of the atmosphere at the place and during the time of the observation on the supposition that the emanation is in equilibrium with the amount of radium stated.*

I venture to call this the *radium equivalent per cubic metre.*

The remaining columns give the approximate means of the temperature in degrees Fahrenheit, the barometric pressure in inches, and the wind direction, during the time of the experiments. Remarks have been added to indicate the weather conditions, when well defined. The figures and remarks are deduced from notes made at the time, from the weather reports of the McGill University Observatory, issued by Professor C. H. McLeod, and from the weather maps issued daily by the United States Department of Agriculture.

Discussion of Results.

In the first place it will be seen that temperature has little or no appreciable direct effect on the amount of emanation in the atmosphere near the earth's surface. The results for July and August with a mean temperature of 65° F. are not very different from those made in the month of January with a mean temperature of 12° F.

Again, during the month of March there was, at Montreal, an average depth of snow between two and three feet, and yet the radium equivalent, $45{\cdot}5 \times 10^{-12}$, was but little less than that for April, $51{\cdot}5 \times 10^{-12}$, after the snow had melted. These results agree with the observations of Rutherford and Allen, that the active deposit collected from the atmosphere varied little in magnitude between summer and winter, even when the wind blew from cold regions deeply covered with snow. This fact suggests that the radium emanation escapes from considerable depths in the ground.

It may be noted, however, that in the winter 1907–8 the snow preceded any severe frosts and so protected the earth that the ground was scarcely frozen.

It may be stated generally that, so far as these experiments go, they indicate that a well-defined cyclone, accompanied by heavy rain or a quick thaw of snow, gives maximum values to the radium equivalent. On the other hand, anticyclones, with dry weather, and, in winter, very low temperatures, give minimum values.

If curves are plotted which show the variations of barometer pressure and radium equivalent, it is found that the fluctuations are not markedly synchronous, and that a connexion can only be established when the changes of pressure are exceptionally large. The reason for this has already been indicated, and depends upon the slow rate of decay of radium emanation and the necessarily long period of each experiment.

Series 1.

Date.	Electroscope reading.	Less "rest" value.	Radium grms. $\times 10^{-12}$.	Temp. Fahr	Bar. ins.	Wind.	Rain ins.	Remarks.
1907								
July 13	·331	·081	41·7	70	29·8	S.W.	...	Shallow cyclones & thunderstorms. 1·8 inches total rainfall.
19	·383	·133	68·6					
25	·335	·085	43·8					
Aug. 1	·390	·140	72·2	65	29·9	S.W		
6	·373	·123	63·4					
9	·360	·110	56·6					
Mean	...	...	57·7					
Oct. 17	·419	·169	87·1	51	30·1	S·W.	...	Anticyclone.
24	·331	·081	41·7	40	29·9	W.	1·2	
31	·361	·111	57·3	35	30·2	N.W.	...	Anticyclone.
Nov. 5	·415	·165	85·1 ?	40	29·6	...	·63	
11	·420	·170	87·6	37	29·8	W.	...	Heavy rain previously.
Mean	...	...	71·9					

Series 2.

Date.	Electroscope reading.	Less "rest" value.	Radium grms. $\times 10^{-12}$.	Temp. Fahr	Bar. ins.	Wind.	Rain ins.	Remarks.
1907								
Dec. 9	·880 ?	·43	108 ?	36	30·0	S.	...	Thaw after frost and snow.
12	·617	·167	42	29	29·6	W.	0·5	Cyclone, rain, then frost.
20	·571	·123	31	21	30·0	W.		
23	1·24 ?	·79	198 ?	30	30·0	W.	0·35	
26	·84	·39	98	27	29·7	S.	...	Cyclone, some snow.
Mean	...	...	95·2					

SERIES 2 (*continued*).

Date.	Electroscope reading.	Less "rest" value.	Radium grms. $\times 10^{-12}$	Temp. Fahr.	Bar. ins.	Wind.	Rain ins.	Remarks.
1908 Jan. 2	·726	·276	69·3	18	30·0	W.	0·3	Thaw on 30th Dec.
6	·60	·150	37·6	16	29·8	S.W.	...	A cold spell.
9	·877	·427	107·0	24	29·5	S.W.	...	8 ins. snowfall. 20 ins. on ground.
13	·583	·133	33·4	17	29·7	N.E.		
16	·688	·238	60·4	6	29·9	N.W.	...	Cold spell.
20	·544	·094	24·8	11	30·1			
23	·858	·408	102·4	31	29·9	W.	0·34	*Well marked thaw.*
27	·750	·300	75·4	13	29·5	N.E.		
30	·509	·059	14·7	−4	30·3	W.	...	Very cold spell, and anticyclone.
Mean	...	...	58·2					
Mar. 10	·524	·074	18·5	21	30·3	W.	...	2½ ft. snow on ground.
13	·611	·161	40·4	27	29·9			
16	·712	·262	65·5	24	29·6	S.W.	0·9	Thaw.
19	·625	·175	43·8	15	30·0	E.		
23	·710	·260	65·2	29	29·9	W.	0·16	*
26	·618	·168	42·2	29	29·9	W.	0·21	
31	·621	·171	42·9	32	30·0	W.	...	1 ft. snow on ground.
Mean	...	...	45·5					
Apr. 3	·582	·132	33·2	25	29·7	W.	0·02	1 ft. snow on ground.
6	·594	·144	39·9	29	30·0	W.	0·1	
9	·678	·228	57·3	32	30·0	E.	0·3	
13	·560	·110	31·3	35	29·7	W.		
16	·627	·177	37·0	32	30·2	S.W.	...	Snow nearly gone.
20	·610	·160	40·2	35	29·6	S.W.	0·2	
23	·684	·234	58·6	38	29·8	W.		
27	·821	·371	93·0	53	29·7	S.E.	1·0	Thaw, rain, cyclone.
30	·745	·295	74·1	46	29·8	S.W.	0·1	
Mean	...	...	51·5					

Mean of monthly Means ... **59·7**

* During March and early April thaw and frost alternated. Snow went mainly by evaporation.

The best examples of cyclone effects were

9 Dec. 1907.	108 ?	grm. × 10^{-12}
23 " "	198 ?	"
23 Jan. 1908.	102	"
27 April "	93	"

and of anticyclones

20 Dec. 1907.	31	grm. × 10^{-12}
20 Jan. 1908.	25	"
30 Jan. "	15	"
10 March "	19	"

On 30th January the barometer rose to 30·5, and the thermometer fell to 20° below zero, Fahr. The natural leak of the electroscope, and the "rest" experiments, were not affected by the changes of weather, as the laboratory was dry and at a steady temperature.

The reading of 23rd December was nearly twice as great as any other, and may perhaps have been incorrect. Excepting this, the ratio of the greatest to the least values was 7 to 1, and this is less than the corresponding ratio 16 to 1, found by Elster and Geitel in the case of the active deposit collected from the atmosphere by a negatively charged wire. The variations in the amount of active deposit are modified by the influence of smoke, dust, and mist—disturbing factors which are avoided in measurement of the emanation.

There are many reasons why the amount of radium emanation in the atmosphere should be increased when a cyclone prevails, for then :—

(1) The air is moving along the surface of the earth in large spiral paths towards the centre of the depression where the air rises. Thus the air near the earth's surface contains much of the emanation escaping from the ground. But with an anticyclone, air is descending from altitudes where the contained emanation has decayed, and where fresh supplies are not forthcoming.

(2) Diminishing pressure causes radium emanation, with other gases, to pass out from the ground into the atmosphere.

(3) Rain usually accompanies a cyclone, and in winter higher temperatures prevail and cause the snow to melt. In both cases water enters and moistens the soil, and emanation escapes more readily from radium salts when these are moist or in solution.

After experimenting for some months it was found possible to make fairly good forecasts of the radium equivalent, when weather of a pronounced type prevailed. The gradual thaw of March and April produced fairly steady values, until the well-defined cyclone of 27th April arrived from the westward with a south wind and an inch of rainfall, and then there was a considerable increase.

The month of February was spent in calibrating instruments, and in vain endeavours to obtain daily measurements. The quantity of emanation collected between 5 P.M. and 9 A.M. proved too small for measurement with any approach to accuracy.

The mean of the results is $59{\cdot}7 \times 10^{-12}$ grm. of radium as the amount in equilibrium with the emanation present in a cubic metre of air. This is in fair agreement with the determination 82×10^{-12} described in a previous paper (Phil. Mag. July 1905). In the latter case, the active deposit on a negatively charged wire was measured and compared with similar deposits from the emanation arising from a standard solution.

I regret that pressure of other work prevented me from making simultaneous observations on the active deposit, ionization and potential gradient. At present there is much waste of labour in the incomplete work of many observers who have not time or opportunity to make more thorough investigations. The time has certainly come for a complete radioactive survey at a well-equipped laboratory with a sufficient staff of skilled observers. Simultaneous and continuous experiments are needed on the meteorological conditions, amount of radium emanation in the atmosphere, active deposit obtainable, potential gradient, penetrating radiation, and ionization (Ebert's and Langevin's methods). In the measurement of penetrating radiation too much reliance has sometimes been placed on the readings of a single instrument. It is desirable to observe the fluctuations with both electroscope and electrometer, and to ascertain if the variations agree with different types and arrangements of apparatus.

Those engaged in balloon, or kite, experiments might obtain useful information on the penetrating radiation at high altitudes, by observations on the rate of discharge of electroscopes at the earth's surface and at considerable elevation. The active deposit on the wires employed should also be measured.

The ionization of the atmosphere near the ground appears to be largely due to radioactive matter, and meteorological conditions are dependent on ionization to a large and unknown extent, so that a thorough radioactive survey cannot fail to be of interest and advantage.

Summary.

(1) The amount of radium which would be in equilibrium with the average amount of radium emanation present in a cubic metre of air, as measured at Montreal at intervals extending over a year, 1907–8, is 60×10^{-12} gram.

(2) The amount of radium emanation in the atmosphere varied so that the maximum is to the minimum as about 7 is to 1.

(3) The amounts in summer and in winter are not widely different, and large changes of temperature appear to have little or no direct influence on the quantity.

(4) The approach of a deep cyclone, accompanied by heavy rain or a quick thaw of snow, cause an increase, whilst anticyclonic conditions, with dry or very cold weather, give a decrease of the radium emanation in the air.

I am grateful to Professor Rutherford for proposing to me this experimental work and for suggesting the general methods adopted.

Hornsea, 27th June, 1908.

LII. *The Relation between Uranium and Radium.* III.[*]

By Frederick Soddy, *M.A.*[†]

MORE than a year has elapsed since the last published tests in the second series of experiments with large quantities of uranium, purified with great care by Mr. T. D. Mackenzie. The subsequent tests on these preparations and some new experiments are given in the present paper. The only change of method to be recorded is the use of a glass electroscope of globular form, silvered internally, which being air-tight and capable of standing a vacuum, is more suited for the measurement of minute quantities of radium emanation, as the observations can be extended over longer intervals without fear of loss. In Experiments I. and II. the emanation has been extracted by the mercury pump exactly as before; but this arrangement has now been dispensed with and the solutions sealed up in large flasks. Subsequent

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[*] I. Soddy, Phil. Mag. June 1905, p. 768. II. Soddy and Mackenzie, Phil. Mag. Aug. 1907, p. 272.

[†] Communicated by the Author.

tests will be carried out without the pump in the manner previously described (*loc. cit.* II. p. 281). All the other radium tests described in the paper are carried out also in this way, as it involves less labour than the pump method. Before the results in the main experiments (I. and II.) are described, the less important, but gratifying result of Experiment VI. will be first dealt with,

Experiment VI.—The residues from the uranium used in experiments I. and II. (*loc. cit.* II. pp. 285 & 293), had been purified from radium by the original barium sulphate method employed in 1904, and the quantity of radium then present (June 20th and July 3rd, 1907) was found to be only 4×10^{-12} gram. In two agreeing consecutive tests on May 22nd and July 1st, 1908, the amount of radium found was 3×10^{-11} gram. Thus in a year the quantity of radium had increased about seven times. This establishes, indeed, what was all along to be expected, first the existence of a radium-producing body in commercial uranium salts, and secondly that the original barium sulphate method of purification of uranium from radium does not remove all this substance. Though, in the present state of the subject, not of much importance, these results are personally very gratifying as they bear out the original observation of a growth of radium, which was ascribed to experimental error by a subsequent investigator who employed one tenth part of the amount of uranium, a shorter period of observation, and a different method of purification.

The original experiment was of necessity terminated, as it was necessary to prove that the sulphuric acid present, by causing the radium formed to assume the non-emanating condition, was not interfering with the results. The solution of the barium sulphate precipitate, used at the end of the experiment to precipitate the radium formed, has however been preserved unchanged. In 1905 the leak it produced in an electroscope, by the bubbling test, was much less than when tested by the same method a few weeks ago. It is therefore being examined to see if it does not contain some of the original radium-producing substance precipitated with the barium sulphate.

The amount of the radium parent in commercial uranium salts probably varies very much. In some commercial uranyl nitrate recently purchased the total impurities present amounted only to a few tenths of a per cent., whereas from one of the kilograms used in the earlier work over 200 grams of the sulphate of an alkali-metal were extracted.

The very first uranyl nitrate examined, in 1903, was divided into two halves; the one was purified by means of barium sulphate, and the other is still in its initial condition. The first now (May 1908) contains $4 \cdot 5 \times 10^{-12}$ gram of radium, and the second $2 \cdot 7 \times 10^{-11}$. Even assuming that in both the whole of the radium has been formed within the last five years the amount of the parent of radium is only one-sixtieth per cent. and one-tenth per cent. of the equilibrium quantity in the two cases.

The growth of $2 \cdot 6 \times 10^{-11}$ gram of radium in about a year from the residues, probably, of about 1500 grams of commercial uranyl nitrate, indicates the presence of about one-thirtieth per cent. of the equilibrium quantity of the parent. Marckwald and Keetman (*Ber. d. D. Chem. Gesell.* 1908, li. p. 43) point out that, since the radium-bearing insoluble residues of pitchblende are poor in the parent of radium, the main quantity of the latter must go into solution with the uranium. These results show that it is almost all separated before the uranium comes into the market. It is not difficult to see therefore that it must be almost wholly contained in the mother-liquors from the crystallization of the uranium salts, which are probably wasted. The curious preferential restrictions woven around the supply of radioactive material to scientific workers, which have resulted in many of the original investigators being deprived of material for their researches (see *Zeit. Elektrochemie,* 1907, xiii. p. 369) close this avenue of search except to the privileged.

Experiment I.—The solution, containing about 255 grams of uranium, initially contained $1 \cdot 9 \times 10^{-11}$ gram of radium. The last published test (July 3rd, 1907), 617 days from the start, showed $2 \cdot 7 \times 10^{-11}$gram. The last test, performed on Aug. 7th, 1908, 1018 days from the start, showed $2 \cdot 9 \times 10^{-11}$ gram. This increase, which, though slight, appears to be real, is in all probability due to a small fraction of the parent of radium, present in commercial uranium salts, escaping removal during the purification with ether, and being still present with the uranium. In any case, the experiment proves that the amount of radium formed per kilogram of uranium is less than 5×10^{-11} gram in the first 1018 days, or $2\frac{3}{4}$ years.

Experiment II.—408 [*] grams of uranium in the initial test showed $1 \cdot 3 \times 10^{-11}$ gram of radium. In the last published test (July 9th, 1907), 208 days from the start, the result

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[*] A recent analysis has shown that the solution contains 408 grams of uranium instead of 480 as previously stated. The analysis of the solution of Experiment I. showed the presence of 255 grams of uranium, confirming the previous estimate of about 250 grams.

was $1 \cdot 2 \times 10^{-11}$ gram. In the last test on August 8th, 1908, 586 days from the start, which was an exceptionally perfect one, the amount of radium was found to be only $0 \cdot 7 \times 10^{-11}$ gram. This test is more trustworthy than the earlier ones and is in accord with one performed on June 10th, 1908. For these extremely minute amounts of radium the figures previously were rather maximum estimates than accurate measurements; but with the slight improvements already referred to smaller quantities of radium can be more accurately determined than formerly.

The increase in this experiment, if any, is certainly less than 5×10^{-12} gram. The amount of radium formed per kilogram of uranium is certainly not above 10^{-11} gram in the first 586 days, or $1\frac{2}{3}$ years.

From these data the period of average life, or its reciprocal the radio-active constant, of the intermediate parent of radium, may be calculated, at least so far as to indicate a minimum value for the average life, as shown by Rutherford (*Jahr. Radioaktivität*, 1908, v. p. 164). The calculation is here reproduced. Let P_0 refer to the quantity of uranium under observation, and Q_0, R_0, to the quantities of the parent of radium, and of radium, respectively in equilibrium with P_0. λ_1, λ_2, and λ_3 denote the respective radioactive constants, or fractions changing per year, of uranium, the parent of radium, and of radium. Then

$$\lambda_1 P_0 = \lambda_2 Q_0 = \lambda_3 R_0.$$

The intermediate body UrX is neglected in the calculation, being of too short period to affect the result, and the assumption is made that the time, t in years, is short compared with the period of average life of the intermediate parent, while the latter is short compared with that of the primary parent, uranium.

The amount of uranium changing, and the amount of the parent formed, in the time of the experiment is $\lambda_1 P_0 t$. The amount of radium formed in short time dt is $\lambda_2 (\lambda_1 P_0 t) dt$. If R is the amount of radium formed in the time of the experiment,

$$R = \int_0^t \lambda_2 (\lambda_1 P_0 t)\, dt = \tfrac{1}{2} \lambda_1 \lambda_2 P_0 t^2 = \tfrac{1}{2} \lambda_2 \lambda_3 R_0 t^2.$$

From this λ_2 may at once be deduced from the data given. If R is made to represent the amount of radium formed per kilogram of uranium in time t, the numerical value of $\lambda_1 P_0$ or $\lambda_3 R_0$ is $3 \cdot 5 \times 10^{-4} \times 3 \cdot 4 \times 10^{-4} = 1 \cdot 2 \times 10^{-7}$.

Experiment I.

$$R < 5 \times 10^{-11}, \qquad t = 2\tfrac{3}{4} \text{ years},$$
$$5 \times 10^{-11} > \tfrac{1}{2}\lambda_2(1{\cdot}2 \times 10^{-7})(\tfrac{11}{4})^2,$$
$$\lambda_2 < 1{\cdot}1 \times 10^{-4}.$$

Experiment II.

$$R < 10^{-11}, \qquad t = 1\tfrac{2}{3} \text{ years},$$
$$10^{-11} > \tfrac{1}{2}\lambda_2(1{\cdot}2 \times 10^{-7})(\tfrac{5}{3})^2,$$
$$\lambda_2 < 6 \times 10^{-5}.$$

The result of the second experiment is thus the best at the present time. It shows conclusively that, if only one intermediate parent exists between uranium X and radium, its period of average life must be far greater than that of radium. According to the second experiment the period is not less than 16,500 years. This is six times that of radium, so that the quantity in minerals should be at least six times greater than that of radium.

Other considerations, however, indicate that there may be two or more intermediate bodies in the series. For, the difference between the atomic weights of uranium and radium is 12, which is equal to the mass of three α particles, and rayless changes are certainly to be expected if the initial decay of the activity of UrX is, as hitherto supposed, complete.

Rutherford's method of calculation appears to be applicable to a general solution for the initial rate of production of radium, however many intermediate bodies intervene, provided the life of each is long compared with the time of observation. The method of calculation in reality neglects decrements of the quantities of the changing substances, and considers only the increments. Any member of the changing series being considered, except the first, it experiences an increment of quantity due to the preceding change, and, including the first, a decrement of quantity due to the succeeding change. The decrement is consistently neglected throughout, as by hypothesis in the initial stage of the change it is insignificant, the fraction of the total changing being always small. Changes of very short periods compared to the time of observation, on the other hand, like that of UrX, may be omitted altogether without serious error.

If the radium is formed after n changes, so that the change of the radium is the $(n+1)$th change, the general expression is

$$R = (1/n\,!)\,\lambda_1\lambda_2\ldots\lambda_n U t^n,$$

where U is the quantity of uranium. If, as before, a kilogram of uranium is considered, since

$$\lambda_1 U = 1{\cdot}2 \times 10^{-7},$$
$$R = (1/n\,!)\,\lambda_2\lambda_3 \ldots \lambda_n t^n \times 1{\cdot}2 \times 10^{-7}.$$

It is interesting to note that the experimental results, when they have been obtained, will enable the number of intermediate changes to be at once determined, this number being the power of the time to which the initial rate of production is proportional. Of the intermediate bodies, the products of their periods may be deduced, and the geometrical mean period, but not the individual periods.

For the case of two intermediate bodies, $n=3$, and the expression becomes

$$R = \tfrac{1}{6}\lambda_2\lambda_3 t^3 \times 1{\cdot}2 \times 10^{-7}.$$

From Experiment I.,

$$5 \times 10^{-11} > \tfrac{1}{6}\lambda_2\lambda_3 \times \left(\tfrac{11}{4}\right)^3 \times 1{\cdot}2 \times 10^{-7}.$$
$$\lambda_2\lambda_3 < 1{\cdot}2 \times 10^{-4}.$$

From Experiment II.,

$$10^{-11} > \tfrac{1}{6}\lambda_2\lambda_3 \times \left(\tfrac{5}{2}\right)^3 \times 1{\cdot}2 \times 10^{-7},$$
$$\lambda_2\lambda_3 < 1{\cdot}1 \times 10^{-4}.$$

On the assumption of the existence of two intermediate bodies, therefore, both experiments indicate that the products of the two periods is at least 10,000 years, so that if the two periods are similar each is above 100 years. It is probable that several intermediate bodies will ultimately be found to intervene.

With regard to *Experiment* IV., which was an attempt to detect a production of actinium from uranium, no further tests have yet been done. In *Experiment* V., the wire made active by exposure to an actinium preparation for five months now shows no detectable activity, and no detectable amount of radium emanation was obtained from it on heating to redness in a recent test, though 2×10^{-12} gram could have been detected.

Summary of Results.

(1) The results of the second series of experiments have confirmed the original experiment, started in 1903, in showing the existence of a radium-producing substance in minute amount in commercial uranyl salts. The amount is, in the

specimens tested, always below one part in a thousand of the theoretical equilibrium amount which should be present in the natural mineral. The main part by far of the parent of radium in minerals is probably contained in the mother-liquors from the crystallization of the uranium salts, and so is lost.

(2) In the carefully purified uranium salts prepared by Mr. T. D. Mackenzie in 1905–06, the growth of radium in one case is not greater than 5×10^{-11} gram per kilogram of uranium in $2\frac{3}{4}$ years, and in the other it is not above 10^{-11} gram per kilogram of uranium in $1\frac{2}{3}$ years. It can be shown from these data that if there exists only one long-lived intermediate body between uranium and radium, its period of average life must not be less than 16,500 years, or six times that of radium; so that at least six times more of it than of radium must exist in minerals. If there be two such bodies, the product of their periods must be at least 10,000 years; and if they are equal each must be not less than 100 years.

Physical Chemistry Laboratory,
The University of Glasgow.
10 Aug. 1908.

LIII. *A Directive System of Wireless Telegraphy.*
By E. Bellini *and* A. Tosi *.

Part I.—Bilateral Directive Wireless Telegraphy using Closed Oscillatory Circuits: (i.) for Transmission; (ii.) for Reception; (iii.) for both Transmission and Reception.

Part II.—New Unilateral Directive Method: Simultaneous Use of Closed Oscillatory Aerial Circuits and the Open Oscillator or Vertical Antenna.

THE authors, having lately obtained some interesting and very remarkable results in the course of their work upon a further development of their directive system, propose to give an account of the arrangements employed and the results attained.

Since the complete understanding of these experiments depends upon the properties shown by the closed oscillatory circuits used by the authors, it is considered desirable, in the first part of the paper, to recapitulate, as briefly as possible, the main features of the original method, thus enabling a more comprehensive view to be taken of the later

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* Communicated by the Physical Society: read June 12, 1908.

arrangements, as well as supplying the necessary information to those who are not familiar with the earlier work, which has been fully dealt with elsewhere*.

PART I.

The aerial of the bilateral system is composed of vertical closed oscillatory circuits.

The closed oscillatory circuit is, as is known, an oscillatory circuit, the metallic portion of which forms a geometrically "nearly closed" figure, the electric field of which is concentrated in a very narrow region, and the conditions of vibration of which are independent of the position of the spark.

Although in such circuits the electric field is situate almost exclusively between the armatures of the condenser, none the less there always exists an electric field of dispersion the lines of force of which go from different points of the circuit to neighbouring conductors and to earth. Consequently, if one of these circuits be vertically placed in proximity to the ground, and with the condenser at the upper part, a number of lines of force will reach the earth, giving rise to an electromagnetic field which propagates itself in space. Since one of the armatures of the condenser has at the same instant an equal potential of opposite sign to that of the other, the electromagnetic field of one side will be opposed in phase relative to the field of the other side. As a result it is evident that in the direction perpendicular to the plane of the circuit there is no radiation whatever; that is to say, the said type of circuit radiates principally in its own plane.

An oscillatory circuit placed in an electromagnetic field will become the seat of an E.M.F. due to the variation of magnetic flux across the surface bounded by the circuit. This E.M.F. will vary with the cosine of the angle which the plane of the circuit makes with the direction of propagation of the field.

Using the Duddell thermogalvanometer, the authors have determined the diagrams of the energy emitted or received by such a circuit. The energy diagrams obtained were

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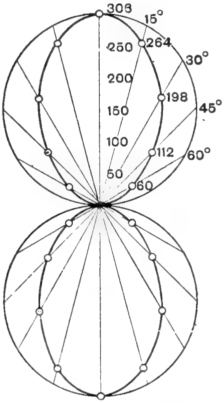
* Electrical Engineering, ii. pp. 771–775 (1907), and iii. pp. 348–351 (1908). The blocks referring to this part of the paper have been kindly lent by the Kilowatt Publishing Company.

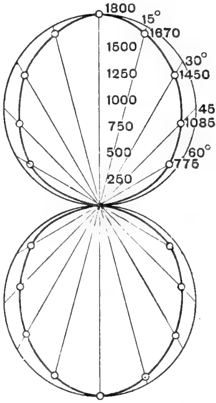
equal and composed of two equal tangent curves (fig. A) whose equation is $E = E_0 \cos^2 \alpha$, where α is the angle which the direction of propagation makes with the plane of the circuit. The diagram of the electromagnetic field is composed of two equal tangent circles (fig. B).

Fig. A.



Energy Transmission Diagram (Microwatts).

Fig. B.



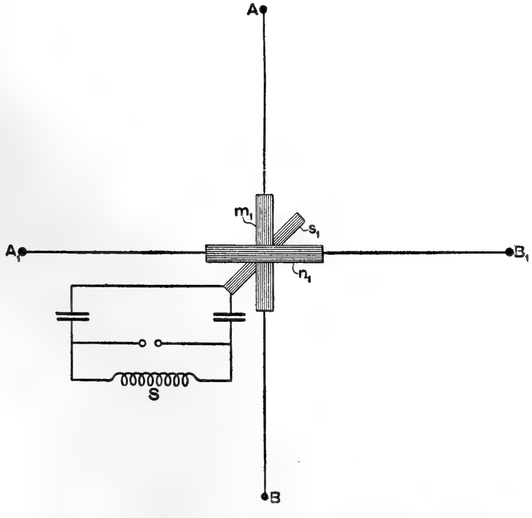
Transmission Diagram of Electromagnetic Field Intensity (Microamperes).

It is owing to these properties possessed by closed oscillatory circuits that such circuits were chosen by the authors for use as directive aerials; and the triangular form of circuit, open at the apex, was employed, owing to the fact that it could easily be sustained by a single mast. In order to be able to transmit and receive to or from any direction whatsoever, without having to turn the aerial, or having recourse to a large number of aerials in fixed positions, the aerials were built up of two equal closed oscillatory circuits, vertically placed and mutually perpendicular. This aerial system is connected up to special instruments for transmission and reception which the authors have called "Radiogoniometers."

The radiogoniometer for transmission comprises two fixed windings, m_1, n_1, mutually perpendicular, one of which is inserted in each of the two aerial circuits AB, A_1B_1, as shown diagrammatically in horizontal projection in fig. C. A third winding *s*, enclosed by the two first, is arranged so as to be movable on its vertical axis, which axis is that of the intersection of the planes of the two fixed windings. This winding *s* is included in the oscillatory exciting circuit, by means of contact brushes. S is the secondary of the spark coil or transformer.

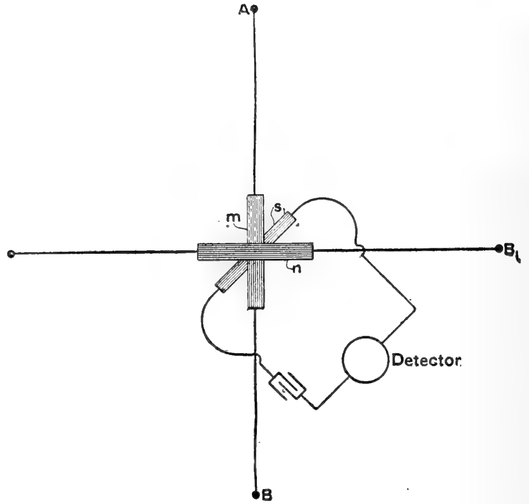
It is evident that on placing the movable winding in different positions the magnetic flux which passes through the two fixed windings will vary, as also will the oscillatory currents in the aerials. The electromagnetic field in space will be produced by the superposition of the partial fields created by the two aerial circuits. Its intensity will be independent of its direction, and this latter will coincide with the direction of the central plane of the movable winding. The law of angular variation of the energy and of the magnetic field is the same as for a single circuit.

Fig. C.



The apparatus is provided with a fixed dial over which moves a pointer rigidly attached to the movable winding. On setting the pointer in the direction of the station to which the signals are to be sent, the emission will be a maximum in the vertical plane which contains the transmitting and receiving stations—that is to say, both towards the receiving station, and at 180° from this. The receiving radiogoniometer is similar in construction to that for the transmission. The fixed windings *m*, *n* (fig. D) are connected to their respective aerial circuits. The movable winding s_1 is suitably connected up to the detector, through two brushes.

Fig. D.



The oscillatory currents set up in the two aerials, when these latter are subjected to the influence of an electromagnetic field, create, in the interior of the fixed windings, a resultant magnetic field of an intensity which is independent of the direction of the transmitting station. When, therefore, the movable winding is perpendicular to this resultant field, that is, its central plane is oriented towards the transmitting station, the effect on the detector will be a maximum. In this position the reception is practically limited to the plane containing the transmitting station, and the pointer indicates on the dial the direction of this plane. One is, however, not able to determine *which* side of the receiving station the transmitting station is located.

The receiving radiogoniometer is provided with special contacts for tuning the fixed windings to the lengths of the waves to be received, which is effected by varying the number of active turns equally and simultaneously on the two windings.

The experiments with the system have been carried out at three stations on the French side of the English Channel, at Dieppe, Havre, and Barfleur respectively. The distance Dieppe-Barfleur is 107 miles, all over sea; that between Dieppe and Havre 54 miles, entirely over land; the angle made by the three stations Havre-Dieppe-Barfleur is 23°.

Employing this bilateral system it has been possible to transmit from Dieppe to either Havre or Barfleur without the emission which was directed towards the one post troubling the other one. The energy sufficing for this purpose was about 500 watts.

By the use of the receiving radiogoniometer at the Dieppe and Havre stations the authors have been able to determine the direction of stations both known and unknown. Further, by receiving the same transmission (signals) simultaneously at both Dieppe and Havre, and determining at each station the bearing of the unknown station, it has been possible to locate, by intersection, the actual position of the station which was transmitting. The accuracy obtainable by the use of the receiving radiogoniometer is about one degree of arc.

The triangular closed oscillatory circuits comprising the aerial system were 45 metres high, with a base of 55 metres.

Part II.

The system of wireless telegraphy reviewed in the first Part allows of transmission and reception in the plane in which the station with which one is communicating is situated. That is to say, in transmitting, one is sending the signals to the corresponding station and at the same time in the opposite direction also. As regards the reception, either of two diametrically opposite transmitting stations will affect the receiver in the same way, and it will not be possible to decide as to which side of the receiving station the transmitting station is actually located.

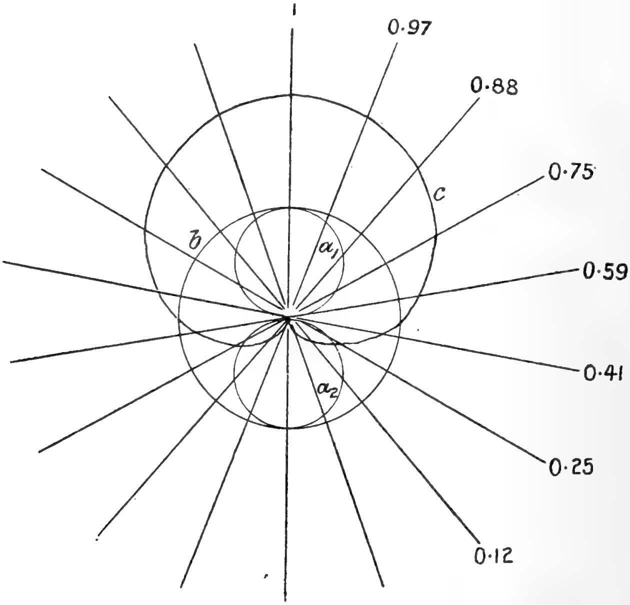
Since the sending of the waves in a single useful direction is often of great importance, and it is desirable to be able to decide not merely the direction but the azimuth, the authors have worked out a method of achieving this object, and have solved the problem in the following manner.

Transmission.—The diagram of the electromagnetic field of the bilateral directive system already described is composed of two equal tangent circles, and the one half-field, represented by one of the circles, is opposite in phase to the other half-field.

If one operates simultaneously, at the same station, both the directive system and an ordinary system giving a circular emission, whose vertical antenna is symmetrically placed with reference to the directive aerial, the resultant electromagnetic field of the simultaneous emissions of the two systems, can, in general, be obtained by vectorially adding the partial diagrams of the two systems.

As an example, let a_1 and a_2 (fig. 1) be the two tangent circles forming the diagram of the electromagnetic field of the directive system; the circumference b represents the diagram of the system with circular emission, of amplitude equal to the maximum amplitude of the directive system; let the phase-difference between b and a_1 be zero, and that between b and a_2 180°. The resultant diagram c is obtained in this case by adding algebraically the *radii vectores* of the curve a_1 to those of the diagram b and by subtracting the *radii vectores* of the curve b from those of curve a_2. The resultant diagram is represented by a "cardioid."

Fig. 1.



It is evident from the figure, that the resultant maximum electromagnetic field is directed to one side only ; that it has a value double that of the component electromagnetic fields ; and that the field on the other side is zero.

The intensity of the electromagnetic field set up by the directive system at a point whose direction makes an angle α with the maximum radiation, is expressed by $C \cos \alpha$. Let M be the intensity of the electromagnetic field produced by the circularly radiating system at the same point, and let ϕ be the phase-difference between the electromagnetic field of the circular system and that of one side of the directive system.

The intensity of the resultant electromagnetic field at the point considered will be

$$\begin{aligned} I &= \sqrt{(M+C\cos\alpha\cos\phi)^2 + C^2\cos^2\alpha\sin^2\phi} \\ &= \sqrt{M^2 + C^2\cos^2\alpha + 2MC\cos\alpha\cos\phi}. \end{aligned}$$

The minimum of I with reference to α is obtained when

$$\cos\alpha = -\frac{M}{C}\cos\phi.$$

This value of $\cos\alpha$ is imaginary when $M\cos\phi > C$.

In the case when $M\cos\phi \leqq C$, one has $I_{\min} = M\sin\phi$; when $M\cos\phi > C$ one has

$$I_{\min} = \sqrt{M^2 + C^2\cos^2\alpha - 2MC\cos\alpha\cos\phi}.$$

In the special case when $\phi = 0$ the equation of the resultant electromagnetic field transforms itself into

$$I = M + C\cos\alpha,$$

which is the equation of a curve that can have three different forms according to the value of the ratio M/C. The curve represented by the condition $M = C$ is the cardioid above mentioned.

But since in wireless telegraphy the action depends chiefly upon the energy, it will be useful to consider this in preference to the intensity of the electromagnetic field.

In the general case the energy radiated in the different directions is expressed by the equation—

$$W = M^2 + C^2\cos^2\alpha + 2MC\cos\alpha\cos\phi,$$

and in the case of the cardioid by the equation—

$$W = M^2(1+\cos\alpha)^2,$$

The corresponding curve is given in fig. 2.

Fig. 2.

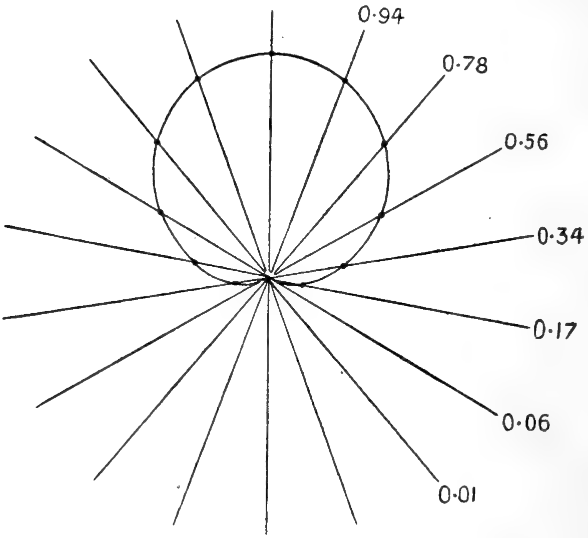


Fig. 3 represents the energy diagram in the case where $M/C = 0{\cdot}72$ and $\phi = 53°$.

Fig. 3.

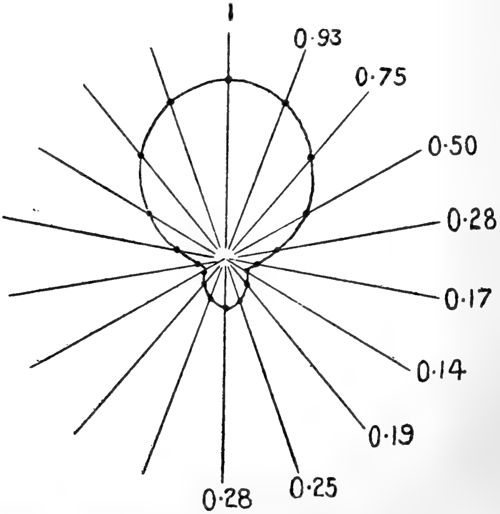


Fig. 4 shows the same diagram for the case where $M = 2C$

and $\phi=0$, and finally fig. 5 the same diagram for $M=C$ and $\phi=90°$.

Fig. 4.

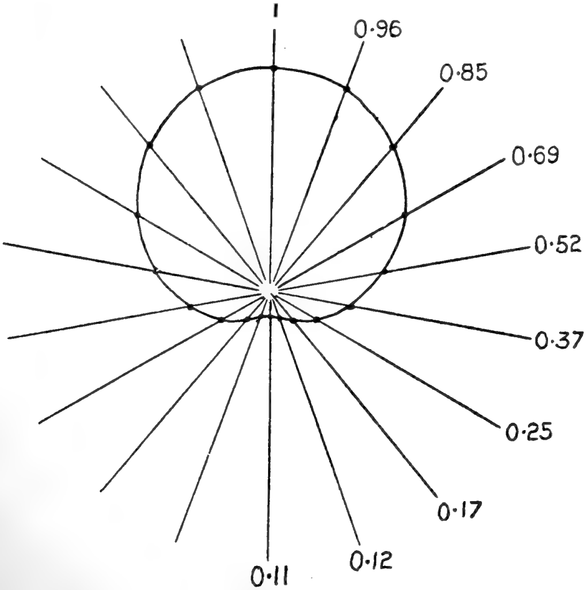
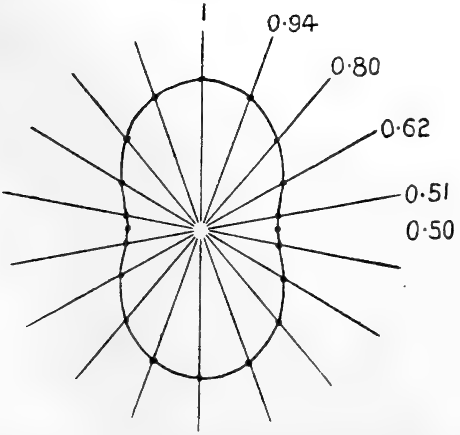


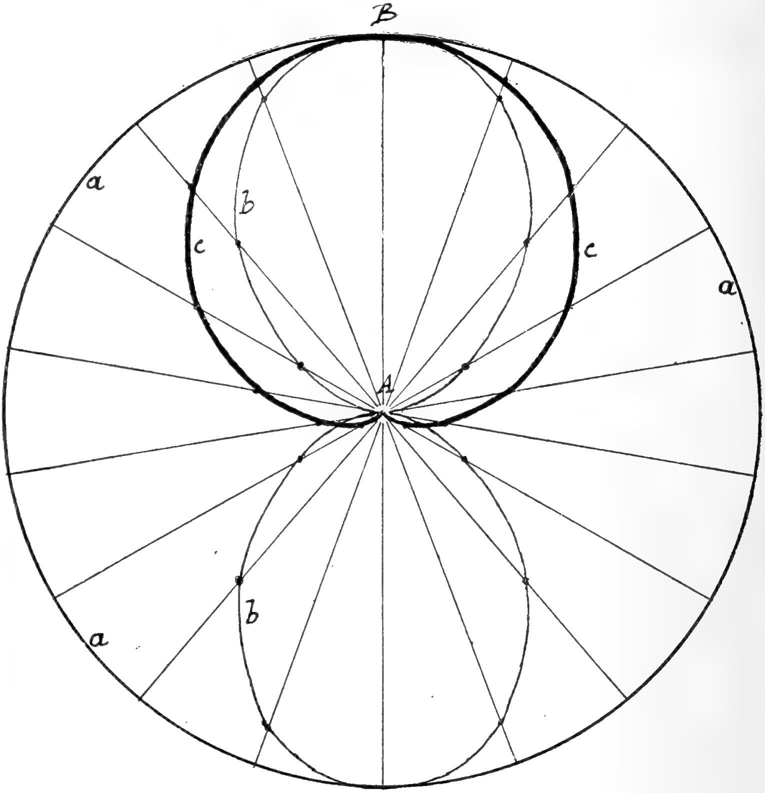
Fig. 5



In consequence, one can conclude that the shape of the diagram of the energy radiated in the different directions depends upon the value of the phase-difference of the component electromagnetic fields, and that the superposition of a circular system on a directive system allows of the concentration of the emitted energy in the desired direction and in the useful sense only.

Fig. 6 shows diagrammatically the advantages which the employment of the mixed unilateral system has over the ordinary circular, or the simple bilateral directive method.

Fig. 6.



Let it be supposed that a station A ought to transmit to a station B. If the station A uses a circular system the energy is radiated all over the circular region a, affecting all the stations comprised within this region. If A uses the bilateral directive system the active area is the region bounded by the two tangent curves b, b. If the station uses the mixed unilateral system adjusted for $M=C$ and $\phi=0$, the active area is considerably smaller than that with the other methods.

The practical realization of the superposition of the two systems has been effected by employing as the directive system the bilateral system already dealt with in Part I. It was evident *a priori* that, owing to the different conditions under which the radiation from the directive circuit takes place with reference to the radiation from the vertical antenna, a phase-difference between the emissions of the two systems should exist, for equality of phase in the excitations. As will be seen further on, the experiments have shown that this phase-difference is 90° or near to that value. The aerial of the unilateral system is formed by the aerial of the directive circuit to which has been added a vertical antenna in a position symmetrical with reference to the first. To secure the simultaneous excitation of the closed oscillatory circuits and of the vertical antenna, various arrangements have been employed which are diagrammatically depicted in figs. 7, 8, 9, 10.

Fig. 7.

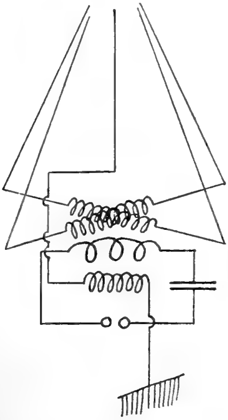


Fig. 8.

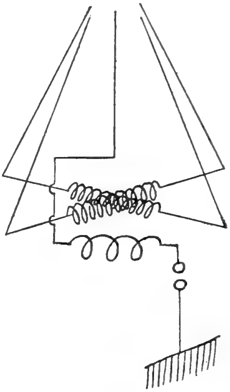


Fig. 9.

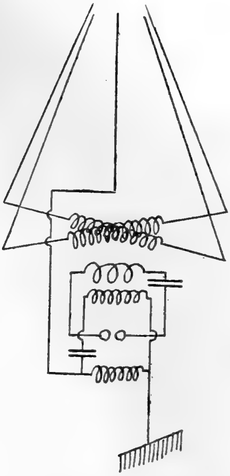
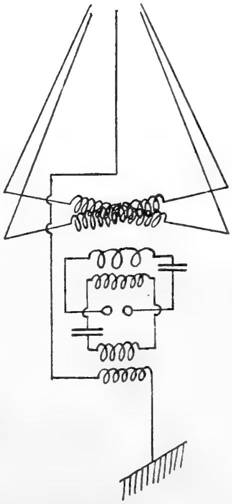
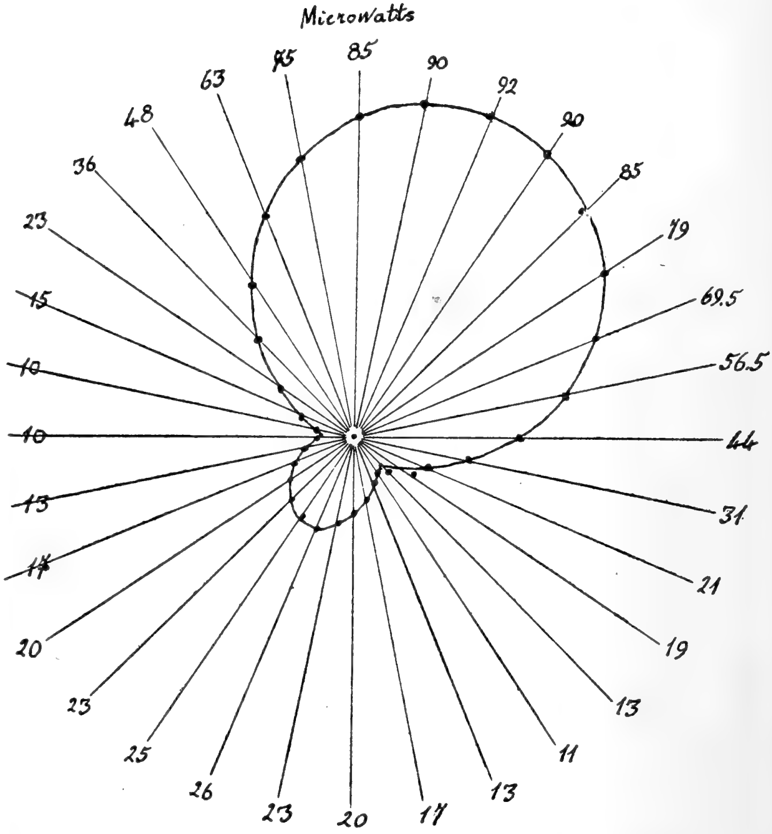


Fig. 10.



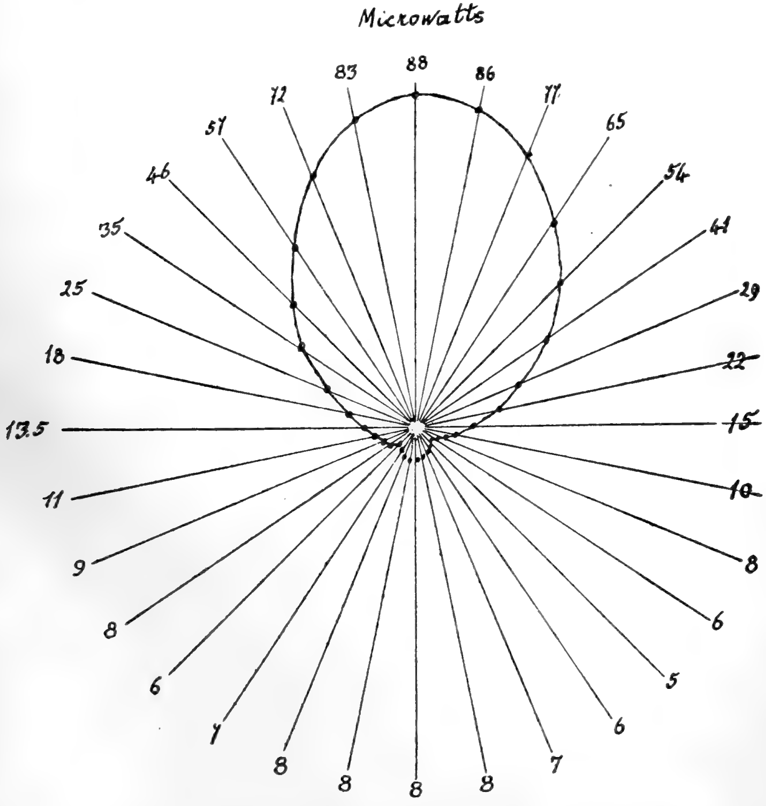
In the first of these arrangements (fig. 7) the excitations of the two systems are in phase; in the other three cases they are in quadrature. The diagrams of the energy radiated in the different directions (figs. 11 and 12) are selected from among the large number which have been determined. They were obtained with the thermo-galvanometer in a similar manner to that employed in the case of the bilateral directive system. In particular the diagram of fig. 11 was obtained when using the arrangement shown in fig. 7; and that of fig. 12 with the arrangement of fig. 10. In the last diagram (fig. 12) the phase-difference between the radiation from the two component systems turns out to be much smaller than in the preceding diagram, and only by means of this last arrangement (fig. 10) have the very small values of the

Fig. 11.



backwardly radiated energy been obtained. This proves the existence of a phase-difference of 90°, or thereabouts, between the emissions from the two systems. The diagram of fig. 12 shows besides, that the problem of the emission of the energy exclusively on the useful side can be considered as having been practically solved.

Fig. 12.



It is interesting to note that, even if the phase-difference between the radiation from the two systems is as much as a certain number of degrees, and the ratio of the partial fields is slightly different from unity, the backward radiation is always practically zero. The phase-difference has to be over 45° for the backward radiation to become noticeable. In order to see if the energy emitted by each component of the system and by the resultant system satisfied the theoretical predictions, these have been measured in several cases with the thermo-galvanometer. The results were always in practical agreement with the theory.

The simultaneous excitation of the two systems was effected by adding, internal to the primary of the transmitting radiogoniometer, a winding, fixed in position relatively to the primary and inductively excited by it. To this winding is connected the vertical antenna. On turning the movable winding of the apparatus the excitation of the vertical antenna remains constant whilst the excitations of the closed circuits forming the aerial of the bilateral system, vary. Consequently, to transmit by the unilateral system in a given direction, one has merely to turn the movable pointer until it points in this direction.

The tests of the unilateral system at long distance were made between the stations of Dieppe and Havre, and have confirmed the results obtained at short range—that is to say, on placing the pointer of the transmitting radiogoniometer in the direction of Havre, reception was effected ; on turning the pointer to 180° from this the reception ceased entirely.

Reception.—The same principle of the superposition of the two systems has been applied to the case of the reception. Considering the case of a receiving station provided with an aerial composed of a single closed oscillatory circuit, fixed in position, and of a vertical antenna symmetrically placed with respect to the closed oscillatory circuit, let it be supposed that any transmitting station is moving along a circumference of which the receiving station is the centre ; it is evident that the intensity and phase of the oscillatory current in the vertical antenna of the receiving station will remain constant, whilst in the closed oscillatory circuit they will vary with the position of the transmitting station. The intensity passes through two maxima and two minima, and its phase varies by 180° when the transmitting station passes from one side to the other of the plane perpendicular to the closed oscillatory circuit. Further, although a closed oscillatory circuit utilises the variation of magnetic flux across the surface bounded by such circuit, the E.M.F. generated in it will be in quadrature with the E.M.F. generated in the vertical antenna, and the same phase-displacement will exist between the currents in the two types of aerials if these latter are both tuned to the length of the waves received.

Let it be supposed, for instance, that the closed oscillatory circuit is oriented in a certain meridian and that the transmitting station in moving about arrives in the plane of the closed oscillatory circuit, on the north side. In such a position, by bringing the actions of the two systems on the detector into phase by any means, the effects of the two will be added. When the transmitting station finds itself, similarly, in the plane of the closed circuit but on the south side, the effects of the two systems counteract one another. If the directive aerial of the receiving station is composed of two closed oscillatory circuits connected to the receiving radiogoniometer, the phase of the E.M.F. induced in the movable winding of the apparatus will vary by 180° when the coil is turned through 180°. So that the action of the directive aerial in one case will add itself to that of the vertical antenna, and in the other case will subtract itself therefrom. It follows that, to the position of maximum reception of the movable coil, there corresponds a position of zero or minimum reception when the coil is turned through 180°, which thus permits of the determination not merely of the direction of the transmitting station, but also of the side which it is on.

The action of the detector depends, as in the case of the transmission, upon the values of the phase-difference between the actions of the two systems and on the ratio M/C. The law of variation of this action is the same as that of the variation of the resultant electromagnetic field at the transmitter and the diagrams are the same.

Fig. 13.

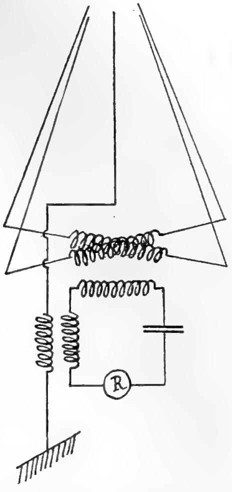
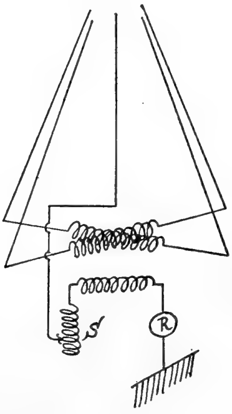


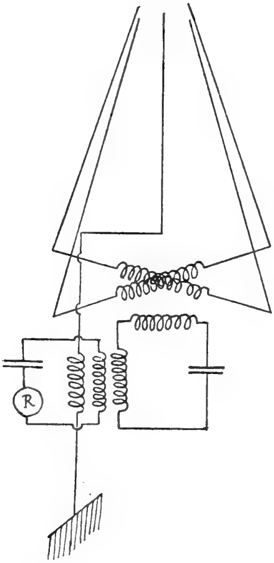
Fig. 14.



To obtain quadrature between the actions of the vertical antenna system and that of the directive bilateral system several arrangements have been tried which are shown in figs. 13, 14, 15.

In the case of fig. 13 the phase displacement was obtained by inserting an excess of self-inductance in one or other of the aerial circuits; in the arrangements of figs. 14 and 15

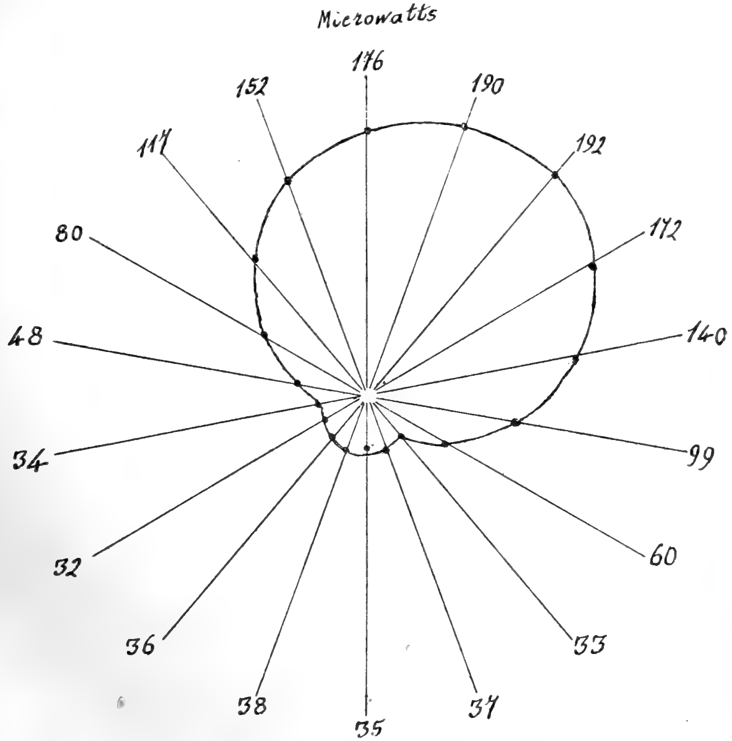
Fig. 15.



the shift of phase was produced automatically when the circuits were all carefully tuned, but the arrangement of fig. 14 is preferable owing to its simplicity, rapidity, and certainty of operation. In this case, as can be seen from the figure, the vertical antenna is joined to one end of the secondary circuit of the receiving radiogoniometer, through a self-inductance S; the other end of the secondary is earthed through the detector R. The working of the arrangement is very simple, since it only requires the tuning of the two circuits as in ordinary cases of circular reception. The diagrams of the reception were obtained in the same way as those of the transmission, by means of the thermo-galvanometer in place of the detector, and by turning the movable secondary of the receiving radiogoniometer, the transmitting station being fixed. The curve of fig. 16 in particular was obtained by means of the arrangement shown in fig. 13; the curve of fig. 17 (p. 656) by that of fig. 15; and the curve of fig. 18 (p. 656) by the arrangement of fig. 14.

The arrangements have always enabled the sense of the received transmissions to be determined, and in many cases to get no reception when the pointer of the movable coil of the receiving radiogoniometer was turned in the opposite direction, which was precisely the object to be achieved.

Fig. 16.



The directive system of wireless telegraphy described can be employed in many ways, according to the requirements, owing to the facility with which one can pass from one system to the other. For example, when the operator expects a message from a station whose position is unknown, he could employ the single vertical antenna system; a soon as reception is effected he can, by using either the bilateral or unilateral system, determine the direction and upon which side the transmitting station lies, and make himself independent of other transmissions.

For the transmission the operator could, similarly, employ the system with circular radiation when he does not know the position of the receiving station or when he wishes to send the same message to several stations. He could in other cases use the unilateral or bilateral system according to the position of the stations which should not receive the messages.

Fig. 17.

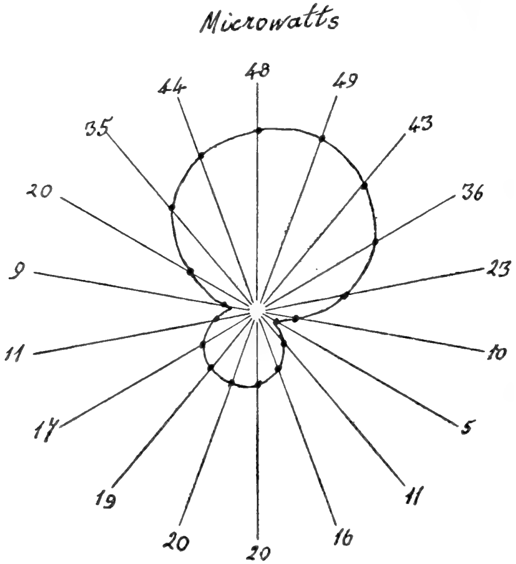
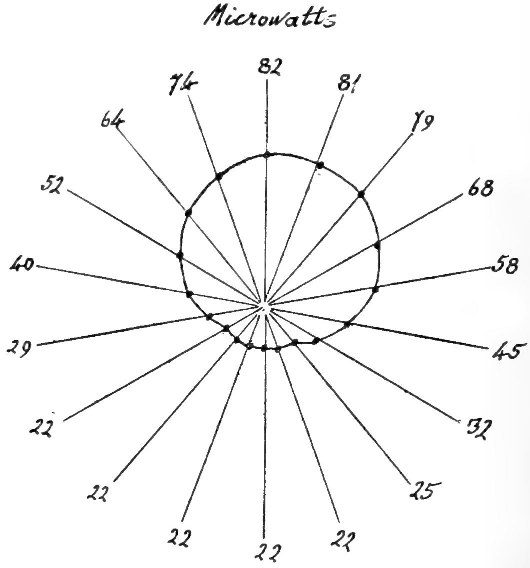


Fig. 18.



The directive system described presents some advantages over other systems, which are very important either from the commercial or the strategic point of view.

So far as the commercial services are concerned, the possibility of transmitting messages to one station without affecting the others, results in the stations having an increased working capacity and consequently in an enhancement of their commercial value. The ability to receive from one determined direction renders the receiving station independent of extraneous transmissions, and even owing to this circumstance alone the working capacity of the stations is raised. Further, the ability to determine the origin of a transmission, apart from its obvious advantages, presents the advantage of enabling the route to be followed by a ship proceeding to the assistance of another in danger, to be indicated.

From the strategic point of view the directive reception enables one to learn of the presence of the enemy in a certain direction and to follow him in his movements. The directive transmission will allow, when suitably employed, of transmitting to one's friends without the enemy being able to receive the waves—for the simple reason that there are no waves there to be detected in the undesired region.

In conclusion, the following is given as one practical example of the main strategical advantage of the directive system. Supposing it were necessary to send radiotelegraphic messages to the cruiser squadrons on the north-east, north, north-west, and west coasts of the United Kingdom; if the messages were sent by an ordinary vertical antenna system they would be perceived in Denmark, in Germany, in Belgium, Holland, and France. Employing, on the other hand, the unilateral system, the messages sent from London to the Fleet would not be received outside the United Kingdom.

The authors desire to thank Mr. L. H. Walter for translating this paper from the original.

LIV. *Positive Rays.* *By* J. J. THOMSON, *M.A., F.R.S.; Cavendish Professor of Experimental Physics, Cambridge; Professor of Natural Philosophy at the Royal Institution* [*].

THOUGH the ordinary cathode rays are the most conspicuous of the rays spreading out from the cathode in a vacuum-tube, there are other rays mixed with them, which as Goldstein (*Verhandl. d. Deutsch. physik. Gesellsch.* iv. p. 228, 1902) and the writer (Proc. Camb. Phil. Soc. ix. p. 243) showed long ago are not appreciably deflected by weak magnetic fields. The very complete study of the region near the cathode made by Goldstein, the results of which are

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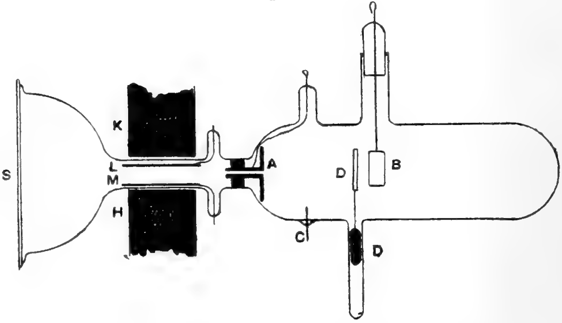
[*] Communicated by the Author.

described in a paper read before the Physical Society of Berlin (republished Phil. Mag. Mar. 1908), has led him to distinguish five kinds of rays besides the cathode rays. Recent experiments made by Villard (*Comptes Rendus*, cxliii. p. 673, 1906) and the author (Phil. Mag. xiv. p. 359, 1907) have shown that some of these rays are deflected in electric and strong magnetic fields, and the direction of the deflexion indicates that they carry a positive charge of electricity. The fact that these positively charged rays travel with high velocities away from the cathode, and thus against the direction of the electric force, makes the investigation of their properties a very interesting problem, and I have lately made a series of experiments with the object of obtaining some information as to their nature and origin.

The tube used in the first series of experiments is represented in fig. 1. A is a perforated electrode through which rays can pass on their way to the phosphorescent screen S covered with Willemite; the rays on their journey to the screen traverse strong electric and magnetic fields, the former produced by charging the plates L M to different potentials and the latter by placing the tube between the poles of a powerful electromagnet. From the deflexions which these produce on the rays, the velocities and values of e/m for the rays can be determined in the usual way. B is a flat electrode at the other end of the tube; this electrode is carried by a stopper working in a ground-glass joint, and can be rotated about a vertical axis. C is an auxiliary electrode at the side of the tube. D is a side tube in which a metallic obstacle is placed at the end of a rod, this end is fastened to a closed glass vessel containing a piece of iron. By moving this vessel along D by means of a magnet, the obstacle can either be inserted in the line of fire of the rays

Fig. 1.



coming from B and passing down the hole in A, or withdrawn into the tube; the obstacle is in metallic connexion with a wire leading out of the tube, so that it can be used as a cathode if required. The discharge through the tube was produced in some cases by a large induction-coil, in others by a Wimshurst machine.

If the stopper carrying the electrode B was turned so that the normal to the electrode coincided with the axis of the tube A, or made only a small angle with it, and if B were made cathode and a discharge sent through the tube, then in addition to the cathode rays other rays passed through the tube in A and excited phosphorescence on the screen. The direction of the deflexions of the phosphorescence under electric and magnetic forces showed that these rays were charged with positive electricity.

If A were made cathode, the ordinary Canalstrahlen produced bright phosphoresence on the screen. The first point investigated was to make sure that the positive rays observed when A was anode, were not due to reversals of the induction-coil making A at times a cathode and sending ordinary Canalstrahlen down the tube. Very simple observations, however, showed that this could not be the explanation. In the first place, the positive rays still passed down the tube when A was disconnected from the coil and the auxiliary electrode C used as an anode; secondly, A being connected with the coil, the rays down the tube disappeared when B was twisted round, so that the normal to its plane made a considerable angle with the axis of the tube; and thirdly, the rays down the tube were stopped when the obstacle in the side tube was pushed forward so as to be in the line between the cathode and the aperture in the anode.

The next point investigated was to see whether the effect might not be due to A acting at times as a cathode in virtue of the negative charge given up to it by the cathode rays starting from B. That this is not the explanation is proved by the following experiments. When the cathode rays were diverted by a magnet so that they no longer fell upon A, the brightness of the phosphorescent patch due to the positive rays going down the tube in A was not appreciably diminished, although the tendency for A to become cathode must have been almost entirely removed. The conclusions drawn from this experiment were confirmed by the results obtained when the obstacle in the side tube was used as a cathode instead of B. When the obstacle was not pushed far enough across the tube for its normal to pass down the tube in A, no positive rays passed down the tube, but as soon as the obstacle had advanced into such a position that its normal went down the aperture in A, the phosphorescence on the screen due to the positive rays appeared. The contrast between the brightness of the phosphorescence when the normal to the obstacle went down the hole in A and when it did not was very sharp, though there was very little variation in the number of cathode rays striking against the anode as a whole. These experiments show that the positive rays under discussion are not due to reversals of the induction-coil nor to the negative electrification of A by the bombardment of cathode rays, but that they originate at the cathode and travel away from it down the tube.

By means of the rotating cathode B we can determine whether the positive rays coming from the cathode are emitted normally to its surface, or whether, like some of the rays observed by Goldstein, they come off in all directions. When the normal to the cathode went down the tube in A, a plentiful supply of positive rays went down the tube. When the cathode was rotated, the phosphorescence due to the positive rays did not immediately disappear, although it became very much fainter; it could, however, be detected until the normal to the cathode made an angle of about 15° with the axis of the tube. The positive rays under discussion appear to follow much the same path as the cathode rays, for it was found that the angle of rotation required to prevent these getting down the tube was much the same as that required to extinguish the phosphorescence due to the positive rays.

Properties of these Positive Rays.

These rays get exceedingly faint at very low pressures, and cease to be observable at pressures when the Canalstrahlen are still quite bright. It is probably due to this that I have never been able to observe the resolution of the phosphorescence, under the action of electric and magnetic forces, into separate patches as in the case of Canalstrahlen (Phil. Mag. xiii. p. 561, 1907) when the pressure is low. The spot of phosphorescence due to the positive rays coming out in front of the cathode is, under the action of electric and magnetic deflexion of the rays, drawn out into a continuous band, even when the pressure is such that the phosphorescence due to the Canalstrahlen shows well-developed patches. In the case of the Canalstrahlen, there are some rays whose deflexion shows that they are negatively charged and have a mass comparable with that of the positive rays. We find, too, in the case of the rays travelling in the opposite direction to the Canalstrahlen, that a considerable number of them are negatively charged particles, indeed I think the proportion of the negative to the positive is greater in this case than in that of the Canalstrahlen. I have observed cases in which the phosphorescence due to the negatively charged particles was little, if at all, less than that due to the positively charged ones.

A large number of determinations were made, by the method described in my first paper (Phil. Mag. xiii. p. 561, 1907), of the velocity and values of e/m for these rays; in consequence of the spot of phosphorescence being drawn out into a band, the values of e/m ranged continuously from 0 to a maximum value.

Two tubes were used for this purpose, in one of them (fig. 1) the electrode B was connected with a stopper ground into the tube, one side of the electrode was aluminium, the other calcium; by turning the stopper either side could be made to face the tube A, down which the rays passed. L M are parallel plates, which can be connected with a battery of storage-cells; when this is done rays passing between the plates are acted on by a strong electric field. S is the screen at the end of the tube. H, K the pole-pieces of the electromagnets. C is a wire fused into the tube, to serve as an electrode, thus allowing A to be insulated or connected with one or other of the electrodes at will. The dimensions of the parts of the tube which affect the deflexions of the phosphorescence are as follows:—

Distance between the plates L and M	=·45 cm.
Length of these plates	=3·8 cm.
Distance between the screen and the end of the plates	=4·0 cm.

If V is the potential in volts between the plates, e the charge, m the mass, and v the velocity of the rays, D the deflexion due to the electrostatic field, we can easily prove that

$$\frac{e}{mv^2}=\frac{\mathrm{D}}{5\times 10^9\mathrm{V}}.$$

While if d is the deflexion due to the magnetic field when a current of 1 ampere is passing through the coils, it was found by the method described in Phil. Mag. xiii. p. 561, that

$$\frac{e}{mv}=\frac{d}{2\cdot 8\times 10^4}.$$

From these equations the following determinations of e/m and v were made; the value of V was 420 volts.

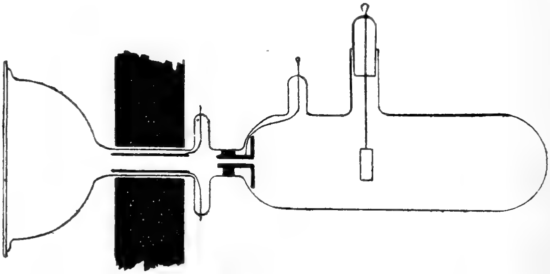
Tube filled with Air.

D.	*d.*	*e/m.*	*v.*
·5	1·4	10^4	2×10^8 cm./sec.
·4	1·1	$·78\times10^4$	2×10^8 ,,
·5	1·4	10^4	2×10^8 ,,
·45	1·3	$·96\times10^4$	$2·1\times10^8$,,
·4	1·4	$1·25\times10^4$	$2·5\times10^8$,,
·4	1·3	$1·08\times10^4$	$2·3\times10^8$,,
·3	1·1	$1·04\times10^4$	$2·6\times10^8$,,
	Mean	$1·01\times10^4$	

Tube filled with Hydrogen.

D.	*d.*	*e/m.*	*v.*
·7	1·7	$1·05\times10^4$	$1·8\times10^8$ cm./sec.
·4	1·3	$1·08\times10^4$	$2·3\times10^8$,,
·6	1·5	$·96\times10^4$	$1·7\times10^8$,,
·4	1·3	$1·08\times10^4$	$2·3\times10^8$,,
	Mean	$1·04\times10^4$	

Fig. 2.



The other type of tube (fig. 2), in which there were no auxiliary electrodes, had the following dimensions :—

Distance between the plates L and M = ·4 cm.
Length of plates . . . . = 4 cm.
Distance between screen and plate = 3·5 cm.

Hence if V is the potential-difference in volts between the plates, and D, as before, the deflexion in the electrostatic field,

$$\frac{e}{mv^2}=\frac{D}{5\cdot5\times10^9V}.$$

The magnet had been readjusted and furnished with new pole-pieces. If *d* was the magnetic deflexion, it was found that when 1 ampere was the current through the coils

$$\frac{e}{mv}=\frac{d}{4\cdot5\times10^4}.$$

With this tube the following values of *e*/*m* and *v* were obtained for the positive rays proceeding from the cathode in the opposite direction to the Canalstrahlen. The value of V was 400 volts.

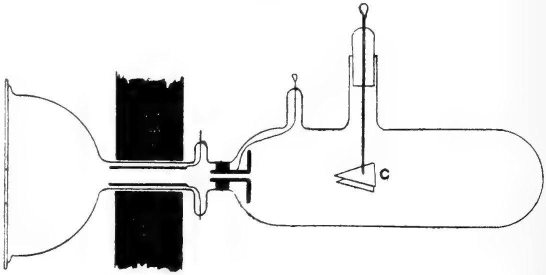
Tube filled with Air.			
D.	*d.*	*e*/*m*.	*v*.
·4	1·7	$·83\times10^4$	$2·2\times10^8$ cm./sec.
·3	1·6	$·9\times10^4$	$2·6\times10^8$,,
·5	1·9	$·72\times10^4$	$1·7\times10^8$,,
·5	2·0	$·9\times10^4$	$2·0\times10^8$,,
·4	1·8	$·9\times10^4$	$2·2\times10^8$,,
·2	1·3	$·9\times10^4$	$3·2\times10^8$,,
·4	1·7	$·83\times10^4$	$2·2\times10^8$,,
	Mean	$·85\times10^4$	
Tube filled with Helium.			
·5	20	$·9\times10^4$	$2·0\times10^8$ cm./sec.
·5	22	$1·08\times10^4$	$2·2\times10^8$,,
·5	21	1×10^4	$2·1\times10^8$,,
	Mean	$·99\times10^4$	

The deflexions of the Canalstrahlen in the same tube were also observed: this could easily be done by making the tube A the cathode. It was found that the structure of the Canalstrahlen was more complicated than that of the retrograde positive rays, the former showing two types of rays, characterized by values of e/m in the ratio of 2 to 1: the latter showed only one type of ray, this type coinciding, however, both as to value of e/m and the velocity with the type of Canalstrahlen rays having the maximum value of e/m. Some of the retrograde rays, as well as some of the Canalstrahlen, are deflected in a direction which shows that they carry a negative charge, and that their mass is comparable with that of the positively charged particles. I have determined the value of e/m and the velocity of these negative constituents of the retrograde rays, and find that the value of e/m for the negative particles is numerically equal to that of e/m for the positive ones; while the velocity of the negative ones is slightly, but only slightly (about 15 per cent. in my experiments), less than that of the positive ones.

Experiments with Goldstein's Double Cathodes.

Goldstein (*loc. cit.*) found that when the cathode consists of two parallel plates in metallic connexion, rays other than the cathode rays proceed from the space between the plates. If the plates are triangles, Goldstein found that a pencil of easily deflected cathode rays start from the middle points of the sides, while pencils of undeflected rays start from the corners of the triangle. The difference in the character of the rays can be strikingly shown by using helium in the discharge-tube, when the rays from the corners are red and those from the sides blue. I have examined the electric and magnetic deflexion of these rays, using for the purpose a tube such as that shown in fig. 3.

Fig. 3.

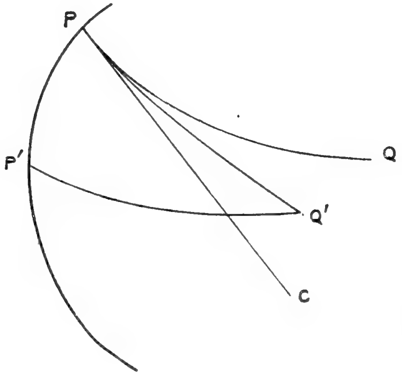


The cathode consists of two parallel triangles, and is carried by a stopper working in a ground-glass tube. By turning the stopper the different parts of the triangular cathode could be brought opposite to the opening in the tube and the distribution of the rays round the triangle studied. I found that this distribution depended a good deal upon the pressure of the gas in the discharge-tube. At all the pressures I tried, I found that the maximum emission of ordinary cathode rays was along the line starting from the middle points of the sides; at the higher pressures, this was the only direction in which the cathode rays could be detected; at very low pressures, however, rays could be detected starting from the corners of the triangle as well as from the middle points of the sides, few, if any, however, were given out in any intermediate position. With regard to the positive rays, I found at all the pressures I tried that these streamed off from both the corners and the middle points of the sides, there were but few in any intermediate position; the most abundant stream came, as was the case for cathode rays, from the middle points of the sides, but the disproportion between the streams from the corners and from the sides was nothing like so great for the positive as it was for the cathode rays; so that the ratio of the quantity of the positive rays to the quantity of cathode rays was greatest at the corners of the triangle.

I also measured the velocity and the value of e/m for the positive rays. I found that this was the same whether the rays came from the corners or from the sides, and the same as that of one type of Canalstrahlen (the type for which $e/m=10^4$), which went down the tube when A was made cathode. In the case of the positive rays coming from the triangular cathode, often only a small fraction were at all affected by electric and magnetic forces, by far the larger portions were quite undeflected by these forces; so that the phosphorescence of the screen when the magnetic force was applied to the tube presented the appearance of a bright central undeflected patch with a faintly luminous tail.

We can, I think, explain this distribution of the rays from the triangular cathode on the view that there is a reciprocity between the cathode rays and the positive rays of the following kind. The corpuscles in the cathode rays are due to the impact of positive ions at or near the cathode, while the positive rays are due to the impact of the corpuscles at some distance from the cathode. Let us consider now what happens when the lines of electric force in the neighbourhood of the cathode are curved as in fig. 4. A corpuscle starting along the normal from P would on account of its inertia not follow the line of force PQ but some path PQ′ between PC and PQ, PC being the normal to the cathode. If, now, the corpuscle produces a positive ion at Q′, this ion as it moves up to the cathode will not follow the path Q′P but some such path as Q′P′, striking the cathode at P′, and producing a cathode ray at P′. Thus the positive particle, if it strikes the cathode at all, will not give rise to a cathode ray to replace the one which produced it, but a ray starting from some other region. If, however, the line of force starting from P were a straight line, the positive particle produced by the ray at P would strike the cathode at P. When the discharge is in a steady state the number of corpuscles coming from *any region* must be proportional to the number of positive particles falling on that region. Now this will be the case when and only (except perhaps in very special cases) when the positive rays which strike the region are those produced by the corpuscles coming from it. For this to happen, the lines of force from that region must be straight lines. In the case of the triangular cathode there are six regions where the lines of force are straight, the middle points of the sides and the corners; and it is therefore from these regions that we should expect the discharge to be concentrated; and inasmuch as the region over which the lines are approximately straight is much greater at the middle points of the sides than at the corners, we should expect the maximum discharge to come from the middle point of the sides.

Fig. 4.



Magneto-Cathodic Rays.

Among the rays which sometimes occur near the cathode are some observed by Villard (*Comptes Rendus*, cix. p. 42, 1905) and called by him magneto-cathodic rays. These rays occur when the discharge-tube is placed in a strong magnetic field ; they are in the direction of the lines of magnetic force, and when subject to an external electric field they are displaced in a direction at right angles to the electric and also to the magnetic force. Ions moving through a medium in which they are under the action of electric and magnetic forces, and which resists their motion with a force proportional to their velocity, would behave exactly in this manner. For, just as a stone falling through a resisting medium moves at first with nearly uniform acceleration but after a time settles down into a state where the velocity is constant and equal to what is known as the limiting velocity, so ions, when exposed to electric and magnetic forces and to a resistance proportional to their velocity, will after a time settle down to a state where the velocity is uniform. The time required to reach this state is inversely proportional to the resistance when the velocity is unity and directly proportional to the mass of the ion. I have shown in my 'Conduction of Electricity through Gases' (2nd edition, p. 106) that when the ions have reached this state, and the magnetic force H is so large that Hu_0 is large compared with unity, u_0 being the velocity acquired by an ion when unit force acts upon it, and inversely proportional to the pressure, then the ions move nearly along the lines of magnetic force, but have a small component in the direction at right angles to both the electric and magnetic forces. In these respects they resemble Villard's magneto-cathodic rays ; the ions, however, would carry electric charges, while Villard could detect no charge when the magneto-cathodic rays entered a Faraday cylinder. It is perhaps possible that the absence of charge may have been due to the rays making the gas round the Faraday cylinder so good a conductor of electricity, that no appreciable charge could accumulate in the cylinder.

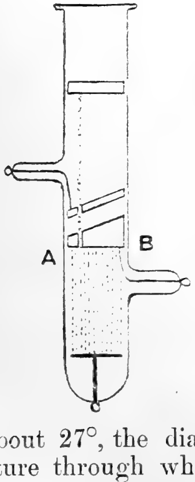
On the Method by which the Retrograde Rays acquire their Velocity.

We have seen that the velocity of those positive rays which move away from the cathode, and which are, when under observation, free from the influence of the electric field in the tube, is practically the same as that of the Canalstrahlen which have moved up to and then passed through the cathode. This result is remarkable, for in the latter case the action of the electric field which produces the discharge in the tube would increase the velocity of a positively charged particle, while in the former it would diminish it. The fact that the velocities in the two cases are very much the same suggests, at first, the suspicion that the electric field may not be accountable for any considerable portion of the velocity in either case, and that perhaps the particles forming these rays may, like the α particles given out by radioactive substances, start with a high initial velocity, much higher than they could acquire under the electric field. If we refer to the table of velocities given on pages 662–3, we shall see that there is not, in the different experiments, much variation in the velocity of the particles; these are always about 2×10^8 cm./sec., and could be generated by a fall through a potential-difference of about 20,000 volts. We must not, however, attach too much importance to the constancy of the velocity, for the range of pressure over which we can make accurate observations on the retrograde rays is very limited. For when the pressure gets very low, and the discharge requires a high potential-difference to send it through the tube, the rays are not bright enough to be observed; while if the pressure is more than a small fraction of a millimetre, the rays either do not reach the screen, or when they do reach it are so diffuse that the phosphorescent patch is not definite enough for its position to be measured with accuracy. And although even rough measurements show that at these high pressures the velocity of the particles is less than when the pressure is low, we should not be justified without further evidence in concluding that the initial velocity was less, for before reaching the screen the rays have had to make a long journey through the gas, and if the pressure is high, they will in their journey lose more of their velocity than when the pressure is low.

To test whether or not the velocity of the rays was due to the electric field, I tried the following experiments:—

In the first experiment, a piece of wire gauze was placed about 2 mm. in front of the perforated electrode of the tube represented in fig. 2 and well insulated from it; the gauze was used as the cathode and measurements of the velocity of the particles were made (1) when the perforated electrode was connected with the gauze, (2) when it was connected with the anode. In the second case, a particle if it retained its charge during the whole of its path, would in its journey between the gauze and the perforated electrode be at least as much retarded as it had been accelerated before reaching the gauze, and any velocity it possessed after passing through the perforated electrode must have been acquired from sources independent of the electric field; while in the first case its velocity would be measured by the electric field in the tube. On trying the experiment, it was found that though the Canalstrahlen were not nearly as bright in the second case as in the first, they were still quite perceptible, and that the velocity of those which got through was the same as the velocity of those reaching the screen in the first case. The fact that a large proportion of the rays are stopped by connecting the perforated electrode with the anode, while those which get through are not affected, shows that the velocity of the majority of them is not great enough to travel against the potential-difference between the electrodes; while the fact that some get through without diminution of velocity, indicates that when they are passing between the gauze and the perforated electrode, they are for the moment electrically neutral and without charge, and that they re-acquire, by losing a corpuscle, a positive charge after passing through the opening in the electrode by collision with the molecules of the gas. The following experiment shows in perhaps a simpler way than the preceding one that some of the Canalstrahlen are uncharged during a portion of their path. The perforated cathode (fig. 5) was wedge-shaped, the angle of the wedge being about 27°, the diameter of the cathode was 2 cm., the aperture through which the Canalstrahlen passed was about 5 mm. from the sharp end, the length of the path of the rays from one side of the cathode to another

Fig. 5.



was about 2·5 mm. A flat piece of wire gauze was fixed parallel to the upper face of the cathode (the face most remote from the anode), and insulated from it: the distance of the gauze from the cathode was about 3 mm. The Canalstrahlen travel at right angles to the lower face AB of the cathode. If the wire gauze is connected with the anode, and if the particles in the Canalstrahlen are charged, they will after passing through the cathode be acted on by a force which has a component at right angles to their direction of projection: thus if they are positively charged they will be bent to the right, if they are negatively charged to the left, while if they are uncharged they will be undeflected. The path of the rays when the pressure of the gas is not too low, can readily be traced by the luminosity they produce in the gas as they pass through it. On trying the experiment, it was found that when the gauze was connected with the anode the path of the few rays which got through the gauze was a straight line, coinciding in direction with their path before passing through the cathode. An easy way of seeing this is to connect by means of a key the gauze in quick succession with the anode and the cathode, when it is easily seen that though the Canalstrahlen are much more numerous in the latter case than in the former, the paths of those which do get through are identical, so that even when the gauze is connected with the anode some of the rays get through the space between *cd* and *cf* without suffering any deflexion, showing that they must be uncharged as they pass through this region. It is thus evident that a considerable number of the positively charged Canalstrahlen lose their positive charge by attracting when in the neighbourhood of the cathode a negatively electrified corpuscle; the mass of the corpuscle is so small in comparison with that of the particles forming the Canalstrahlen, that the addition of the corpuscle will not materially reduce the velocity of the Canalstrahlen. These rapidly moving uncharged particles will soon get ionized by collision, and by losing a negatively electrified corpuscle again become positively charged.

In my first paper on the positive rays (Phil. Mag. xiii. p. 561) I showed that at not too low pressures the appearance presented by the phosphorescence on the screen indicated that many of the particles in the Canalstrahlen were positively charged for only a portion of their path; the experiments just described are very direct evidence of this effect.

Again, at not too low pressures the Canalstrahlen are accompanied by negatively electrified particles having masses and velocities equal to those of the positive particles;

the negatively electrified particles in my experiments always being less numerous than the positive ones, in most cases very much so, in others the difference was not very great. We should expect the negatively electrified particles to be less numerous than the positive ones, since they would more readily lose their charges by collision.

I think that the positive rays which travel away from the cathode arise in the same way as the negative rays which accompany the Canalstrahlen. Let us consider what happens to the Canalstrahlen as they approach the cathode. When they reach the cathode some of them, as we have seen, get neutralized there, some will go further than this, and by gathering another corpuscle will become negatively electrified; those negatively electrified ones will, however, be repelled from the cathode, and under the action of the electric field will acquire a velocity of the same order as that acquired by the positive particles in their approach to the cathode. The rapidly moving electrified particles will in their course through the gas soon lose corpuscles by collision and thus become positively electrified, forming the positive rays which come from the cathode. Such rays, however, on the view just given start their journey with a negative charge.

The Canalstrahlen and the positive retrograde rays are not found with all types of discharge, thus in the type of discharge sometimes called the flash discharge: which occurs when a condenser of large capacity is earthed through the discharge-tube, the discharge passes as a column of uniform luminosity stretching from one electrode to the other, and there is no dark space in the neighbourhood of the cathode. In this case I have never been able to detect positive rays of any kind, either in front of or behind the cathode.

It is important to distinguish between the positive ions to be found in a gas, ionized by Röntgen rays and not exposed to electric fields strong enough to give to them very high velocities; and the positive ions which, like those in the Canalstrahlen, have very great kinetic energy. For between the positive charges and the molecules there are forces comparable in intensity to those which exist between the atoms of different elements having the greatest chemical affinity for each other. Thus, unless the positive ions possess more than a certain amount of kinetic energy, combination will go on with great rapidity and positively charged aggregates will be formed. If, however, the positive ions are moving with great rapidity, they will be in a state analogous to a gas at a very high temperature, and at these very high temperatures chemical combination does not take place. We have seen that the particles in the Canalstrahlen have a velocity of the order of 2×10^8 cm./sec. With a velocity such as this their kinetic energy would be equal to the mean kinetic energy of the molecules of a gas at a temperature of many hundred thousand degrees absolute; and though, as I have shown in 'Conduction of Electricity through Gases,' 2nd edition, p. 360, a positive ion might be expected to combine with a corpuscle if its velocity were but a little less than this, it would not be likely to do so with an uncharged molecule where the attraction would be very much less. If we take the case of a positive ion of mass m projected with a velocity V at right angles to the line joining it with a molecule of mass M, and at a given distance from it, the condition that the ion should be able to get away from the molecule is that

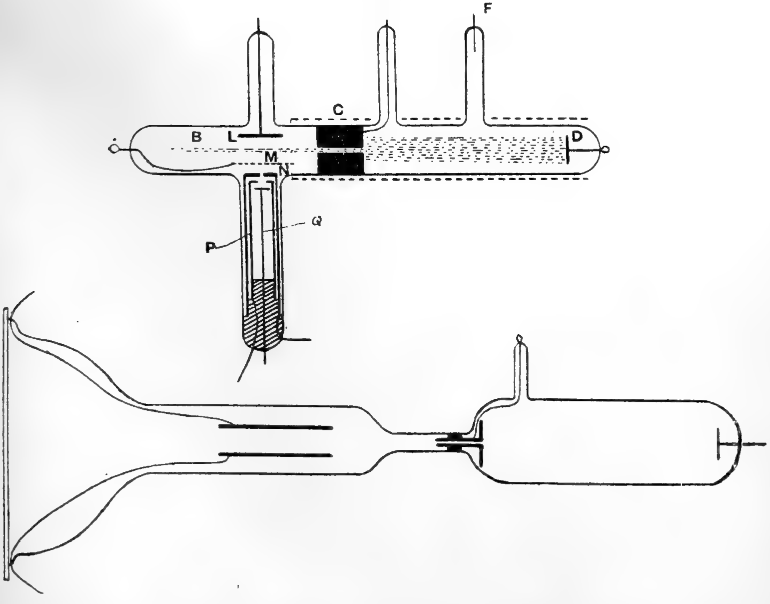
$$mV^2 \cdot \frac{M}{m+M}$$

should be greater than a certain quantity depending on the force between the molecules and the ion and the apsidal distance between them. Now if the force were independent of the mass of the molecule, we see that it would require a greater value of mV^2 to separate the ion from the molecule, when M is small compared with m, than when it is large. Thus if the kinetic energy of the ions were gradually to diminish say by collisions with the molecules, then if there were molecules of different masses in the gas through which the Canalstrahlen are moving, combination would occur first with the molecules of smallest mass, while the heaviest molecules would be the last to combine. The lightest molecules would thus have the first pick of the ions, which would therefore tend to be absorbed by the lightest gases. The force between an ion and a molecule is proportional to the volume of the molecule; and if the volume of a molecule were to increase as rapidly as its mass, the preceding considerations would not be valid. We have every reason, however, to believe that the changes in the volume of the molecules are not comparable with the changes in the masses: that, for example, the volume of a molecule of oxygen, instead of being sixteen times that of a molecule of hydrogen, is hardly more than twice, so that the increase in the forces exerted by the heavier molecules is not sufficient to counteract the influence of the increased mass.

The Nature of the Positive Ions in different Gases when the Ionization has settled into a steady state.

The Canalstrahlen are formed in very intense electric fields, and the kinetic energy which they possess tends to prevent them combining with the molecules and corpuscles around them; they are thus under quite different conditions from the ordinary ions produced in a region where the electric force is small or absent, for these have time before being removed from the field to enter into combination with the molecules, the system of molecules and ions getting into a steady state if the source of ionization is constant. The difference between this case and that of the Canalstrahlen may be compared with the difference between the state of a mixture of different chemical substances after they have entered into combination and settled into a state of equilibrium and when they were first mixed. I thought that it would be interesting to determine the values of e/m for the ordinary ions simultaneously with the determination of e/m for the Canalstrahlen in the same discharge-tube. The method used to determine e/m for the ordinary ions was as follows. A tube represented in fig 6 was sealed on to the tubes such as have already been described in connexion with the determination of e/m for the Canalstrahlen. B is an ionization chamber, the gas in it

Fig. 6.



being ionized by cathode rays coming down through the tube C which was connected with the earth. The cathode was at D in front of the tube, the anode in a side tube F. Three parallel electrodes, L, M, N, were put in the ionization chamber. The first, L, was a plate at the top of the tube ; the second, M, near the bottom of the tube was a piece of wire gauze about a millimetre above N, which was the top of an earth-connected cylinder, with a small hole ·9 mm. in diameter bored through the centre, the thickness of this plate was 1·6 mm. By means of these electrodes ions could be collected and some of them sent through the hole with a definite and known velocity. Suppose for example we wish to send a stream of positive ions through the hole. A small difference of potential (in our experiments generally that due to two Leclanché cells) was maintained between the plates L, M, L being at the higher potential. The electric field produced in this way caused a stream of slowly moving positive ions to pass downwards through the gauze ; by means of a potential divider any potential-difference between 10 and 800 volts could be established between the gauze and the top of the cylinder, the gauze being positive to the cylinder. The ions collected by the upper plates thus entered into a much stronger field which gave to them a velocity much greater than that with which they entered it, so that when they passed through the hole they were all moving with practically the same velocity.

Beneath the top of the box there was an insulated Faraday cylinder (P) connected with a Wilson electroscope. The distance between the top of the cylinder and the bottom of the plate was 1 mm. in one piece of apparatus, ·5 mm. in another ; the diameter of the hole in the Faraday cylinder was 2·3 mm. Beneath this hole there was a metal disk insulated and connected with another Wilson electroscope; the plane of the disk was parallel to N and thus at right angles to the undeviated path of the ions, the axis of the hole in N passed through the centre of the disk. The part of the tube below N was placed between the poles of a powerful electromagnet, the lines of magnetic force being at right angles to the undeviated path of the ions, and parallel to the direction of the cathode rays. To protect the cathode rays coming from D from the magnetic field, a deep cutting was made in one of the poles of the electromagnet and the portion from C to D of the tube placed in this and then covered over with layers of soft iron. This tube was sealed on to the tube T of the kind already described, for the determination of e/m for the Canalstrahlen.

If the ions travelled without deviation parallel to the axis of the tunnel in N, they would all strike against the disk Q, and the Faraday cylinder would not receive any charge. If, on the other hand, they were very much deflected by the magnetic field, they would all strike against the Faraday cylinder and the disk would not receive any charge. If we measure the charges received by the disk and the Faraday cylinder during any time, the ratio of the charges will be the ratio of the number of ions which strike against the disk to the number striking against the cylinder. The readings of the electroscopes do not give us directly the charges received by the systems to which they are attached, but the potentials to which these systems are raised. We can, however, if we know the ratio of the potentials easily deduce that of the charges. For let E_1V_1 be the charge and potential of the Faraday cylinder, E_2, V_2 the corresponding quantities for the disk.

Thus if the q's represent coefficients of capacity, we have

$$E_1 = q_1V_1 + q_{12}V_2$$

$$E_2 = q_{12}V_1 + q_2V,$$

so that

$$\frac{E_1}{E_2} = \frac{q_1V_1 + q_{12}V_2}{q_{12}V_1 + q_2V}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

To determine the q's by experiment we proceed as follows. Given a charge to the disk, the cylinder being insulated and uncharged, then if V_1' and V_2' are respectively the potentials of the cylinder and disk as determined by their electroscopes,

$$q_1V_1' + q_{12}V_2' = 0, \quad \text{since } E_1 = 0.$$

Thus if α is the ratio of the potential of the cylinder to that of the disk when the cylinder is uncharged,

$$q_1 = -q_{12}\frac{V_2'}{V_1'} = -\frac{q_{12}}{\alpha}.$$

Similarly, if β is the ratio of the potential of the disk to that of the cylinder when the disk is uncharged, we have

$$q_2 = -\frac{q_{12}}{\beta}.$$

Substituting in equation (1) we have

$$\frac{E_1}{E_2} = \frac{\beta}{\alpha}\,\frac{(V_1 - \alpha V_2)}{V_2 - \beta V_1}.$$

The quantities α and β are very easily determined, and from this equation we can deduce the ratio of the charges when we know that of the potentials. By using two electroscopes and determining by means of them the *ratio* of the charges received by the cylinder and disk, we eliminate any irregularities that might arise from variations in the working of the coil used to produce the cathode rays which ionize the gas in the ionization chamber.

If an ion is projected through the tunnel in N along the axis of the tunnel, it will, if there is no magnetic field acting upon it, travel along a straight line and hit the disk. If there is a magnetic field its path, after getting through the hole, will be a circle, since if it is free when once it has got through the hole from any electric force, it will, however, continue to hit the disk until the radius of this circle is less than the radius of the circle passing through the hole, the edge of the disk, and touching at the hole the axis of the tunnel. If d is the distance of the disk below the hole, a the radius of the disk, r the radius of this circle is equal to $\frac{d^2+a^2}{2a}$. When the radius of the path of the ion is less than this, the ion will give up its charge to the Faraday cylinder; when it is greater than this it will give up its charge to the disk.

If H is the magnetic force acting on the ion, e its charge, m its mass, and r the radius of its circular orbit,

$$\mathrm{H}er=mv,$$

if V is the potential-difference between the gauze and the top of the box

$$\mathrm{V}e=\tfrac{1}{2}mv^2;$$

thus

$$\mathrm{H}^2r^2\frac{e}{m}=2\mathrm{V}.$$

Thus when H increases through the value given by the equation

$$\mathrm{H}^2\left(\frac{d^2+a^2}{2a}\right)^2\frac{e}{m}=2\mathrm{V}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

there ought to be a large increase in the ratio of the charge on the Faraday cylinder to that on the disk. If the pencil of ions coming through the hole were indefinitely thin, and if all the ions travelled with the same velocity in the same direction, the transference of the charge from the disk to the cylinder would be quite abrupt. With a magnetic force less than a certain value, all the charge would be on the disk, while with a force greater than this all the charge would be on the cylinder. In my experiments the diameter of the hole, ·9 mm., was a considerable fraction of the length 1·6 mm. of the tunnel, so that there was a considerable latitude in the direction of propagation of ions through the hole. This has the effect of making the ratio of the charges on the cylinder and disk change much less abruptly than if they were all projected in the same direction, since those ions which are projected towards the side of the cylinder to which they are bent by the magnetic field, will be carried to the side by a smaller magnetic force than those which are projected at right angles to the disk. When the hole is very small, the charge carried by the ions passing through it in a given time is also very small, and the potentials of the disk and cylinder change very slowly. The purpose for which these experiments were made was not so much to get accurate values of *e*/*m* for the ions as to find out whether these had masses comparable with the mass of an atom of hydrogen, or of oxygen, &c. The arrangement used was adequate for doing this, and had the advantage of giving a supply of ions which could produce measurable effects in a minute or so, thus avoiding many difficulties as to insulation which crop up when the experiments have to be extended over very much longer periods. Experiments with very much smaller holes are, however, in progress.

The strength of the magnetic field between the poles was determined by comparing the currents induced in a small coil when suddenly withdrawn from the magnetic field with the current obtained by turning an earth inductor through 180° in the earth's magnetic field. When the pole-pieces were 1·15 cm. apart, the magnetic forces H for different currents through the coils of the electromagnet were as follows :—

Current through Electromagnet in amperes.	H.
·5	1330
1	2570
2·5	4000
2	4900
2·5	5600
3	6000
3·5	6400
4·0	6660

When, as in our Faraday cylinder, $d=5$ mm. $e=2$ mm., the radius of the critical circle $\frac{d^2+a^2}{2a}=\cdot 725$ mm., we see by the application of equation (2) that if $e/m=10^4$, the potential-difference V required to reduce the radius of the orbit to the critical value would, when the currents through the electromagnets were 1, 2, 3, 4 amperes, be respectively 170, 620, 900, 1100 volts. These are the potential-differences between the gauze and the top of the cylinder N required to send the ions to the plate. The following table gives the charge acquired by the disk when the sum of the charges on the disk and Faraday cylinder was 100 for different strengths of magnetic fields; assuming that all the ions carry the same charge, these numbers represent the percentage of the ions passing through the hole which reach the disk. In the table V is the potential-difference between the gauze and N in volts, ι the current through the electromagnet in amperes, and n the percentage of ions which reach the disk. The gas in the tube was hydrogen.

	V=10.	V=20.	V=30.	V=40.	V=50.	V=60.	V=80.
ι	n	n	n	n	n	n	n
1......	17	18·4	18	18	18	19	22·8
2......	18	23	23	22	22	20	19
3......	11	16	22	23	25	26	21
4......	8	9	20	22·5	25	27	26

	V=100.	V=120.	V=140.	V=160.	V=180.	V=420.
1.....	23	25	24	28	31	50·5
2... ..	16	17	22	14	12	12
3......	21	19	19	16	9	9
4......	25	23	21	18	15	8

On looking at the numbers we see that until the voltage exceeds 160 volts there is no appreciable difference between the number of ions going to the disk when the magnetic field is due to a current of 1 ampere, and when it is due to 2 amperes. We saw, from the preceding calculation, that a voltage of 170 volts would carry ions for which $e/m=10^4$ to the disk against the electric current, while it would require about 700 volts to drive them across when the current was

2 amperes, thus the difference which sets in between the results when $\iota=1$ and $\iota=2$ at 160 volts indicates the presence of a considerable number of ions for which $e/m=10^4$.

For voltages between 30 and 160 there is no appreciable difference with currents ranging from 1 to 4 amperes, while for voltages less than 30 there is an appreciable diminution in the number which get to the disk when the current through the electromagnet is raised from 1 to 4 amperes. This indicates that there are some ions which, under a voltage of say 25 volts, are stopped when the magnetic field is that due to 4 amperes, but can get across when it is due to 2 amperes. Since 1100 volts would just drive particles for which $e/m=10^4$ across the field due to 4 amperes, 25 volts will drive particles for which $e/m=10^4/(1100/25)=10^4/44$ across this field. For the field due to 2 amperes 620 volts are required to drive particles for which $e/m=10^4$, 25 volts will drive particles for which $e/m=10^4/(620/25)=10^4/25$. From the preceding results we infer the presence of ions for which e/m is between $10^4/44$ and $10^4/25$. Such ions might be molecules of nitrogen or oxygen due to traces of air in the discharge-tube; these, however, are only a small fraction of the whole number of ions. The pressure of the hydrogen in this case was about ·003 mm. It is necessary to work at pressures so low that the mean free path of the ion is large compared with the distance d.

Let us now compare the results obtained when the apparatus had been repeatedly filled with oxygen obtained by heating permanganate of potash in a tube fused on to the discharge-tube, running the coil with the gas at the pressure when the discharge passes most easily, and then filling and repumping; the oxygen on its way from the permanganate to the discharge-tube went through a worm immersed in liquid air to free it from any traces of water vapour given off from the permanganate. No hydrogen lines could be detected in the spectrum. The Faraday cylinder had been taken down between this experiment and the preceding one, and slightly altered so that the radius of the critical circle in this case when $d=4$, $a=2{\cdot}5$, is ·47 cm., hence the potentials required to force ions for which $e/m=10^4$ across to the disk when currents 1, 2, 3, 4 amperes flow through the coils of the electromagnet are respectively 72, 270, 400, and 480 volts. The pressure of the oxygen was ·009 mm.

The following are the results of the experiments, n as before being the percentage of ions which reach the disk :—

	V=10.	V=15.	V=20.	V=25.	V=30.
ι	n	n	n	n	n
1.........	75	82	81	81	80
2.........	56	62	68	72	72
3.........	36	43	50	58	61
4.........	28	27	43	50	56

	V=40.	N=100.	V=200.	V=300.	V=400.
1.........	82	81	81	81	81
2.........	78	80	80	80	81
3.........	68	78	76	79	80
4.........	63	76	79	80	80

The figures in this case are quite different from those for hydrogen. We see that for voltages over 100 the charge on the disk is not appreciably diminished when the current through the electromagnet is raised from 1 up to 4 amperes; this shows that the number of ions with masses comparable with those of a hydrogen atom is too small to be detected, for such ions under a field of 100 volts would have been able to make their way to the disk against a magnetic field due to 1 ampere, but not that due to 2 amperes or more; thus if these had been present in any considerable number, the number reaching the disk when $\iota=1$ would have been appreciably greater than when $\iota=2$.

The fact that 20 per cent. under these voltages reach the Faraday cylinder is due, I think, to the obliquity of the ions as they come through the hole, and to the diffusion they suffer in passing through the gas. Under the smaller voltages the effect of the magnitude of the magnetic field is very apparent; thus until the voltage is above 20 the majority of them are stopped by a field of 4 amperes, indicating that the mass of the majority of the ions is not greater than 480/20 or 24 times the mass of an atom of hydrogen. In fact that the majority of the ions have masses comparable with that of the molecule of oxygen, and are not aggregates of several molecules.

Though the preceding list shows that the number of ordinary hydrogen ions in this gas was too small to be detected, yet when the Canalstrahlen produced in a tube in direct connexion with the one in which the ionization occurred were investigated they were found to be well developed, and to give exactly the same value for e/m as when the apparatus had been filled with hydrogen, as in the experiments discussed on pages 678, 679.

By measuring the relative numbers of ions carried to the cylinder and the disk by different voltages against a constant magnetic field we can readily estimate the relative amounts of heavy and light ions in the gas. Indeed I think that by using a very small hole in the plate N a very fair analysis of the gas in the ionizing chamber might be made. Thus suppose the magnetic field were that due to 3 amperes through the coils of the electromagnet; then with apparatus of the dimensions used in one of the experiments the ions for which $e/m=10^4$ would not reach the disk until $V=900$, while those for which $e/m=\frac{1}{2}10^4$ would reach it when $V=450$, those for which $e/m=\frac{1}{16}10^4$ when $V=56$, those for which $V=\frac{1}{32}10^4$ when $V=28$. Thus for ions of different atomic weights the stages are well separated, and the relative numbers of the ions of the different kinds could be determined. With the comparatively large hole used in the experiments described above it was quite easy to observe the gradual diminution in the number of the lighter ions, as each dose of oxygen was supplied to the tube and then pumped out. This method of analysis is applicable at pressures far below those at which even spectrum analysis is available.

By reversing the potentials in the ionization chamber we can collect and send through the opening in the plate negative ions and corpuscles which are present in large numbers in the gas. The corpuscles, on account of their small mass, are prevented from reaching either the Faraday cylinder or the disk by a comparatively small magnetic force, and then only negative ions get through to the conductor. The proportion of these reaching the disk and cylinder with changes in the electric and magnetic fields show variations of a similar character to those observed for the positive ions.

The relative rates at which the cylinder or disk charged up according as positive or negative ions were supplied to them from the ionization chamber was determined. When the magnetic field was weak the rate of charging was much more rapid with negative than with positive ions; this was due to the excess of corpuscles in the ionization chamber; when, however, the magnetic field was strong enough to stop the corpuscles, the rate of charging under potential-differences of the order of about 200 volts was about the same for the negative as for the positive ions, while with smaller differences of potential, say 25 volts, the rate of charging with negative ions was only about 1/6 of that with positive. The positive ions seem, in the ionization chamber, to be moving more rapidly than the negative, for with no electric field in that chamber both cylinder and disk acquire a positive charge when the magnetic field is strong.

With the apparatus we have been describing we can measure simultaneously the values of e/m for the ions and the Canalstrahlen in the same vessel, and the experiments we have described show that we can get a complete change in the character of the ions without any change in the nature of the Canalstrahlen ; this is, I think, strong evidence that the particles composing the Canalstrahlen are the same from whatever source they may be derived.

It might, however, be urged that although the tube might be cleared of hydrogen to begin with, this gas might be driven by the discharge out of the cathode and that this might be the source of the Canalstrahlen, and I have noticed a phenomenon which at first sight suggests this view. I have observed that under some conditions there is a lag amounting in some cases to half a minute or so between starting the discharge and the appearance of the phosphorescence due to the canal-rays; this might be explained by supposing that it takes time to liberate sufficient hydrogen to produce appreciable Canalstrahlen. I have made many experiments on this lag and these show that it has no special connexion with hydrogen, but is due to an alteration in the pressure of the gas produced by the discharge. It is well known that the Canalstrahlen are only well developed when the pressure in the tube is between certain limits. It is only when the initial pressure is near to, but outside, one of these limits that the lag occurs, and then the alteration in pressure which occurs when the discharge passes may accumulate until the pressure is brought within the required limits. That this, and not the introduction of hydrogen rather than any other gas, is the explanation of the lag is I think proved in the following experiments:—If the presence of hydrogen were all that is wanted for the Canalstrahlen, then the lag should not occur when the tube is filled with hydrogen : we find that the lag occurs when the tube is filled with hydrogen, as well as when great precautions have been taken to remove this gas from the tube. Again, in a tube from which hydrogen has been removed and the lag is well developed, the admission of a small quantity of dry air will remove the lag just as effectively as the admission of hydrogen. When once the lag has been got rid of it is necessary to give the tube a long rest from the discharge before it returns. The fact that the lag may be destroyed by admitting a small quantity of gas shows that it is due to the alteration in pressure and not to a change produced by the discharge in the surface of the electrode. This can also be proved in the following way: two discharge-tubes A and B are connected together and with the pump, and the pressure is adjusted so that both A and B show the lag; then if the discharge is sent through A until the lag disappears from that tube, it will be found to have simultaneously disappeared from B, though no discharge has been running through this tube.

It is somewhat remarkable that we do not, when the tube is filled with oxygen, get any trace in the Canalstrahlen of particles having masses comparable with those of the ions in oxygen. For though such ions would not be formed in very intense electric fields, there are places in the discharge-tube where the electric field is weak, as, for example, outside the cathode dark space; we might expect positive ions to be formed in these regions, and then dragged by the electric field up to and through a perforated cathode mingling with the Canalstrahlen. The reason that we get no evidence of these oxygen ions in the Canalstrahlen is, I think, as follows: Let A be a positive ion, B a corpuscle, and let the relative velocity of A and B at the instant under consideration be at right angles to AB and equal to V. Then it is easy to show that A and B will not part company if $\frac{mV^2}{2}$ is less than $\frac{e^2}{AB}$, where m is the mass and e the charge of the corpuscle, M the mass of the ion being supposed very large compared with m. Thus if the relative velocity falls below a certain value the ion and the corpuscle will form a neutral doublet and will cease to be a possible constituent of the Canalstrahlen. If the ion is moving much more rapidly than the corpuscle, then V will be the velocity of the ion, and we see that the smaller this velocity the more likely is it to have its charge neutralized. M being the mass of the ion $\frac{1}{2}MV^2=Pe$, where P is the potential-difference moved through by the ion, thus the ion will be neutralized unless $P > \frac{M}{m} \cdot \frac{e}{AB}$. Thus to protect a heavy ion, for which M_1 is large, from being neutralized it must be subject to a much stronger electric field than would be necessary for a light ion; thus, if there were a mixture of different gases in the discharge-tube, the ions formed from the lighter gases would persist longer than those formed from the heavier ones.

An illustration of this result is furnished by the fact that, as I showed in the paper (Phil. Mag. ser. 5, vol. xiii. p. 561), the only ions besides those of hydrogen which can be observed in the Canalstrahlen are those of the next highest gas helium, which, when the discharge passes through helium, can be observed in the Canalstrahlen without difficulty.

The places where the neutralization of the positive ions by the corpuscles takes place will be either quite close to the cathode or when the cathode is perforated in the region behind the cathode; for in front of the cathode where the positive ions are produced, though the velocity of these ions will be small, since they are in a feeble electric field, yet the corpuscles which have come from the cathode will have passed through a great potential-difference and will have a very high velocity; thus the relative velocity of the positive ions and the corpuscles will be very large. Quite close to the cathode the velocity of the corpuscles will be very small, and though the velocity of the ion will be much greater than in the former case, yet since the mass of the ion is so much greater than that of the corpuscle, the velocity acquired by the ion under the same potential-difference will be small compared with that acquired by the corpuscle, so that the relative velocity of the two close to the cathode will be much less than at a greater distance in front of it, so that combination is much more likely to occur near to the cathode, or if the cathode is perforated behind it.

If the forces between a small positive ion and an uncharged molecule are independent of the atomic weight of the molecule, or only increase slowly as the atomic weight increases, then such an ion is more likely to attach itself to a light molecule than to a heavy one; for we can show that the condition that the ion and the molecule should separate is that

$$\frac{\mathrm{M}\,\mathrm{M}'\,\mathrm{V}^2}{\mathrm{M}+\mathrm{M}'}$$

should be greater than a certain quantity depending only on the force between the systems and their distance apart when nearest together. M is the mass of the ion, M′ that of the molecule, and V the relative velocity of the two at the absidal distance. If M′ is very large compared with M the condition is that $\mathrm{M}v^2$ should be greater, while if M′ were equal to M, the condition is that $\frac{1}{2}\mathrm{M}v^2$ should be greater than the same quantity; thus in the second case the ion would take twice as much energy to get free as in the first, and so would be more likely to combine with the molecule.

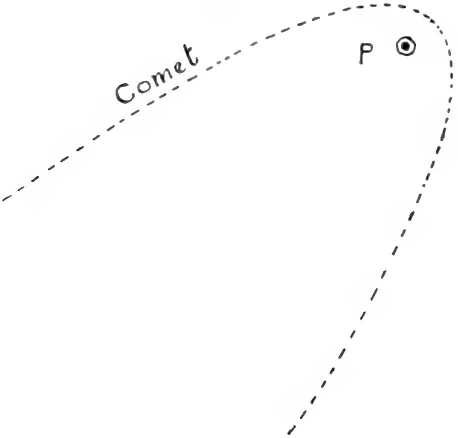
Nature of Ionization by Cathode Rays.

If, as seems most probable, the positively charged particles are produced from the ionization of the gas by cathode rays, the study of the processes by which this ionization is accomplished may be expected to throw considerable light on the nature of the positive rays. When a gas is ionized by cathode rays, secondary cathode rays are generated, and the author has recently shown (Proc. Camb. Phil. Soc. xiv. p. 540, 1908) that the maximum velocity of the secondary rays is independent of the velocity of the primary rays. A comparison of the velocity of the secondary rays from gases, as determined in my experiments, with those from metals, measured by Füchtbauer (*Phys. Zeits.* vii. p. 748, 1908) shows that there is not much difference between the two. The velocity of the rays from gases was that due to a potential-difference of 40 volts, of those from metals that due to a potential-difference of 33 volts; the difference between these results is not greater than could be explained by errors of experiment. Thus, as far as our present knowledge goes, the velocity of a secondary cathode ray is independent both of the velocity of the primary ray and varies but little with the nature of the molecule from which the secondary ray is projected. The first result shows that the energy of the secondary ray is not acquired by a corpuscle in the primary rays striking against one in a molecule of a gas and imparting to it sufficient energy to force it out of the molecule, for if this were the case we should expect the energy of the secondary ray to vary quickly with that of the primary. Neither does it seem likely that the energy in the secondary ray is due to a general explosion of the molecule of the gas produced by a gradual accumulation of energy in the molecule from impacts with the primary rays, for then we should expect the energy in the secondary rays to depend largely on the chemical nature of the molecules.

As a working hypothesis to account for these very striking properties of the secondary rays I would suggest that perhaps the first stage is ionization by cathode rays, may be the separation from the molecule, not of a single corpuscle, but of an electrically neutral doublet consisting of a negatively electrified corpuscle in rapid rotation round a much more massive particle with a positive charge, and that these doublets may be the same from whatever molecule they may be ejected. The secondary cathode rays are due to the subsequent breaking up of this doublet, their energy being the kinetic energy possessed by the corpuscle when rotating round the positive charge. This hypothesis would also explain the constancy of e/m in the Canalstrahlen produced from different gases.

There are many ways in which the doublet might get broken up after it had escaped from the molecule. Thus, for example, if another corpuscle, which we shall call for brevity a comet, were under the attraction of the positive particle to describe an orbit such as that shown in fig. 7,

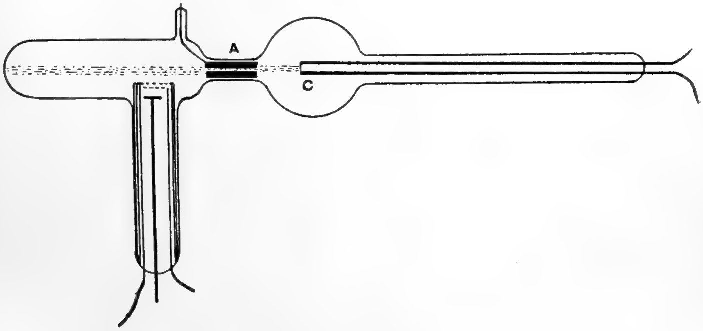
Fig. 7.



then when the comet was in the immediate neighbourhood of the positive particle, it would neutralize the attraction of this particle on the corpuscle in the doublet; thus this will move off with undiminished velocity along a straight line, and when the comet has left the system, will, if not free, be at any rate further from the positive particle than it was before, and still possessed of its original kinetic energy; if it did not get free under the influence of the first comet, a repetition of the process by other comets might liberate it from the doublet. The same effect might be produced if the positive part of the doublet came close to a gaseous molecule, which behaved like a conductor of electricity; the negative charges induced on the conductor would balance the attraction of the positive particle on the corpuscle in the doublet, and just as in the previous case, the corpuscle would be able to get off with undiminished velocity.

The questions now arise, can we get any experimental evidence of the existence of these doublets, and is it possible that such systems, if they existed, could have escaped the careful scrutiny which has been given? The second question is more easily answered than the first, for these doublets being uncharged would not possess the properties which make the positive rays or the cathode rays so noticeable; thus they would not be deflected by uniform magnetic or electric fields, and the absence of the charge might involve also a loss of the power of producing luminosity when they pass through a gas, and thus render them invisible. With regard to the first question I have made some preliminary experiments, the results of which suggest the existence in the neighbourhood of cathode of neutral systems, such as the doublets which dissociate into corpuscles and positive ions. The arrangement used in these experiments is represented in fig. 8.

Fig. 8.



The idea of the experiment was as follows:—If the secondary cathode rays are produced from the primary without the intervention of the neutral doublet stage, then, as the secondary ionization is due to the secondary cathode rays, a strong electric field, arranged so as to stop the negative corpuscles forming the secondary cathode rays, ought to act as a complete screen against this ionization. If, on the other hand, there is an intermediate stage between the primary and secondary rays, and if this stage consists of neutral doublets, then some of these ought to be able to get through the strong electric field, if this is quite close to the primary rays, because it is only those secondary rays which are produced from the doublets whilst the latter are passing through the field which would be stopped; the doublets themselves will not be stopped, and if they last long enough to get through the field they ought to give rise to ionization on the other side. To test this view the apparatus represented in fig. 7 was used. A copious supply of slowly moving primary cathode rays was produced from the hot Wehnelt cathode C, these passed through a hole in the anode A, the anode was earthed, the primary rays passed over the top of the side tube, T; across the top of the tube were stretched two parallel pieces of wire gauze about a millimetre apart: the upper gauze was earthed, the other could be charged negatively by connecting it with the negative terminal of a battery of small storage-cells, the positive terminal of which was earthed. When the lower gauze was earthed as well as the upper, the tube was filled with the glow due to the secondary rays. When the lower gauze was charged to a negative potential of about 40 volts, this glow became exceedingly faint; but that the gas below the gauze was ionized was shown by the fact that when the negative potential of the lower gauze was increased to about 200 volts, a potential quite insufficient to produce luminosity in an unionized gas, the tube again became full of luminous glow. Thus something capable of ionizing the gas was able to traverse the strong electric field. There are two sources of ionization which have to be eliminated before we can assign this ionization to the existence of neutral systems traversing the electric field,—the ultra-violet light coming from the luminous discharge in the main tube, and soft Röntgen rays produced by the slowly moving primary cathode rays. To test whether it was due to ultra-violet, a thin plate of quartz was placed over the top of the upper gauze: with this arrangement no luminosity could be detected in the side tube under the conditions as to potential and so on which gave bright luminosity in the tube when the quartz was absent. Hence I conclude that the luminosity was not due to ultra-violet light. To test whether it was due to soft Röntgen rays, taking the quartz away, I got a bright luminosity in the side tube with the primary rays passing horizontally down the tube, then by means of a magnet I bent the primary rays so that they struck the glass of the tube just above the side tube, the path of the rays being represented by the dotted line of the figure. This made the rays themselves further from the side tube, but brought the places where they struck the glass, the sources of the Röntgen rays, much nearer to that tube; so that if the ionization in the side tube were due to Röntgen rays it should be increased by the introduction of the magnet, while if it were due to the neutral doublets it would be diminished. As a matter of fact the luminosity in the side tube almost disappeared when the rays were deflected in this way, showing that it was not due to Röntgen rays, while the effect is what we should expect if the ionization were due to uncharged systems.

In the preceding experiments there is the possibility that the ionization might arise in some such way as the following. The secondary cathode rays would have to penetrate some way between the two pieces of gauze before they were stopped, and if they collided against the molecules of the gas they might ionize it: the positive ions so produced would, under the action of the electric field between the pieces of gauze, acquire considerable kinetic energy when they reached the lower gauze, they would travel some distance after passing through before they were stopped and brought back to the gauze, and would thus have an opportunity of ionizing the gas below the gauze by collision. The negative corpuscles produced in this way would be repelled from the lower gauze and might acquire sufficient energy to produce fresh ions by collisions, and thus give rise to the luminosity observed below the gauze. To eliminate this source of ionization, a strong magnetic field was used to prevent any of the secondary cathode rays from straying into a region where they could affect the ionization in the region under observation. Two arrangements were used for this purpose. In the first, the tube with the hot lime cathode (fig. 8) was used. The primary cathode rays were coiled up into a small bunch by means of a strong electromagnet placed just under the tube, from which the cathode rays emerge, the cathode rays in the early part of their path were screened from the effect of the magnetic force by thick iron plates. The magnetic force was strong enough to prevent the primary cathode rays, which were produced under a potential difference of about 250 volts, from travelling more than 2 or 3 millimetres across the lines of force. The path of the rays when not under the influence of magnetic force never approached within this distance of the two pieces of gauze, and the deflexion of these rays by the magnet was away from the gauze. No luminosity could be seen close to the gauze next to the discharge-tube. Nevertheless, when the lower gauze N was at a potential of about 200 volts, the upper gauze being earthed, there was a perceptible luminous discharge in the side tube, showing that in spite of the strong magnetic field something must have passed across the gauze and ionized the gas in the side tube. A modification of this experiment was tried, in which the two pieces of gauze were connected together and with the earth, and an insulated plate connected with a charged electroscope was placed in the side tube at some distance from the gauze; the ionization in the side tube produced a leak of the electroscope. It was found that even when the primary cathode particles were coiled up by the strong magnetic field into a small bundle at the mouth of the tube from which they emerge, there was a rapid leak of the electroscope showing that the gas in the side tube was ionized. The leak was more rapid when the electroscope was positively than when it was negatively charged.

A somewhat similar experiment was also tried with the apparatus represented in fig. 6. A magnetic field of 1200 was established between the pole-pieces, and the plates L, M, N connected with the earth, so that there was no electric field in the ionizing vessel. Under these circumstances neither the cylinder nor the disk received any electric charge when the electric discharge passed through the upper tube. The Faraday cylinder was then disconnected from the electroscope and charged up positively to about 40 volts; the disk now acquired a positive charge, when the cylinder was charged to −40 volts the disk got a negative charge. This shows that the gas between the cylinder and disk was ionized, though the magnetic field prevented any negative corpuscles from entering this region.

Though we have given reasons for thinking that the Röntgen rays are not the cause of the ionization in the side tube when this is exposed to strong magnetic fields, soft Röntgen rays are produced by the impact of the primary cathode rays against the molecules of the gas in the tube. This was proved by covering the end of the side tube (fig. 8) with thin aluminium foil and placing in the side tube behind the foil an insulated metal plate connected with a charged electroscope. The escape of electricity from this plate could not be ascribed to ionized gas making its way from the main tube into the side one, for the only channel of communication was through a long stretch of glass tubing from the main tube to the pump, and then through another long tube from the pump to the side tube; since the opening between the main tube and the side tube was closed, it was necessary to exhaust them separately. When the primary and secondary cathode rays were well developed and the main tube filled with a bright glow, the charge from the electroscope rapidly leaked away whether it were positive or negative. The gas in the side tube is thus ionized by rays which have passed through the thin aluminium foil. The leak was, however, completely stopped when, by means of a strong magnetic field, the primary and secondary cathode rays were rolled up into a small bundle at the mouth of the tube, from which they emerge just above the aluminium foil. In this case the length of the path of the rays after coming through the tube was only 2 or 3 mm., and there was hardly any luminosity in the tube. The aluminium foil prevents the ionization in the side tube in this case, for if the foil is removed the gas, as we have already stated, is ionized.

The preceding experiments are in harmony with the view that neutral doublets are one of the stages in the process of ionization; they must, however, be regarded as only preliminary. More extended experiments are necessary before we can be certain that the effects are not due to some very easily absorbed kind of radiation or to the diffusion of very slowly moving ions.

We have hitherto considered the case when the primary ionization was due to cathode rays, but there are reasons for thinking that similar doublets are produced when the ionization is produced by positive rays. Thus Füchtbauer (*loc. cit.*) found that the velocity of the secondary cathode rays from metals was the same whether they were produced by cathode rays or Canalstrahlen. It is sometimes argued that the much greater difficulty experienced in saturating a gas ionized by α particles than one ionized in any other way, shows that results of ionization are different in the two cases : this result is, however, exactly what we should expect if there were no such difference. For when a gas is ionized by α rays, each α particle produces an enormous number of ions, but there are comparatively few particles, and these are widely separated. Thus in a gas ionized by α rays we have intense ionization in some localities and very weak ionization in others, while other methods give much more uniform ionization. Now the electric force required to saturate a gas depends upon the maximum density of ionization as well as upon the average ; thus it will require a more intense field to saturate a gas ionized by α particles than a gas where the total ionization is the same but the ionization is uniformly distributed through the gas. The researches of Moulin (*Le Radium*, t. v. March 1908) on the ionization by α rays, show that the differences between this kind of ionization and others can be explained as arising from the want of uniformity in the distribution of the α ionization.

I have much pleasure in thanking Mr. E. Everett and Mr. G. W. C. Kaye for the assistance they have given me in this investigation.

LV. *The Quality of the Secondary Ionization due to β Rays.* *By* W. H. Bragg, *M.A., F.R.S., Elder Professor of Mathematics and Physics in the University of Adelaide, and* J. P. V. Madsen, *B.Sc., B.E., Lecturer on Electrical Engineering* *.

THE so-called secondary radiation due to β rays has been studied by many observers. Quite recently McClelland and H. W. Schmidt have contributed important sets of papers upon the subject.

It is usual to estimate the amount or the energy of the primary and secondary streams by measuring the ionization produced within an ordinary ionization-chamber placed in the path of the rays, the principal reason being that such measurements can be made with convenience and accuracy.

But it is only under very special conditions that this procedure is legitimate, because the β particle produces more ions in traversing a given space when its velocity is small than when it is great; in other words, the ionization increases as the speed diminishes. If two streams of β radiation are to be compared by this method, it is one of the essential conditions of success that the velocities of the two streams shall be the same, or similarly distributed. This would not be necessary if the ionization-chamber were made so large that even the fastest β particles spent their ionizing powers within it, and if the whole ionization produced by a β particle might be taken as a measure of its energy. But it is usual to employ a small chamber, placed comparatively near to the source of the rays; and in this way an unfair advantage is given to the particles of smaller velocity.

The experiments to be described in this paper show that the secondary radiations returned by different substances struck by the same primary stream are not uniform in quality, but vary from substance to substance. When the atomic weight of the substance is small, the radiation is relatively soft; it contains a larger proportion of less penetrating rays. If, therefore, the constants of secondary ionization are measured in the usual way, they are exaggerated in the case of substances of low atomic weight, as compared with those the atoms of which are heavier.

For the purpose of observing the secondary ionization due

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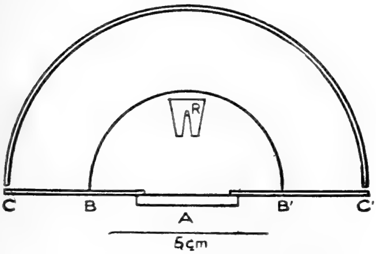
* From the Transactions of the Royal Society of South Australia, vol. xxxi. 1907. Communicated by the Authors.

to β rays we have adopted the form of apparatus shown in the figure. The plate at A scatters in all directions the radiation which it receives from the radium at R. Nearly all the returned particles strike the hemispherical wall BB′ of the ionization-chamber, the larger hemisphere CC′ being connected to the electrometer. The usual shielding devices are used, but not shown in the figure. This arrangement gathers in the effects of all the secondary rays, so that a measurable effect is obtained, even when only a small quantity of radium is used.

Fig. 1.



When the cup or dome BB′ is made of very thin Al foil, stretched on a frame of a few fine wires, the effects obtained by placing plates of different metals at A approximate to those given by McClelland—that is to say, the curve which shows the relation between secondary ionization and atomic weight is of the same general form as McClelland's, though somewhat flatter. But when the dome is thickened by the addition of layers of tinfoil, there is a considerable alteration. The addition of tinfoil of a tenth of a millimetre in thickness is sufficient to make the curve almost linear, and the ionization is then nearly proportional to the atomic weight of the radiator.

The figures in the following table show the results of an experiment of this kind. They give the ionization currents, on an arbitrary scale, for different radiators and different thicknesses of the dome. The smaller figures are only approximate :—

	Pb.	Ag.	Zn.	Fe.	S.	Al.	C.
1. Thin Al leaf	1300	1010	798	679	484	391	166
2. Sn foil ·0065 mm. ...	1124	829	627	519	352	276	141
3. ,, ·043 ,, ...	414	272	189	145	85	57	21
4. ,, ·080 ,, ...	210	129	87	65	35	21	8
5. ,, ·116 ,, ...	125	71	45	32	19	12	5
6. ,, ·153 ,, ...	76	42	29	21	13	7	5

Assuming that the returned radiation is really due to a scattering of the primary beam, there are two ways of interpreting these results. The β radiation of radium is heterogeneous, and consists of rays of various velocities. According to H. W. Schmidt there are a certain number of groups, each homogeneous in itself (*Ann. der Phys.* Nov. 1906). It is conceivable that the effect of varying the atomic weight of the radiator might depend on the velocity of the β particle, and that the smaller atomic weights might return a relatively small amount of fast primary rays. Assuming the velocity of the secondary rays to be of the order of that of the primary, it would then follow that the constitution of a heterogeneous primary beam would be altered by scattering, the alteration depending on the atomic weight of the scattering substance or radiator, and being of the nature indicated by experiment. Crowther (Phil. Mag. Oct. 1906) has described an experiment which appears to show a considerable effect of this kind. He found that the secondary ionization due to the β rays of UrX was much more nearly proportional to atomic weight than in the case of radium, as studied by McClelland, and he has suggested that the difference "may be due to to the presence in the radium radiation of comparatively slowly-moving β rays." On the other hand, H. W. Schmidt has recently found (*Ann. der Phys.* Bd. xxiii. 1907) that the behaviour of substances under radiation from the β rays of UrX is not very different to that found by McClelland in the case of radium. As it was important to settle this point, if we were to find the true interpretation of our own experiments, we put together the apparatus of the form used by Crowther, and repeated his experiments with UrX, using also radium and actinium. The apparatus is not very well suited, as Schmidt points out, for obtaining accurately the proportion between secondary and primary; but it gives a ready answer to the question as to whether or no the speed of the β particle has any effect.

Subtracting the effects of the carbon plate from all the others, and setting lead equal to 200, we obtained the following results :—

	Pb.	Sn.	Ag.	Zn.	Cu.	Fe.	Al.	C.
Ac	200	158	147	110	102	91	37	0
UrX	200	160	147	110	102	87·5	36	0
Ra 1	200	155	145	106·5	99·5	86·5	34·5	0
Ra 2	200	152·5	141	101·5	94·5	79	31	0
Ra 3	200	152	145	99	82	68	25·5	0
Ra 4	200	132·5	123	88	82·5	73	27·5	0

The screens used were as follows:—

Ac—Thin mica + thin tinfoil; the two equivalent to about 10 cm. of air, and enough to cut off all α rays.
UrX—No screen.
Ra 1—Thin mica + tinfoil, the latter ·00366 cm. thick.
Ra 2—Thin mica + tinfoil, the latter ·0293 cm. thick.
Ra 3—Thin mica + tinfoil, the latter ·0586 cm. thick.
Ra 4—Thin mica + lead, the latter equivalent to ·11 cm. of tinfoil.

The figures for Ra 1, Ra 2, Ra 3, are for β rays only, the effects of γ rays having been eliminated. The figures for Ra 4 have not been corrected for γ rays, and must, indeed, refer almost entirely to rays of the latter class.

The velocity of the β rays of Ac is less than in the case of UrX. In the case of radium it varies; some of the rays are as little penetrating as those of Ac, others more than the rays of UrX. The figures seem to show that there is a certain small dependence on the velocity of the β rays, but it is insufficient to account for the variations in quality which have been described above.

We must therefore fall back upon a second explanation, viz., that the scattered rays possess velocities which are less, on the average, than those of the primary; and that the difference is greater in the case of the atoms of small atomic weight. This is in general accordance with other experiments and with expectation. It has been shown by Gehrcke (*Ann. der Phys.* viii. p. 81, 1902) that scattered cathode rays possess a variety of velocities, none greater than that of the primary, some, however, being equal to it. And it is not unreasonable to suppose that β rays lose more energy in being scattered by atoms of less weight or of looser building than by those which are heavier or more rigid. If, therefore, a homogeneous beam of β rays fell upon an aluminium plate, there would be found in the scattered secondary rays a larger proportion of particles of much reduced speed than if the plate had been lead.

When we measure the ionization produced in an ionization-chamber, and insert successive thicknesses of absorbing material between the radiating substance and the chamber, placing them in contact with the wall of the latter, the effect is the same as if we gradually removed the chamber to greater distances; if we may assume that the law of absorption in air and in the given absorbing material is not greatly affected by the alterations in quality which we are considering. We may, therefore, take the figures in any vertical column of the first table given above as showing the effects of the secondary radiation at various distances from the radiator. If we plot an ionization-distance curve the whole area between the curve and the axes is the true measure of the ionization due to the returned rays. The usual plan is to accept as a measure the one figure at the head of the column.

We find that in each case the curve may be nearly expressed as the sum of two exponentials as $Ae^{-\lambda_1 x}+Be^{-\lambda_2 x}$. Whether this has a physical meaning or not does not concern our immediate argument. Commencing with one thickness of tinfoil on the dome, the actual figures are :—

I.	II.	III.	IV.
Pb	$564e^{-60x}+560e^{-13\cdot 6x}$	200	200
Ag	$492e^{-57x}+337e^{-14x}$	125	140
Zn	$409e^{-57x}+218e^{-14x}$	83	98·5
Fe	$365e^{-54x}+154e^{-14x}$	61·5	76·5
S	$264e^{-59x}+78e^{-13\cdot 5x}$	35	43
Al	$218e^{-73x}+58e^{-14x}$	19·5	27·5
C	$117e^{-73x}+23e^{-14x}$	0	0

The area of the curve is given by $A/\lambda_1+B/\lambda_2$, and the relative values of the areas are placed in the third column, that of C being first subtracted and that of Pb being set equal to 200. In the last column are the corresponding figures when the amount of radiation is measured by $A+B$, *i. e.*, the ionization found when one layer of tinfoil is placed over the chamber. It is clear that there is a considerable difference.

When tinfoil is placed over the radium itself so as to cut out a large proportion of the slower β rays, the secondary radiation is also hardened correspondingly.

The figures here given are not sufficiently accurate to be taken as absolute. The measurements were made as carefully as possible, but more numerous and more varied experiments are needed before it will be possible to map out the phenomena with exactness. But the results show clearly that—

(1) The secondary radiation from different substances, due to the β and γ rays of radium, varies in quality, those of lower atomic weight returning a greater proportion of less penetrating rays.

(2) When the less penetrating portion of a primary beam of β rays from radium is sorted out, the secondary rays also become more penetrating.

(3) In view of these considerations the ionization current due to secondary radiation, measured in a chamber of the ordinary form, does not give a simple or accurate determination of the nature of that radiation.

LVI. *Positive Rays.* *By* John Trowbridge[*].

My intention in undertaking this investigation was to endeavour to measure the group velocity of the positive rays by producing a standing wave; or a stratum of maximum collisions in an exhausted tube in the space between the anode and the cathode. In the case of an oscillating circuit, if we call λ the wave-length, v the velocity of light, t the time of a half oscillation, s the distance between the anode and the cathode, v the velocity of the positive rays, we have

$$\lambda = vt, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(Eq. 1)}$$

$$s = v't, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(Eq. 2)}$$

$$t = \frac{\lambda}{v}, \qquad v' = \frac{vs}{\lambda}.$$

If, by tuning a circuit containing a condenser, self-induction, and the exhausted tube, the stratum of maximum collisions could be formed at the orifice in the cathode, it was thought that none of the positive rays would enter the canal region; if, on the other hand, the positive rays swung, so to speak, with the oscillations of the circuit, a maximum fluorescence could be obtained on a suitably placed willemite screen.

The circuit was arranged as follows: a leyden-jar L, fig. 1, was charged by a storage-battery of ten thousand cells,

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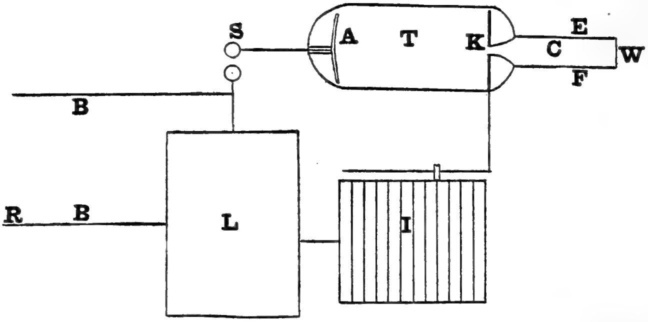
[*] Communicated by the Author.

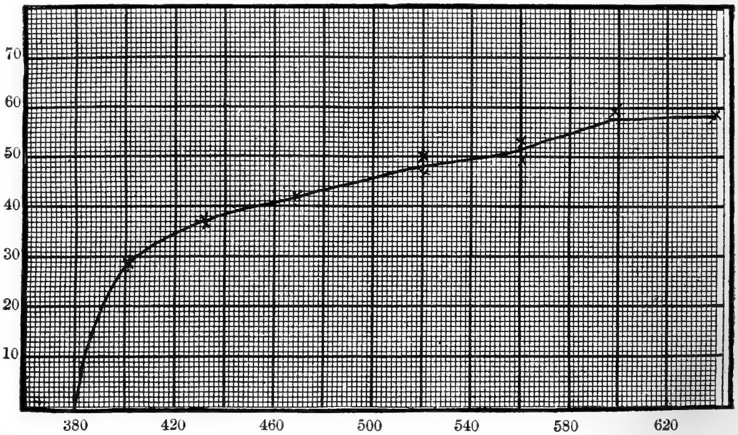
through a large resistance of running water B. The discharging circuit included an adjustable self-induction I, a tube filled with rarefied hydrogen T, and a spark S. K was an iron electrode with an orifice two millimetres in diameter at its centre, a glass tube welded to the sides of the tube C entered this orifice. The end of the tube C was coated with willemite.

Fig. 1.



At first I studied the effect of increasing the self-induction on the admittance of the mixture of anode and cathode rays to the region C. The phosphorescence on the screen at the end of the tube was observed with a spectrophotometer and also with a photometer consisting of crossed Nicol prisms.

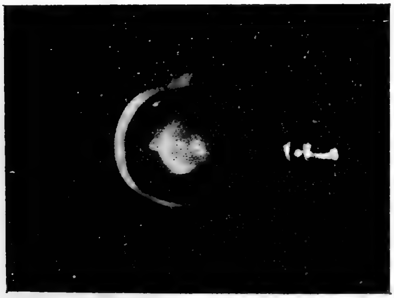
Fig. 2.



In fig. 2 the intensity of light is plotted along the axis of Y, and the wave-lengths of the circuit along X. The phosphorescence appeared suddenly at wave-length 380 metres and increased to a maximum at wave-length 620, the curve then continued parallel to the axis of X. In determining the wave-lengths I employed the admirable wave-meter of Professor G. W. Pierce *. This instrument enabled me to make measurements in a few moments which otherwise would have required days of labour.

On placing the tube C between the poles of an electromagnet, which produced a field just sufficient to divert the cathode rays from the screen, I found that the changes in the phosphorescence represented in fig. 2 were produced by the cathode rays ; for the phosphorescence due to the positive rays remained constant through the range measured. The positive rays were deflected in the direction opposite to that in which the cathode rays were thrown by a field of 530 lines to the centimetre, and produced a narrow band on the willemite screen which showed a slight discontinuity, fig. 3, although the pressure did not exceed $\frac{1}{3}$ mm. I was surprised to find that the group of positive rays were so readily deflected by a comparatively weak magnetic field. The length

Fig. 3.



of the band of phosphorescence was 1·5 cm. It is to be noted that the band occurred only on one side of the middle point of the phosphorescent screen.

On discovering that changes in self-induction had no effect upon the intensity of the phosphorescence produced by this

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* Contributions from the Jefferson Physical Laboratory, vol. iv. 1906.

group of positive rays, I resolved to damp all oscillations by introducing a large water resistance in the oscillating circuit. While the dimensions of the discharge-tube between the anode and the cathode remained the same as in the experiments described above, the canal region was changed from a circular tube of 3 cm. diameter to the form shown in fig. 4 in plan P and end section E. The width of the cross section was 3·5 cm. It will be noticed that it had a flattened egg-shaped section to enable me to place it between the poles of an electromagnet. When all oscillations were damped and a magnetic field of 500 lines to the centimetre was excited, the positive rays produced a narrow sharply defined band of fluorescence which is represented in the photograph fig. 5. The middle of the end of the tube is indicated by the sharp pointers on the photograph; and it will be seen that the phosphorescent band extends to approximately equal distances on both sides of the middle of the screen. At first I thought that I was dealing with a mixture of positive and negative rays, and various theories

Fig. 4.

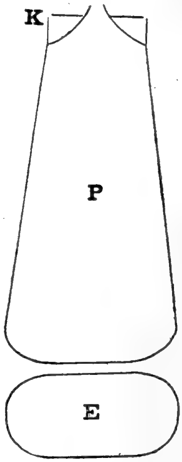
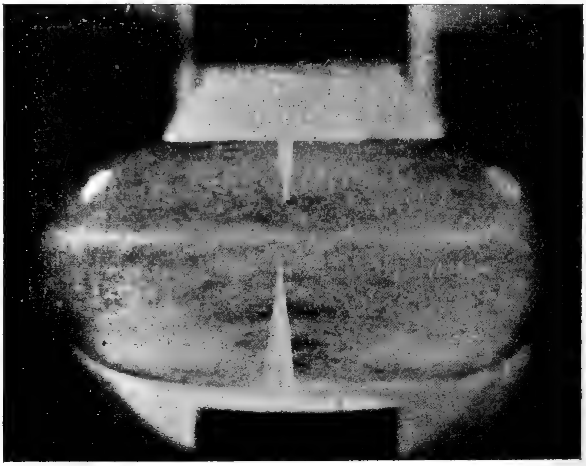


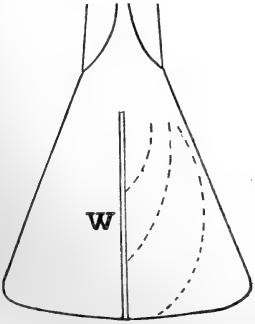
Fig. 5.



of molecular attraction occurred to me; but experiment showed that all negative rays had been driven out of the field. Moreover, by producing a difference of electrostatic potential the entire phosphorescent band or magnetic spectrum moved in the direction the positive rays should move. In fig. 5 it will be noticed that the band moved to the smaller pointer; whereas if the portion of the band to the right of the pointers was made up of negative rays and that to the left of positive rays, the band would not have moved parallel to its original position.

In order to ascertain why the band spread to the right and left of the middle of the screen, I introduced a septum of glass in the middle of the tube constituting the canal region, fig. 6. This septum was welded to the end of the tube and was coated on both sides with willemite. The band of phosphorescence now appeared mainly on one side of the partition. By greatly weakening the magnetic field the negative rays were brought upon the screen to the left of the partition: while the positive rays appeared on the right of this partition; thus proving again that the unobstructed band was made up of positive rays. A large storage-battery proved the best means of studying the positive band; for the phenomenon was not confused by the make and break of mechanical or electrolytic interrupters. It was soon discovered that a narrow phosphorescent band was formed on the side of the septum which shielded the end of the tube.

Fig. 6.



The explanation of the band in the tube without the septum was evidently this: the pilot spark produces a number of positive rays of different velocities which spread out in the form of a cone of which the apex is the narrow orifice in the cathode terminal; under the influence of the magnetic field these rays whirl around in the field somewhat in the manner indicated by the dotted lines, fig. 6.

In the expression $\rho = \frac{\epsilon v'}{m\text{H} \sin \theta}$ can have many values depending upon the values of v. The narrowness of the band results from the electrodynamic attraction of the whirls in a manner similar to the attraction of electrical currents moving in the same direction.

W. Wien * has shown that positive rays emanate from the anode and that these rays can be diverted in a direction opposite to that in which the negative are affected by an ordinary horseshoe magnet. The rays which form the subject of the present paper are undoubtedly of the same nature as those studied by Wien. Their connexion, however, with the pilot discharge of a condenser is an added point of interest.

Jefferson Physical Laboratory,
Harvard University.

LVII. *Notices respecting New Books.*

Thermodynamics of Technical Gas Reactions. By Dr. F. **Haber.** *Translated by* Dr. **Arthur** B. **Lamb.** Pp. xix+356; illustrations. Longmans, Green & Co., 1908. Price 10*s*. 6*d*. net.

NO one familiar with Dr. Haber's *Thermodynamik Technischer Gasreactionen* will be surprised that a translation has so speedily appeared. Dr. Haber brought to the task a mind adequately trained on the mathematical side to deal with thermodynamic problems, and was thus able to reduce to order much that is customarily left vague and unsatisfactory in treatises on physical chemistry. Physicists have been slow to recognize the great merits of the advances that have been made; and this tardiness is largely due to the mode in which the subject has been presented. We feel sure that Dr. Haber's book, besides its immediate object of throwing light on technical processes, will do much to increase contact between physicists and chemists.

Attention should be called to one characteristic. No use is made of the atomic hypothesis. As explained in the author's preface, this is not due to any antagonism, but is based on a conviction that the application of the mechanical theory of heat to chemistry becomes easier and more comprehensible the closer we restrict ourselves to the heat and work effects of masses directly perceptible to our senses. Although suckled on the atomic theory, we are convinced that Dr. Haber is right in excluding it from the present course. It should be understood that this exclusion does not involve the exclusion of the chemical molecule or atom as indicated by the law of combining weights. This is recognized throughout. But all attempts that have been made to derive the properties of systems by direct applications of mechanics to vast congeries of unitary bodies, are studiously put aside in preference for the much more powerful and fruitful methods of thermodynamics. The whole of the German text has been specially revised by the author purposely for this translation. Several new appendices have been added, these being necessitated by the great developments that have been made in the years 1905 and 1906. One of

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* Wied. *Ann.* lxv. pp. 449–450 (1898).

them deals with Nernst's "Third" law of Thermodynamics, and another (translated by Mr. Rossignol) on recent work upon the dissociation of CO_2, and especially on the use of cells containing glass or porcelain septa through which decomposition takes place electrolytically. These appendices include some of the most interesting matter in the whole volume.

We commend the mode in which the translation has been made throughout; and we are glad to think that the book in its translated form will become still more widely known and appreciated than heretofore.

LVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 496.]

May 6th, 1908.—Prof. W. J. Sollas, Sc.D., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'Solution-Valleys in the Glyme Area of Oxfordshire.' By the Rev. E. C. Spicer, M.A., F.G.S.

A triangular area whose sides are defined by the converging Evenlode and Cherwell with a strike-valley, containing the upper Swere for its base, contains a smaller triangular area defined by the confluent Glyme and Dorn. This area is part of the gently-tilted Great Oolite limestone-plateau, which is indented by a number of sunken valleys running in various directions, principally with a strike-and-dip trend, that show no marks of erosion but appear to be subsidence-valleys. They begin suddenly at any part of the area, and descend with sinuous curves to a main valley into which they open quietly without disturbing the main valley's contour, and without bringing any surface-débris. The main valley likewise enters a stream-valley in a similar manner. The stream-valley quietly develops into a broad sinuous river-valley, with a floor, level in transverse section, over which a small river-stream aimlessly meanders with the Evenlode characteristics. A gradation is shown from the plateau dry valleys to the meander-valleys, which are sometimes flooded from bank to bank with soakage-water. The plateau-area is quite free from drift or gravels, and from any of the usual marks of surface-denudation, although the valleys have strongly-marked cross-sections. There are no marks of marine currents, of fluvio-glacial scour, or of ice. There are no wind-gaps suggesting beheaded streams, nor any evidence of vanished heights that could produce torrents sufficiently strong to carve out the present surface. At the mouths of several of these dry winding valleys issue streams strongly impregnated with carbonate of lime. It is suggested that percolating water forming an underground course along joint-lines removes enough material in solution to weaken a long, narrow, winding area over which the surface subsides until the underground stream is revealed. Solution then constantly widens the stream-banks into bowls of soakage, and leaves insoluble material to build up a broad, level valley-floor, which rises gradually above and obscures the dry valley outlet-streams, these then forming marshes. It does not appear possible to reconstruct any local conditions that could have produced these valleys by mechanical erosion, and it is suggested that they are formed by underground solution, and are therefore called joint-valleys or solution-valleys. Prestwich (Quart. Journ. Geol. Soc. vol. xxviii, 1872, p. lxvii) estimates that 140 tons of carbonate of lime are annually removed from every square mile of the limestone-area drained by the Thames. This would give an annual amount removed by solution from the small Glyme area of over 10,000 tons.

2. 'On the Stratigraphy and Structure of the Tarnthal Mass (Tyrol).' By Alfred Prentice Young, Ph.D., F.G.S. With a 'Note on two Cephalopods collected on the Tarnthal Köpfe (Tyrol).' By George C. Crick, Assoc.R.S.M., F.G.S.

The immediate occasion for this paper is the discovery of fossils which appear to throw new light on the relations of the rocks of this mountain. The rock-series may be divided into three parts:—(*a*) The lowest portion consists of dolomite, and the Lias is in normal position, the upper beds being the youngest; this portion is scarcely disturbed. (*b*) A middle section, consisting of calcareous schists, with a band of massive dolomite and dolomite-breccia, shows marks of violent disturbance and crushing. (*c*) The uppermost part, a mass of more or less altered quartzite-schists, calcareous schists, and serpentine, retains most of its original character and form, having undergone little mechanical distortion since it left its 'root.' The succession is summarized as follows:—

3. Serpentine.
Ophicalcite.
Tarnthal quartzites, etc.
2. Calcareous schists with green bands.
Dolomite-breccias.
Calcareous schists.
1. Liassic limestone.
'Principal dolomite' (Rhætic).

The explanation of the structure now suggested is as follows:—The line between 1 and 2 marks approximately the lower loop of a big fold, the dolomite-breccia being a repetition in an attenuated form of the 'principal dolomite' below. The interpretation of the relations of 2 and 3 is not so clear. Either the whole series 2 and 3 is in inverted sequence, or else the dolomite-breccia represents the whole of the 'principal dolomite' in a flattened fold (nappe of Termier), the serpentine and quartzite having been brought into their present position by a long overthrust, representing the traîneau écraseur of the French geologists. The question whether the lower dolomite and the Lias are *in situ* or not is left undecided. A petrographical note is furnished on the amphibolite of Gufidann.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

NOVEMBER 1908.

LIX. *A Revision of the Fundamental Laws of Matter and Energy.* By GILBERT N. LEWIS, *Ph.D., Associate Professor of Physical Chemistry, Massachusetts Institute of Technology, Boston* *.

RECENT publications of Einstein † and Comstock ‡ on the relation of mass to energy have emboldened me to publish certain views which I have entertained on this subject and which a few years ago appeared purely speculative, but which have been so far corroborated by recent advances in experimental and theoretical physics that it seems desirable to subject these views to a strict logical development, although in so doing it will be necessary to modify those fundamental principles of the mechanics of ponderable matter which have remained unaltered since the time of Newton.

The recent experiments which indicate a change in the mass of an electron with the speed, together with the phenomenon of radioactivity, have in some minds created a doubt as to the exact validity of some of the most general laws of nature. In the following pages I shall attempt to show that we may construct a simple system of mechanics which is consistent with all known experimental facts, and which rests upon the assumption of the truth of the three great conservation laws,

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* Communicated by the Author.

† *Ann. Phys.* xviii. p. 639 (1905).

‡ Phil. Mag xv. p. 1 (1908).

namely, the law of conservation of energy, the law of conservation of mass, and the law of conservation of momentum. To these we may add, if we will, the law of conservation of electricity.

The Relation of Mass to Energy.

When a black body * is placed in a beam of light it is subject to a pressure or force which tends to move it in the direction in which the light is moving. If $\frac{dE}{dt}$ denotes the time-rate at which the body receives energy, f the force, and V the velocity of light, we have in rational units the formula

$$f=\frac{1}{V}\frac{dE}{dt}. \qquad \qquad (1)$$

This important equation, which was obtained by Maxwell as a consequence of his electromagnetic theory, and by Boltzmann through the direct application of the laws of thermodynamics, has recently been verified with remarkable precision in the beautiful experiments of Nichols and Hull †.

A body subjected to the pressure of radiation will acquire momentum, and if we are to accept the law of conservation of momentum, we must conclude that some other system is losing in the same direction an equivalent momentum. We are thus led inevitably, as Poynting has shown, to the idea that the beam of radiation carries not only energy but momentum as well.

The body subject to the constant force of radiation f, will obviously acquire momentum at the rate

$$\frac{dM}{dt}=f. \qquad \qquad (2)$$

Combining equations (1) and (2) gives

$$\frac{dE}{dM}=V. \qquad \qquad (3)$$

The ratio of the acquired energy to the acquired momentum is equal to the velocity of light. The beam of radiation must, therefore, possess energy and momentum in the same ratio. Hence for the beam itself, or any part of it,

$$\frac{E}{M}=V. \qquad \qquad (4)$$

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* In place of a black body we might consider a partially reflecting one. The equations thus obtained are more complicated but lead also to the simple equation (7).

† Phys. Review, xvii. pp. 26 and 91 (1903).

To anyone unfamiliar with the prevailing theories of light, knowing only that light moves with a certain velocity and that in a beam of light momentum and energy are being carried with this same velocity, the natural assumption would be that in such a beam *something possessing mass moves with the velocity of light and therefore has momentum and energy.* Notwithstanding its apparent divergence from the commonly accepted light theories, I propose to adopt this view and see whither it leads.

Postulating the validity of the fundamental conservation laws mentioned above, we shall need in the following development only this one cardinal assumption, that a beam of radiation possesses not only momentum and energy, but also mass, travelling with the velocity of light, and that a body absorbing radiation is acquiring this mass as it also acquires the momentum and the energy of the radiation. Therefore a body which absorbs radiant energy increases in mass.

The amount of this increase is readily found. If in general we write momentum as the product of mass and velocity, then the momentum of any part of a beam of radiation having the mass m will be given by the equation :

$$\mathrm{M}=m\mathrm{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The increase $d\mathrm{M}$ in the momentum of the body absorbing the radiation will therefore equal the increase dm in its mass, multiplied by the velocity of light,

$$d\mathrm{M}=\mathrm{V}dm. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Combining this equation with (3) we find

$$dm=\frac{d\mathrm{E}}{\mathrm{V}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or if we write $\mathrm{V}=3\times10^{10}$ centimetres per second,

$$dm=1{\cdot}111\times10^{-21}\,d\mathrm{E}.$$

Thus a body receiving or emitting radiant energy gains or loses mass in proportion and by the amount $1{\cdot}111\times10^{-21}$ grams for every erg. This is a small quantity, indeed, but one which is not to be neglected.

Assuming the fundamental conservation law, we must regard mass as a real property of a body which depends upon its state, and not upon its history. Hence it is obvious that if in any other way than by radiation the body gains or loses energy it must still gain or lose mass in just the above proportion. In other words, any change in a body's content of energy is accompanied by a definite change in its mass, regardless of the nature of the process which the energy change accompanies*.

Since therefore when a body loses a given quantity of energy it always loses a definite quantity of mass, we might assume that if it should lose all its energy it would lose all its mass, or, in other words, that the mass of a body is a direct measure of its total energy, according to the equation,

$$m=\frac{E}{V^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We should then regard mass and energy as different names and different measures of the same quantity, and say that one gram equals 9×10^{20} ergs in the same sense that we say one metre equals 39·37... inches.

Plausible as this view seems, it rests upon an additional hypothesis besides the fundamental postulate which we have chosen. We shall use therefore, not equation (8) but equation (7) as the basis of the following work.

It is to be noted that equation (8) has also been obtained by Einstein (*loc. cit.*), who derived it from the general equations of the electromagnetic theory, with the aid of the so-called principle of relativity. That a different method of investigation thus leads to the same simple equation we have here deduced, speaks decidedly for the truth of our fundamental postulate†.

Comstock (*loc. cit.*) from electromagnetic theory alone has also concluded that mass is proportional to energy, but his equation is

$$m=\frac{4}{3}\frac{E}{V^2}.$$

To investigate for the cases studied by Comstock the cause or the justification for this appearance in the equation of the factor 4/3 would lead too far into electromagnetic theory, from which in the present paper I wish to hold entirely aloof.

Before proceeding to develop fully the consequences of equation (7) it may be well to point out an apparent

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* I was first led to an investigation of the relation of mass to energy by the work of Landolt, on the change of weight in chemical reactions. But it is obvious from equation (7) that although there always will be a loss of mass in a reaction which is accompanied by the evolution of energy, this loss in the case of any ordinary reaction will be far too small to measure. In fact Landolt has very recently shown (*Ber. Berlin. Akad.* 1908, p. 354) that when all possible precautions are taken there is no measurable change of weight in the reactions which he studied.

† Einstein, however, obtains (8) as an approximate formula, while we obtain both (7) and (8) as perfectly exact equations.

inconsistency in the equations for the momentum and the energy of a beam of radiation. The momentum of the beam of mass m we have given in equation (5) as

$$M = mV.$$

From our assumption that the energy of the beam is simply the kinetic energy of the moving mass m, we might expect from our knowledge of elementary mechanics to find for the energy the equation

$$E = 1/2\, mV^2\,;$$

whereas in fact we find from equations (4) and (5) that

$$E = mV^2. \qquad \ldots\ldots\ldots \qquad (9)$$

We shall see, however, in the next section that this comparison of equations (5) and (9) instead of demolishing our theory actually furnishes a remarkably satisfactory argument in its favour.

Non-Newtonian Mechanics.

One of the interesting branches of modern mathematics has grown out of the study of those geometries which would result from the change of one or more of the axioms of Euclid. These non-Euclidian geometries present the properties of purely imaginary kinds of space and are therefore so far mere exercises in logic, without any physical significance. But their investigation was doubtless prompted in some cases by the belief that experiment itself may sometime show that there are deviations from the ordinary laws of space when these laws are subjected to tests of a different order from those of common mensuration. Indeed it is not unlikely that Euclidian geometry may prove inadequate when we are able to subject to an accurate metric investigation the vast stretches of interstellar space or the minute regions which we believe to be encompassed within an atom or an electron.

The science of mechanics, like geometry, has been built up from a set of simple axioms, which were laid down by Newton. But the conclusions of the previous section lead us to modify one of these axioms and thus lay the foundation of a system of non-Newtonian mechanics.

The axiom which we must surrender is the one which states that the mass of a body is independent of its velocity. We have concluded that mass is proportional to content of energy. When a body is set in motion it gains kinetic energy and therefore its mass must change with its velocity. In place of the axiom which we have abandoned we must substitute equation (7).

Before investigating the consequences of this step it is necessary to define exactly the principal mechanical quantities which we are to use.

Extension in space (l) and time (t) will be measured in the usual way and the centimetre and the second will be employed as units.

Force (f) will be given its usual significance and the unit, the dyne, will be that force which, acting upon the International standard kilogram, when the latter is at rest, imparts to it an initial acceleration of $\cdot 001\ \frac{\text{cm.}}{\text{sec.}^2}$.

The momentum (M) of a moving body will be measured by the time in which it is brought to rest under the influence of a constant opposing force of one dyne acting in the line of its motion.

The mass (m) of a moving body will be defined as the momentum divided by the velocity (v), that is,

$$m = \frac{\mathrm{M}}{v}. \qquad (10)$$

The limiting ratio of the momentum of a body to its velocity, when it is brought to rest, will be called its mass when at rest. The unit of mass is the gram.

The kinetic energy (E′) of a body will be measured by the distance through which it will move before being brought to rest by a constant opposing force of one dyne, acting in the line of the body's motion. The unit of energy will be the erg.

These definitions, although somewhat unusual in form, are perfectly consistent with the ordinary definitions of Newtonian mechanics. But they have been so chosen as to be consistent also with equation (7) and the fundamental conservation laws. Obviously equation (7) itself is not inconsistent with these conservation laws, for although a body increases in mass as it gains kinetic energy, some other system is losing the same mass as it loses the same energy.

In accordance with the above definitions we may write

$$d\mathrm{M} = f dt, \qquad (11)$$

$$d\mathrm{E}' = f dl. \qquad (12)$$

Let us consider a body originally moving with a velocity v subjected for the time dt to a force f in the line of its motion.

Its momentum and kinetic energy will change according to (11) and (12) by the amounts

$$dM = f\,dt,$$

$$dE' = f\,dl = fv\,dt.$$

Hence

$$dE' = v\,dM. \qquad \text{(13)}$$

So far the equations are those of Newtonian mechanics, but now in substituting for M from equation (10) we must regard m as a variable and write

$$dE' = mv\,dv + v^2 dm. \qquad \text{(14)}$$

This will be our fundamental equation connecting the kinetic energy of a body with its mass and velocity.

Introducing now the relation of mass to energy given in equation (7) we may write,

$$dE' = V^2 dm,$$

and combining this equation with (14) gives

$$V^2 dm = mv\,dv + v^2 dm.$$

This equation, containing only two variables, m and v and the constant V, may readily be integrated as follows. By a simple transformation

$$\left(1 - \frac{v^2}{V^2}\right) dm = \frac{mv\,dv}{V^2}.$$

Writing $\beta = v/V$, and noting that

$$\frac{v\,dv}{V^2} = -\frac{1}{2} d(1-\beta^2),$$

we see that

$$\frac{dm}{m} = -\frac{1}{2}\frac{d(1-\beta^2)}{(1-\beta^2)}.$$

Hence

$$\log m = -\tfrac{1}{2}\log(1-\beta^2) + \log m_0,$$

where $\log m_0$ is the integration constant. Therefore

$$\log\frac{m}{m_0} = \log(1-\beta^2)^{-\frac{1}{2}}$$

or

$$\frac{m}{m_0} = \frac{1}{(1-\beta^2)^{1/2}}. \qquad \text{(15)}$$

This is the general expression for the mass of a moving body in terms of β, the ratio of its velocity to the velocity of light. When β is zero, $m=m_0$. m_0 represents therefore the mass of the body at rest.

If we substitute in this equation numerical values of β we find that, while the quotient m/m_0 becomes infinite when the velocity equals the velocity of light, it remains almost equal to unity until the velocity of light is closely approached. Thus a ton weight given the velocity of the fastest cannon-ball would, according to this equation, gain in mass by less than one millionth of a gram. It is obvious that, except in those unusual cases in which we deal with velocities comparable with that of light, our non-Newtonian equations are identical with those of ordinary mechanics far within the limits of error of the most delicate experiments.

Recently, however, it has been possible to study, in the negative particles emitted by radioactive substances, bodies which sometimes move with a velocity only a little less than that of light. In a series of remarkably skilful experiments Kaufmann* was able to measure the ratio of electric charge to mass (e/m) for negative particles moving at different speeds. Assuming that the charge is constant, the fact that e/m varies with the speed of the particle must be attributed to a variation of the mass with the speed. On this assumption it is possible to calculate from Kaufmann's experiments the values of m/m_0 at the different velocities.

The mass of a negative particle is usually spoken of as electromagnetic mass, but if we are to hold to our definitions we must recognize only one kind of mass. In general we have defined the mass of a moving body as the quotient of the time during which it will be brought to rest by unit force, divided by the initial velocity. It matters not what the supposed origin of this mass may be. Equation (15) should therefore be directly applicable to the experiments of Kaufmann. In the following table are given the values of

$\frac{m}{m_0}$.	β (observed).	β (calculated).
1	0	0
1·34	·73	·67
1·37	·75	·69
1·42	·78	·71
1·47	·80	·73
1·54	·83	·76
1·65	·86	·80
1·73	·88	·82
2·05	·93	·88
2·14	·95	·89
2·42	·96	·91

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* *Phys. Zeit.* iv. p. 54 (1902); *Ann Phys.* xix. p. 487 (1906).

m/m_0 found for the different observed values of β in the second column. The third column shows those values of β which would correspond with the same values of m/m_0 according to equation (15).

It will be seen that the observed values of β follow to a remarkable degree the same trend as those which are calculated by equation (15), but are in every case six to eight per cent. higher[*]. I believe that these differences lie within the limits of experimental error of Kaufmann's measurements. It is true that he claims a higher degree of accuracy, but, notwithstanding the extreme care and delicacy with which the observations were made, it seems almost incredible that measurements of this character, which consisted in the determination of the minute displacement of a somewhat hazy spot on a photographic plate, could have been determined with the precision claimed. Moreover, Planck[†] and Stark[‡] have pointed out certain corrections which probably should have been made by Kaufmann and which would produce a material change in his results[§].

That a charged particle must possess mass in virtue of its charge, and that this mass must vary with the velocity of the particle, was shown to be a consequence of the electromagnetic theory by J. J. Thomson and by Heaviside, and numerous attempts have been made to find the exact expression for the change of mass with the velocity. But before this can be done some assumption is necessary as to the shape of the particle and the distribution of its charge. The three theories of the simple negative particle or electron which are now most discussed are due to Abraham, Bucherer, and Lorentz[‖]. The first assumes that the electron is and remains a rigid sphere, the second assumes an electron which is spherical when at rest but which in motion contracts in the direction of its translation and expands laterally so as to keep a constant volume. The third assumes an electron similar to the second, which contracts in the direction of translation but which does not change its other dimensions. On the basis of these theories and from known electromagnetic principles, three equations have been obtained for the value

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[*] The constancy of the difference between the observed and calculated values of β is striking, and would alone indicate some constant error in Kaufmann's results.

[†] *Verhandlung Deutsch. Phys. Ges.* ix. p. 301 (1907).

[‡] *Ibid.* x. p. 14 (1908).

[§] In reply to Planck see Kaufmann, *ibid.* ix. p. 667 (1907).

[‖] For a discussion of these theories see Abraham, *Theorie der Elektricität*, vol. ii. Leipzig, 1905; and Bucherer, *Mathematische Einführung in die Elektrontheorie*, Leipzig, 1904.

of m/m_0 as a function of β, namely,

$$(a)\quad \frac{m}{m_0}=\frac{3}{4}\frac{1}{\beta^2}\left(\frac{1+\beta^2}{2\beta}\log\frac{1+\beta}{1-\beta}-1\right),$$

$$(b)\quad \frac{m}{m_0}=\frac{1}{(1-\beta^2)^{1/3}},$$

$$(c)\quad \frac{m}{m_0}=\frac{1}{(1-\beta^2)^{1/2}}.$$

The extraordinary significance of the similarity of the first two of these equations and the identity of the third with equation (15), which we have derived from strikingly different principles, needs no emphasis. Kaufmann shows that his results agree better with the first two of these equations than with the third, but to regard this as serious evidence as to the validity of equation (15) would, as Planck has pointed out, be laying too great a stress on the accuracy of the experimental observations.

The agreement of Kaufmann's results with the above equations has led him, and all others who have discussed his results, to the conclusion that all of the mass of an electron is electromagnetic.

Their argument is based on the assumption that ordinary mass, the mass of "ponderable matter," is independent of the velocity, while "electromagnetic mass" varies with the velocity according to one of the above equations. But in this paper we have assumed that all mass is one, and that any bodies, whether charged or not, moving at the velocities of Kaufmann's electrons would show the same values of m/m_0.

There is some hope that the correctness of this view may be decided by an experimental study of the mass of a positive or α particle at different speeds. According to the ordinary view, the mass of such a positive particle as issues from a radioactive source is chiefly that of its "ponderable" matter and only to a very small extent "electromagnetic mass." It would therefore be generally assumed that at the highest velocity of the particle, about one-tenth of the velocity of light, it would have substantially the same mass as at rest. According to our view, on the other hand, the mass of this or any other particle would change with the velocity in the same way as the mass of an electron. From equation (15) we should therefore expect the particle moving with one-tenth of the velocity of light to have a mass two per cent. greater than when at rest. The experimental difficulties in testing this point would be very great, of course, but perhaps not insurmountable.

The plausibility of our fundamental assumption which led directly to equation (15) has been greatly increased by the agreement between this equation and Kaufmann's results, and also perhaps by the similarity between this equation and those deduced from electromagnetic theory. But the simplest as well as the strongest evidence of the correctness of our point of view comes from a consideration of the non-Newtonian equation for kinetic energy.

The integration of equation (14) obviously does not yield the simple Newtonian equation,

$$E' = 1/2mv^2.$$

This equation must be replaced by one that is obtained as follows:—

Let a body, which at rest has the mass m_0, be given the velocity v. As its internal energy changes, its mass will change according to equation (7), and

$$m - m_0 = \frac{E'}{V^2}.$$

where E' is the acquired kinetic energy and $m - m_0$ is the increase in mass.

Eliminating m_0 between this equation and (15) gives

$$E' = mV^2[1 - (1 - \beta^2)^{1/2}]. \quad . \quad . \quad . \quad . \quad (16)$$

This is the general formula for the kinetic energy of a moving body. As usual β represents v/V, the ratio of this velocity to the velocity of light.

From equations (10), (15), and (16) may be constructed the whole science of non-Newtonian dynamics, of which Newtonian dynamics furnishes a limiting case, namely, for velocities which are negligible in comparison with the velocity of light.

For example, expanding (16) by the binomial theorem gives

$$E' = mV^2(\tfrac{1}{2}\beta^2 + \tfrac{1}{8}\beta^4 \ldots .). \quad . \quad . \quad . \quad . \quad (17)$$

For low values of β the higher terms may be neglected and

$$E' = \tfrac{1}{2}mv^2.$$

That is, the limit approached by the kinetic energy of a body as the velocity approaches zero is, as in ordinary mechanics, one half the product of the mass and the square of the velocity. At the other limit of velocity when $\beta = 1$, it follows from (16) that

$$E' = mV^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Between these two limits it is obvious that

$$\tfrac{1}{2}mv^2 < E' < mv^2.$$

The momentum and the kinetic energy of any mass moving with the velocity of light are, therefore,

$$M = mV,$$
$$E' = mV^2,$$

but these equations are identical with (5) and (9) which we obtained for the momentum and the energy of a beam of light.

Further Consequences of the Theory.

The view here proposed, which appears at first sight a reversion to the old corpuscular theory of light, must seem to many incompatible with the electromagnetic theory. If it were really so I should not have ventured to advance it, for the ideas announced by Maxwell constitute what may no longer be regarded as a theory, but rather a body of experimental fact. The new theory is offered, not in any sense to replace, but to supplement the accepted theories of light. I hope in another paper to show that it is entirely consistent with those theories. Such a proof may constitute a step towards one of the obvious goals of present day science, the complete mechanical explanation of electromagnetic phenomena, or, what is very nearly the same thing, an electromagnetic explanation of the phenomena of ordinary mechanics. In the meantime a few of the more salient conclusions of our theory may be cursorily examined.

In the first place it should be noticed that, while the theory is consistent with a modified corpuscular theory of light, it does not necessarily imply that light is corpuscular. The stream of mass issuing from a radiating body may be made up of discrete particles or it may be continuous. Whatever it may be that is emitted it is not matter in the ordinary sense, as is to be seen from the following considerations:—

According to equation (15) any body of finite mass increases in mass as it increases in velocity and would possess infinite mass if it could be given the velocity of light. *Therefore that which in a beam of light has mass, momentum, and energy, and is travelling with the velocity of light, would have no energy, momentum, or mass if it were at rest, or indeed if it were moving with a velocity even by the smallest fraction less than that of light.* After this extraordinary conclusion it would be at present idle to discuss whether the same substance or thing which carries the radiation from the emitting body continues to carry it through space, or, indeed, whether there is any substance or thing connected with the process.

If we assume an æther pervading space, and assume that this æther possesses no mass except when it moves with the velocity of light, it is obvious that an æther drift could in no way affect a beam of radiation nor could it be detected by any mechanical means. If we are to assume such an æther we may as well assume it to be at rest.

The question whether a method is conceivable by which absolute motion in space may be distinguished from relative motion must be answered definitely in the affirmative by one who accepts the above equations of non-Newtonian mechanics. A body is absolutely at rest when any motion imparted to it increases its mass, or when a certain force will give it the same acceleration in any direction. It is true that metaphysicians hold that in the strictest sense absolute motion is not only unknowable but unthinkable, but we may say at least that the above method permits theoretically the detection of absolute translational motion in the same sense that a study of centrifugal forces enables us to detect absolute rotational motion.

Summary.

It is postulated that the energy and momentum of a beam of radiation are due to a *mass* moving with the velocity of light.

From this postulate alone it is shown that the mass of a body depends upon its energy content. It is therefore necessary to replace that axiom of Newtonian mechanics according to which the mass of a body is independent of its velocity, by one which makes the mass increase with the kinetic energy.

Retaining all the other axioms of Newtonian mechanics and assuming the conservation laws of mass, energy, and momentum, a new system of mechanics is constructed.

In this system momentum is mv, kinetic energy varies between $1/2\, mv^2$ at low velocity and mv^2 at the velocity of light, while the mass of a body is a function of the velocity and becomes infinite at the velocity of light. The equation obtained agrees with the experiments of Kaufmann on the relation between the mass of an electron and its velocity. It is, moreover, strikingly similar to the equations that have been obtained for electromagnetic mass.

The new view leads to an unusual conception of the nature of light. It offers theoretically a method of distinguishing between absolute and relative motion.

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
May 14, 1908.

LX. *A Vacuum-Tube Model for Demonstrating the Propagation of Alternate Currents in Cables.* *By* Dr. C. V. Drysdale [*].

[Plates XXII. & XXIII.]

As is well known, the propagation of electric waves along conductors can be conveniently shown on the small scale by means of a helix, fed from a suitable source of high frequency, high potential oscillations. In this case the helix is found to glow with brush discharges at the antinodes of potential, remaining dark at the nodes. Experiments of this kind have been shown by Prof. J. A. Fleming and by G. Seibt [†]. The glow is, however, very faint, and may be rendered much more visible by the use of a vacuum-tube, as Prof. Fleming himself suggests.

When experimenting lately in this direction, the present writer noticed that if a long vacuum-tube was laid parallel to the helix, light and dark portions were observed, but that these did not coincide with the points of maximum and minimum potential respectively; and it was of course evident that such a tube is influenced not by the actual potential, but by its slope or $\frac{\partial V}{\partial x}$ along the tube. As the intrinsic equation of propagation is $\frac{\partial V}{\partial x} = IC$, it is clear that the brightness of the tube is proportional to the current in the helix, and that therefore the whole distribution of current and potential can be exhibited by vacuum-tubes fixed parallel to and perpendicular to the helix respectively. A few photographs of the effects observed were published in a recent paper [‡], but these were obtained by successive exposure of the same tube in different positions.

In order to show these effects with the greatest convenience the model shown in fig. 1 (Pl. XXII.) has been made. The helix is 182 cms. long and 2·65 cms. in external diameter. It is wound on a glass tube with 25·5 turns per cm. of 13 mil. D.S.C. wire; and has a resistance of ·43 ω, an inductance of $\frac{\pi^2 d^2 n^2}{1000} = 44$ microhenrys per cm. The capacity from experiments with a metal tube of similar diameter appears to be $9{\cdot}2 \times 10^{-6}$ mfd. per cm.

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[*] Communicated by the Physical Society: read March 27, 1908.

[†] See 'The Principles of Electric Wave Telegraphy,' by Dr. J. A. Fleming, pp. 251-261.

[‡] "The Theory of Alternate Current Transmission in Cables," Electrician, vol. lx, No. 10, p. 358.

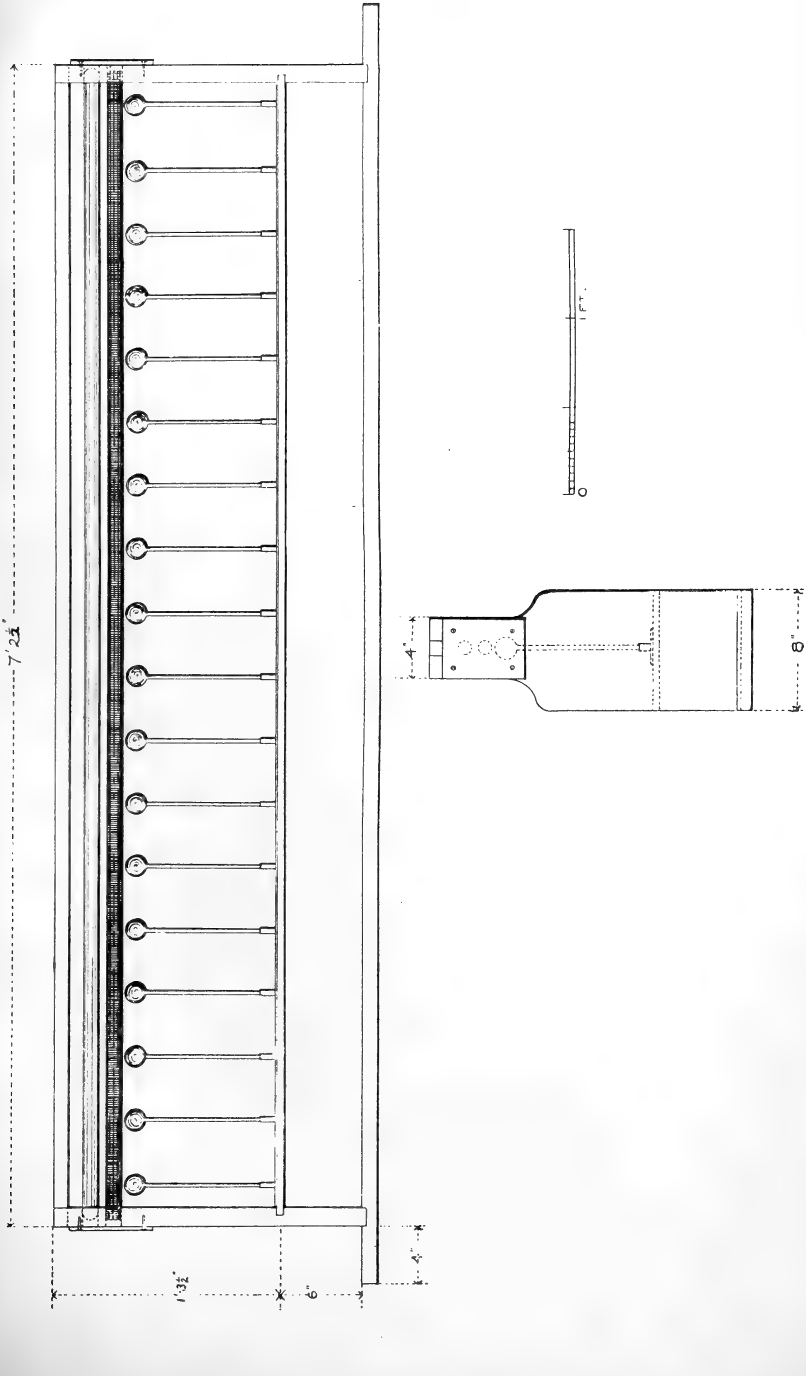

FIG. 1.—General view of apparatus.

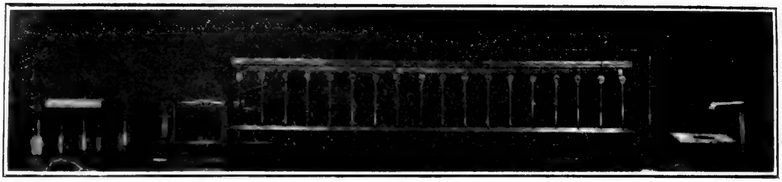

Fig. 2.—Apparatus and accessories.

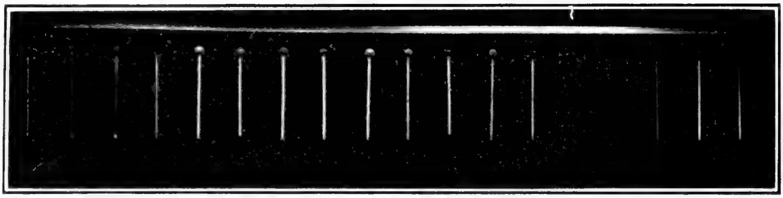

Fig. 3.—Frequency about 600,000. Receiving end open.

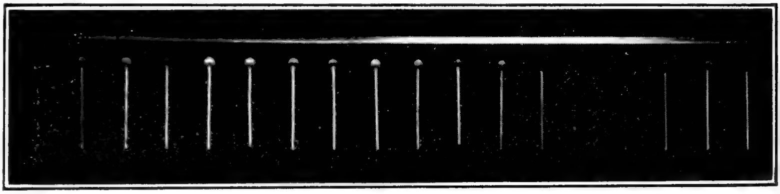

Fig. 4.—Frequency about 1,140,000. Receiving end open.

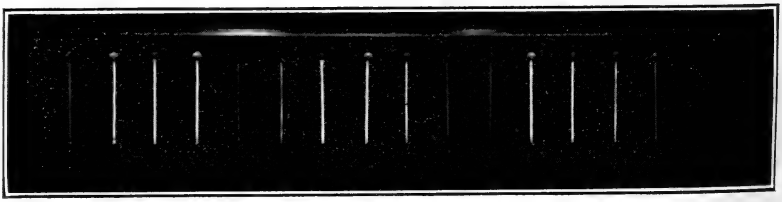

Fig. 5.—Frequency about 1,800,000. Receiving end open.

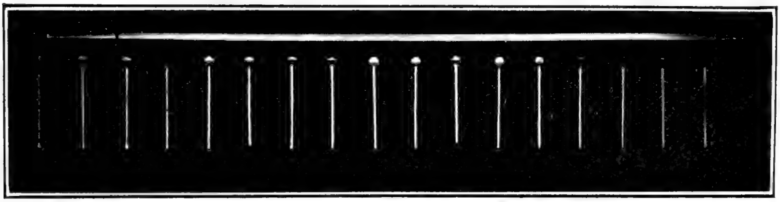

Fig. 6.—Frequency 600,000. Non-inductive receiver.

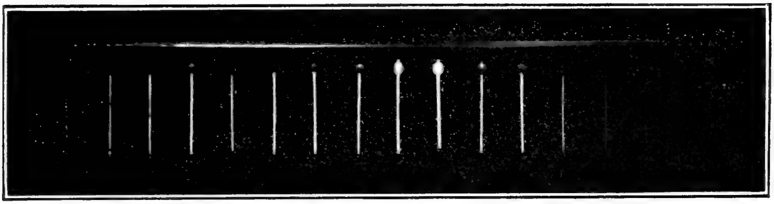

Fig. 7.—Frequency 600,000. Receiving end earthed.

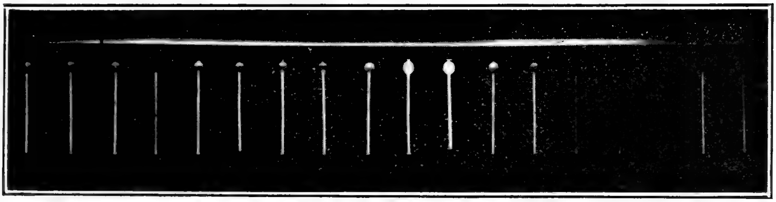

Fig. 8.—Frequency 600,000. Capacity increased by internal wire. Receiving end open.

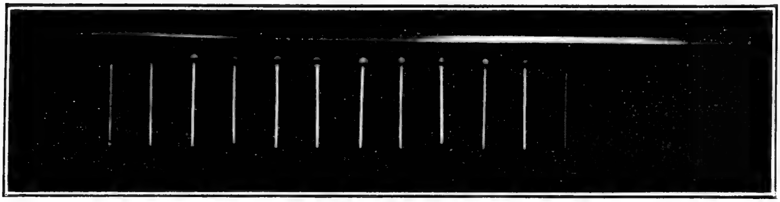

Fig. 9.—Frequency 600,000. Receiving end earthed through condenser.

This helix is supported in a wooden frame, and has above it a carbon-dioxide vacuum-tube 1 inch diameter. Immediately below the helix and about 2 mm. from it are the spherical bulbs of 18 vertical carbon-dioxide tubes, which are mounted in brass sockets on a metal strip fixed to a shelf at the bottom.

The helix is excited from a 10 in.-spark induction-coil with an oscillation-circuit consisting of six leyden-jars of about ·002 microfarad each, which can be connected in series or parallel; and an adjustable helix having a maximum inductance of ·000365 henry.

In order to exhibit the effect of different receivers at the end of the line a water resistance, consisting of a tube about 5 mms. diameter and 30 cms. long, was made up, as well as an adjustable parallel-plate condenser about ·7 sq. ft. in area, and an inductance-coil of 110 yards of No. 16 G.P. covered wire in a hank about 10 in. diameter. By means of mercury cups and paraffin blocks, various arrangements of leyden-jars and loads could be easily made.

The photographs, figs. 2 to 9 (Pl. XXIII.), are of the apparatus, and of the effects observed when currents of different frequency were employed, and different terminal conditions. The sending end was in each case on the left. In figs. 3, 4, and 5 the frequencies were about 600,000, 1,140,000, and 1,800,000∼ per sec. respectively, giving one, two, and three half-waves. In each case the current and potential waves are out of phase; and at the higher frequency, where resistance is of less effect, they are almost exactly in quadrature, as required by theory.

The remaining figures are all with the low frequency and should be compared with fig. 3. Fig. 6 shows the effect of earthing the receiving end through the water resistance; and that, as theory indicates, the current and P.D. become much more uniform in magnitude. In fig. 7 the receiving end is earthed, resulting in a shifting of the waves to the right, so that a second current-loop appears.

Fig. 8 illustrates the effect of increasing the capacity of the helix by introducing an earthed wire inside it, and shows that with the same frequency the wave-length is decreased, so that there are two half-waves instead of one.

Finally, fig. 9 shows the effect of earthing the receiving end through a condenser. The current-loops are shifted forward as when the receiving end was earthed, and at the same time they are much more definite. With inductance the same result is observed, but the shift is backward, as the theory indicates.

No attempt has as yet been made to check the results by theory with great accuracy, nor does it seem probable that this will be of much value, as the presence of such a large number of vacuum-tubes alters the capacity and introduces leakance into the helix. But the general effects observed are of value in illustrating the theory of wave-propagation.

The author's thanks are tendered to Mr. C. M. Dowse who has taken considerable trouble in arranging the apparatus and experiments, and to Mr. A. C. Cossor for the construction of the vacuum-tubes, which were only obtained sufficiently uniform after a considerable amount of trouble.

LXI. *Results of Tests of Materials subjected to Combined Stresses.* *By* E. L. Hancock, *Assistant Professor of Applied Mechanics, Purdue University* *.

During the past four years the writer has conducted tests of steel under combined stresses. These have been carried out in such a way as to combine torsion with tension, flexure, and compression. It is the writer's purpose in this brief report to make a summary of these tests, as well as other tests that have been made along the same lines, and to present these results in such form that they may be readily available for the purposes of the engineer.

Among designers of structures subjected to combined stresses three theories have found favour, namely:—

(1) *The Maximum Stress Theory.*—This theory assumes that the material yields when the tensile (or compressive) stress on any element reaches a certain maximum. It leads to the following relation:

$$q=1/2\left(p\pm\sqrt{p^2+4p_s^2}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where q is the greatest unit-tension (or compression) on any element and p and p_s are the unit-tension (or compression) and unit-shear, found by testing the material in simple tension or compression and simple shear. This theory has been used almost exclusively by American and English engineers.

(2) *The Maximum Strain Theory.*—This theory holds that the material yields when the deformation in tension or compression of any element reaches a certain

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* Communicated by the Author. Read before the American Society for Testing Materials, June 1908.

amount. It holds that Poisson's ratio (the ratio of lateral contraction to longitudinal deformation) is 0·25. Using this ratio the following formula results:

$$q=3/8\,p\pm 5/8\sqrt{p^2+4p_s^2}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the symbols have the same meaning as before. The values of Poisson's ratio for various materials as determined from tests are:

Steel, hard	0·295
,, soft	0·299
Iron	0·277
Brass	0·357
Lead	0·375

It will be seen that these values differ considerably from the value 0·25, so that the formula can hardly be expected to furnish correct results. This formula is in use to a considerable extent in continental Europe.

(3) *Maximum Shear Theory.*—The third theory, and one but little used, is that the material yields when the shear on any element reaches a maximum. This leads to the relation:

$$q_s=1/2\sqrt{p^2+4p_s^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where q_s is the greatest shear on any element. It will be seen from fig. 1 and fig. 2 that this formula fits the results of all the tests much more exactly than either of the others.

Tests made by the writer, by Mr. J. J. Guest, and by Mr. W. A. Scoble (see note *) have been used in making fig. 1. The tests made by Mr. Guest and Mr. Scoble were made by taking the yield-point as a basis, while those made by the writer were made by taking the elastic limit as a basis. Examination of fig. 1 shows very little difference as to which is taken as a basis. The convenience of locating the yield-point suggests an advantage in its favour.

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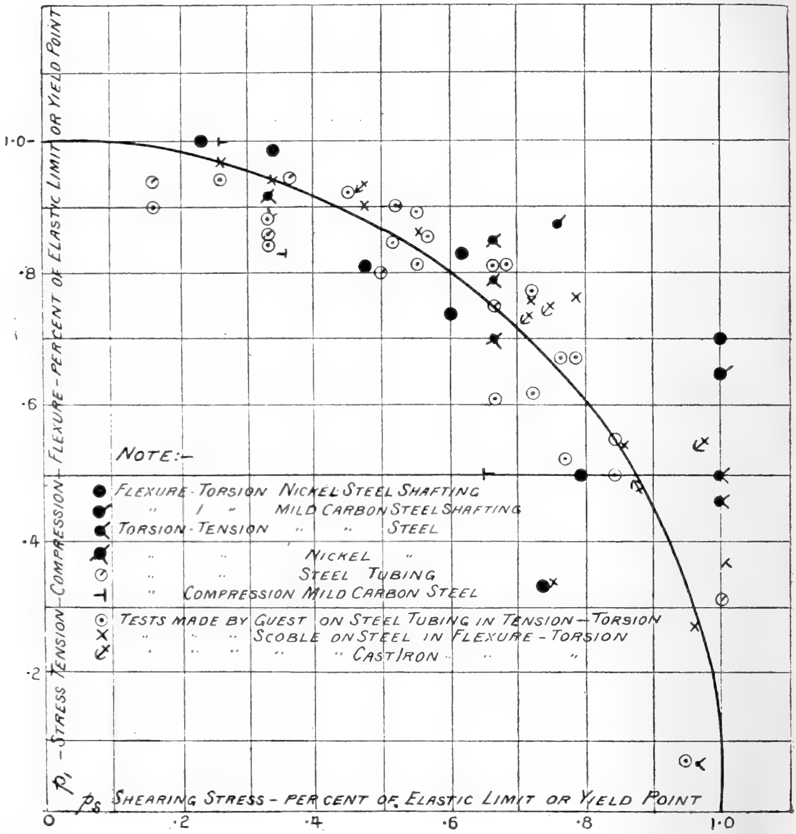
* "Effect of Combined Stresses on the Elastic Properties of Steel," E. L. Hancock, Am. Soc. Test. Mat. vol. v. 1905; vol. vi. 1906; vol. vii. 1907. Also Phil. Mag. Feb. & Oct. 1906 and Feb. 1908. J. J. Guest, Phil. Mag. July 1900, Proc. Physical Soc. of London, Sept. 1900. W. A. Scoble, Phil. Mag. Dec. 1907.

It is seen that the curve is an ellipse with the unit tensile (or compressive) stress as one semi-axis and the unit shear as the other semi-axis. If the shearing strength equals the

Fig. 1.—Results of Tests of Materials subjected to Combined Stresses.



tensile strength, the curve becomes a circle ; this, however, is not generally the case. The equation of the ellipse may be derived as follows :—

Let p be the fibre stress in tension or compression.
" p_s " " " shear.
" b " " " at the elastic limit in tension.
" a " " " " " " shear.
" M_1 be the bending-moment in flexure.
" M_2 " twisting-moment.

Then from the curve

$$\frac{p_s^2}{a^2} + \frac{p^2}{b^2} = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

Knowing a and b from the results of tests of the material in simple tension and torsion and either p or p_s, the other may be determined.

The equivalent twisting-moment for a shaft subjected to combined bending and twisting, derived from (4), is given by the relation

$$M_e^2 = M_2^2 + \left(\frac{4a^2}{q}\right) M_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where M_e is the equivalent twisting-moment.

If the elastic limit in shear be taken as one-half of the elastic limit in tension, (5) becomes

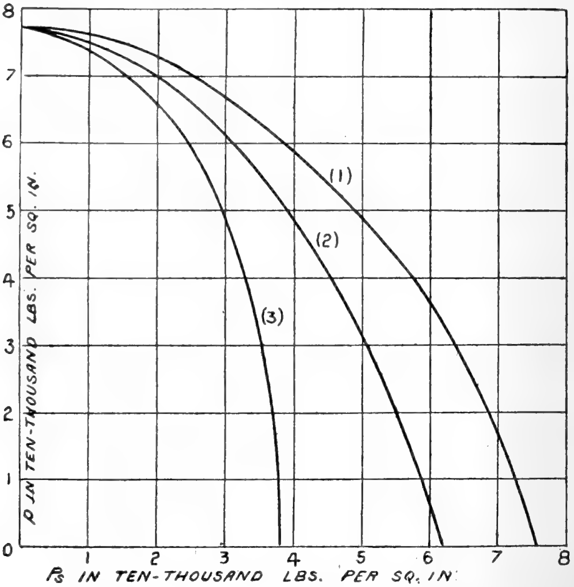
$$M_e^2 = M_2^2 + M_1^2, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

which, lacking a constant factor, is the formula derived by considering the maximum shear theory to hold. This assumption that a equals one-half of b is hardly borne out by the results of tests that have been made, as is shown by the following table :—

Material.	b.	a.	$b/2$.	$a \gtreqless \frac{b}{2}$.	Value of $\frac{4a^2}{b^2}$.
Steel Tubing	21000	10500	10500	=	1·00
Nickel Steel	76500	38000	38200	<	·98
Mild Carbon Steel	47000	30400	23300	>	1·66
Steel (Scoble)	64600	29170	32300	<	·81
Carbon Steel	35500	24400	17700	>	1·84
Rivet Steel.....................	38900	23400	19400	>	1·44
Nickel Steel	56000	36000	28000	>	1·66
Steel Tubing	17000	11500	8500	>	1·82
,, ,, ...	28000	16000	14000	>	1·30
,, ,, ...	20000	12000	10000	>	1·44

An attempt has been made in fig. 2 to show the difference in the shearing strength given by the formulæ representing theories (1), (2), and (3), and expressed in equations (1), (2), and (5). The material under consideration had an elastic limit in tension of 76500 lbs. per sq. inch and an elastic limit in torsion of 38000 lbs. per sq. inch. Equation (5), the equation of the curve in fig. 1, gives the proper elastic limit in shear (the elastic limit in tension was assigned in all cases), while (1) and (2) give an elastic limit much too large. Nearly all values in shear given by (1) and (2) are larger than those obtained from tests. This means that the corresponding bending- or twisting-moment will be too small and if used in design may lead to disaster.

Fig. 2.—Curves showing Shear as given by the Formulæ.



(1) Maximum Stress Theory:—$q=1/2\left(p\pm\sqrt{p^2+4p_s^2}\right)$.

(2) Maximum Strain Theory:—$q=3/8p\pm5/8\sqrt{p^2+4p_s^2}$.

(3) Maximum Shear Theory:—$q=\sqrt{p^2+\frac{b^2}{a^2}p_s^2}$.

The last agrees with the results of tests.

In conclusion, it may be said that both the maximum stress theory and the maximum strain theory give an equivalent moment that is too small. They should not, therefore, be used without a large factor of safety. The maximum shear theory agrees very nearly with the results of tests and the resulting formula, or some slight modification of it should be used in practice. The following formulæ are recommended :—

$$q=\sqrt{p^2+\frac{b^2}{a^2}p_s^2},$$

$$M_e^2=M_2^2+\left(\frac{4a^2}{b^2}\right)M_1^2.$$

LXII. *Some Properties of Artists' Colours.*
By HERBERT EDMESTON WATSON, *B.Sc., A.I.C.*[*]

PART I.—*The Stability of Paints.*

THIS subject is by no means a new one, having probably occupied the attention of colour manufacturers from the earliest times, while in 1888 a report on "The Action of Light on Water Colours" was made to the Government. Up till now, however, not much work seems to have been done in investigating the precise change which paints undergo when they fade.

The chemical reaction which takes place is probably of quite a simple nature, and if it is the same for the majority of paints, it should not be hard to discover. Bearing this fact in mind, the action of hydrogen peroxide on paints was tried, for this substance is known to be formed by the action of air on water in presence of organic matter and light, and moreover it is a very active reagent. The experimental part was carried out as follows :—

A small portion of the pure finely-ground paint to be investigated was well stirred up with water, and a few drops of the suspension poured into each of two small test-tubes. In this way, very minute, but approximately equal quantities were obtained. To one test-tube was added about 1 c.c. of the purest hydrogen peroxide solution (10 vols.), and to the other an equal quantity of water. Both tubes were drawn off in fine capillaries, to avoid loss by evaporation, and kept side by side for a fortnight in the cold ; they were then placed in a steam oven, the usual temperature of which was about 40°, for a year. Observations were made at frequent intervals, and by comparing the two tubes, any change could

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[*] Communicated by Sir William Ramsay, F.R.S.

be at once seen. Below is a table giving the results for a number of paints. In addition, under the heading "Sunlight" is given the effect of light on the same paints. By the courtesy of a well-known firm of colour manufacturers, I was enabled to have access to a number of specimens of water-colours which had been as far as possible exposed to sunlight for 30 years, and also to corresponding specimens which had been kept in the dark. It is from these that the results are taken.

Since writing the above, a paper on "The Action of Ozone on Water-colour Pigments," by Sir William Abney, has appeared [*]. As ozone and hydrogen peroxide are both powerful oxidizing agents, a comparison of the effects produced by them should prove interesting, and consequently the results in the above-mentioned paper are included in the following tables under the heading "Ozone." The figures show the time taken by moist ozonized air to bleach the paint.

Name of Paint.	*Sunlight.*	H_2O_2.	*Ozone.*	
			h	m
Naples Yellow	No change.	Deepened, 1 day.	0	45
Lemon Yellow	No change.	White, 2 weeks.		
King's Yellow	Quite faded.	Colourless on warming.		
Strontium Yellow	No change.	Brown in 10 minutes.		
Gamboge	Browned.	Slight change.	0	50
Indian Yellow	Browned.	Colourless in 1 day.	4	0
Yellow Lake	Quite faded.	Colourless in 3 days.		
Cadmium Yellow	Browned.	Dissolved at once.	4	0
Chrome Yellow	Slightly green.	Paled slightly.	Unchanged.	
Vermillion	Dark brown.	Stable.	Unchanged.	
Scarlet Lake	Brown.	Paler.		
Crimson Lake	White.	Colourless in 2 weeks.	0	30
Purple Lake	White.	Colourless on heating 1 day.		
Carmine	White.	Colourless in 1 day.	0	10
Madder Carmine	Much faded.	Colourless in 1 week.		
Rose Madder	Darkened.	Paler.	4	0
Purple Madder	Greyish.	Colourless in 1 day.	0	20
Madder Brown	White.	Colourless in 1 day.	2	10
Vandyke Brown	White.	Colourless on heating 4 days.	1	15
Sepia	White.	Colourless in 1 week.	0	50
Emerald Green	Darkened.	Brown at once.	0	45
Sap Green	Blue-grey.	Colourless in 1 day.		
Blue Verditer	Greenish.	Brown at once.		
Indigo	White.	Stable.	0	40

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[*] Proc. Roy. Soc., A. vol. lxxx. p. 146 (1908).

The following paints were not treated with hydrogen peroxide, but the effect of sunlight alone is given.

Name of Paint.	*Effect of Sunlight.*
Italian Pink	Quite faded.
Galls Yellow	Quite faded.
Lemon Chrome	Greenish.
Orange Orpiment	Light red.
Fustic Yellow	Quite faded.
*Brown Pink	Quite faded.
Dragon's Blood	Colourless.
Permanent Scarlet	Green brown.
Orange Vermillion	Slightly darkened.
Indian Lake	White.
Deep Rose	White.
Permanent Crimson	White.
Burnt Carmine	White.
Dahlia Carmine	White.
†Violet Carmine	White.
Indian Purple	Grey.
Pink Madder	Darkened.
Cologne Earth	Pale.
Chalon's Brown	Slightly pale.
Roman Sepia	Reddish white.
Warm Sepia	White.
Extract of Madder	Pale.
Hooker's Green 1	Dark.
Hooker's Green 2	Bluish green.
Olive Green	Brown.
Prussian Green	Bluish.

* Bleached by ozone in 30 mins.
† Bleached by ozone in 4 hrs.

Zinc Yellow, Malachite Green, and Verditer were decolorized at once by hydrogen peroxide, Madder Orange after heating for three days.

The following were found to be stable to hydrogen peroxide :—

Alizarin Scarlet.
Alizarin Crimson.
Ivory Black.
Bitumen.

The following to sunlight :—

Permanent Yellow.
Mars Yellow.
Chinese Orange.
Burnt Yellow Ochre.
Burnt Gold Ochre.
Mars Orange.
Turner's Brown.
Leitch's Brown.
Veronese Green.
Veridian.
Ultramarine.
*Ultramarine Ash, 1, 2, & 3.
Mineral Grey.
*French Blue.
Cyanine Blue.
Intense Blue.
Chinese Blue.

And the following to both hydrogen peroxide and sunlight:—

*Yellow Ochre.
Other Ochres.
*Raw Sienna.
Orange Chrome.
Red Lead.
Light Red.
*Venetian Red.
*Burnt Sienna.
*Indian Red.
Madder Red.
Raw Umber ?
Bistre ?
Burnt Umber.
*Terra Verte.
Cobalt Green.
*Chromium Oxide.
Transparent Chromium Oxide.
Smalt.
*Cobalt Blue.
Ceruleum.
*Prussian Blue.
*Antwerp Blue.

* Paints marked with a star were treated with ozone, and remained unaffected.

The most striking fact in connexion with the above tables is the practically identical action of hydrogen peroxide and ozone. Indigo appears to be the only exception, being quite stable towards the former reagent, but easily bleached by the latter. This similarity of action, however, is precisely what would be expected from the chemical nature of the reagents, and, indeed, it seems rather strange that the relative times taken to complete the reaction are not more comparable. The explanation of this is probably to be found in the fact that in neither case were the experiments carried out quantitatively, the weights of paint and bleaching agent being only of the same order of magnitude in each set of experiments. Too much attention must not therefore be paid to the actual times taken.

Bearing this fact in mind, it will be seen that in the majority of cases the action of these oxidizing agents and of light is the same, and this appears to be fairly strong, though of course not conclusive evidence, that in general, the fading of paints is due to oxidation. With regard to the actual active agent, it may be again mentioned that hydrogen peroxide is known to form from moist air in presence of organic matter and light, while the production of ozone under these circumstances is not certain. Moreover, it was found that dry ozone was without bleaching action, and consequently the action may be due to the intermediate formation of hydrogen peroxide in presence of water.

There is one more point of interest. The report of 1888 mentions Antwerp Blue and Prussian Blue as being two of the most fugitive colours, a fact well known to artists. However, it will be seen that neither is attacked by hydrogen peroxide or ozone, and that the pure samples exposed to sunlight were also unaffected.

In conclusion, it may be pointed out that if the fading of paints is due to hydrogen peroxide, much may be done towards their preservation by the employment of a suitable medium. Water-colours are known to be much less stable than oils, and by finding a medium very impermeable to air and moisture, it should be possible to prolong almost indefinitely the life even of a fugitive colour.

PART II.—*The Transparency of Paints.*

The transparency of a paint, or its inverse the opacity, is of more importance to the technical painter than to the artist, for the greater the opacity of a paint, the greater is its efficiency as a covering agent, or in other words, the greater the opacity, the less paint will be required to produce a given effect.

The following experiments were performed with a view of comparing the opacity of various paints. The method employed was to cover a bright metal surface crossed by black lines with a suspension of the colouring material in water. After drying in a level position the effect was observed. If the black lines were visible, more paint was put on, but if not, a little was washed off. The whole was weighed after each operation, and in this way two weights were obtained fairly close together; in one case, however, the black lines were just visible, and in the other they were not. By taking the mean of these, the weight of paint which would just cover the metal was approximately obtained.

These experiments cannot claim any great degree of accuracy, but they afford at least some idea of the relative transparency. The results below (p. 730) show the number of milligrams of paint required to just cover one square centimetre.

In a few cases the paints were so transparent that the thick coating necessary to hide the black lines could not be applied evenly, and in such cases it usually cracked and peeled off. Beyond this, the only point of interest is that gamboge when painted on metal dries as a perfectly transparent yellow varnish, and in this appears to differ from all other paints, the nearest approach to it being sap green.

Baryta	15·05	Indian Yellow	2·07
Flake White	5·52	Gamboge	—
Zinc White	5·32	Yellow Ochre	3·62
Blue Verditer	2·32	Raw Sienna	very great
Ceruleum	3·44	Madder Orange	very great
Cobalt Blue	2·68	Red Lead	6·41
Smalt	2·42	Deep Chrome	3·91
Antwerp Blue	1·32	Vermillion	8·42
Indigo	2·29	Scarlet Lake	2·63
Prussian Blue	0·68	Carmine	1·57
Emerald Chromium Oxide	7·00	Rose Madder	6·27
Emerald Green	4·17	Crimson Lake	3·12
Cobalt Green	4·14	Alizarin Scarlet	2·49
Malachite Green	2·88	Alizarin Crimson	2·15
Verditer	3·57	Madder Carmine	5·6 at least
Sap Green	3·89	Venetian Red	4·42
Artificial Sap Green	4·38	Light Red	2·29
Terra Verte	2·14	Indian Red	1·16
Chromium Green Oxide	2·20	Purple Lake	1·68
Yellow Lake	5·36	Madder Red	1·98
Cadmium Yellow	2·82	Purple Madder	2·22
Aureolin	4·48	Burnt Sienna	6·08
Chrome Yellow	3·83	Brown Madder	1·49
King's Yellow	6·35	Raw Umber	1·64
Zinc Yellow	4·75	Burnt Umber	1·08
Strontium Yellow	6·00	Vandyke Brown	1·86
Lemon Yellow	5·30	Bitumen	1·76
Naples Yellow	7·25	Bistre	1·67
Pale Naples Yellow	4·87	Sepia	—
Bright Naples Yellow	4·23	Ivory Black	1·61

PART III.—*The Absorption Spectra of Paints.*

The absorption spectra of about fifty of the most important paints have been measured. The instrument used was the spectrophotometer designed by Dr. Mees, and kindly lent to me by him. It is fully described in the *Revue des Sciences Photographiques*, Feb. 1905, but the principle of it is that two spectra are brought into juxtaposition by means of an Albrecht's prism. The light forming one of them comes from a standard source, and can be cut down by means of two Nicol prisms until the intensity of the light in any given portion of the two spectra (cut out by means of a slit) is the same. When this is so, the percentage of light coming from the unknown source is proportional to the square of the cosine of the angle through which the nicol is turned. The prism was of the constant deviation type, and the wave-length of the light seen through the slit could be read off on a scale.

For purposes of observation the paints were painted on strips of dull white paper, in size about 3 × 2 ins. Half the paper was left bare, and the whole illuminated with an Auer burner. The light reflected from the white paper formed the standard spectrum.

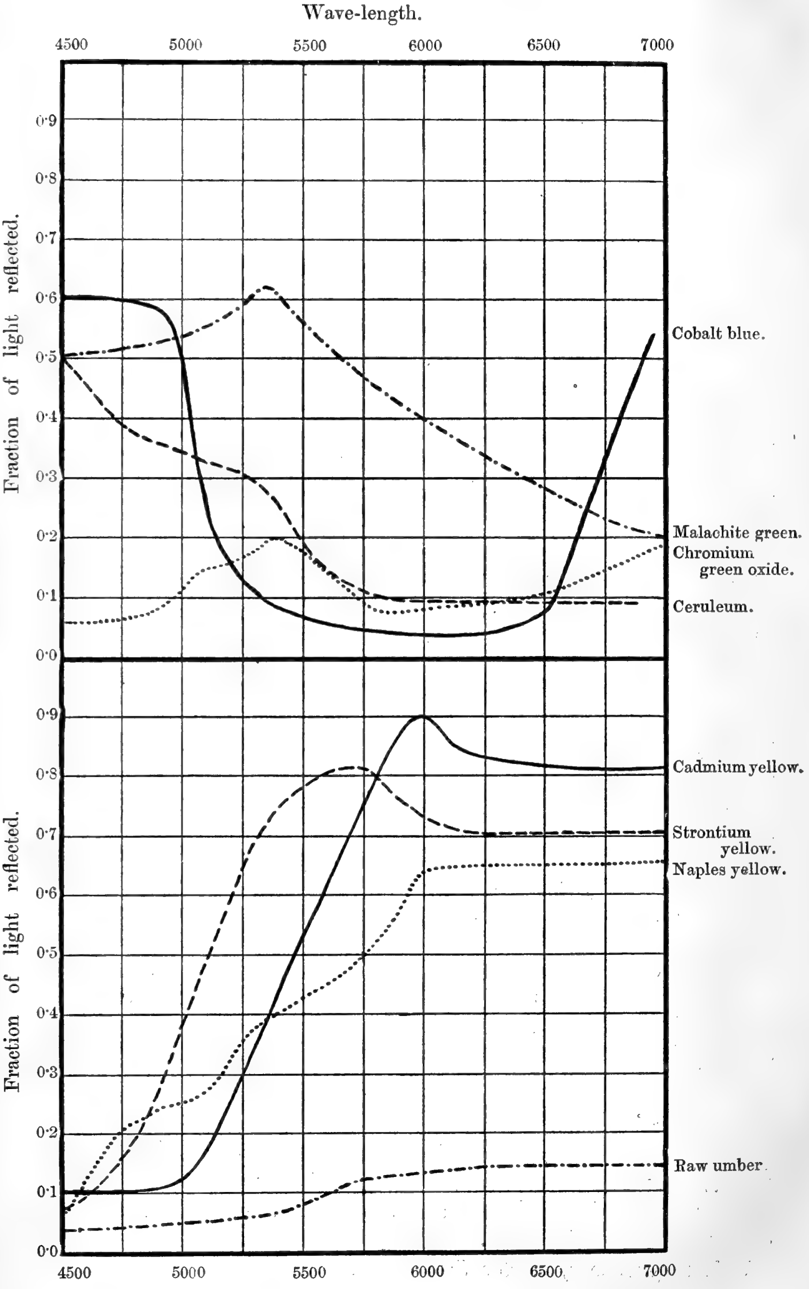
It is difficult to determine the accuracy of the observations, but the errors are practically entirely due to the observer, as the instrument was of exceptionally good quality, and most carefully adjusted. Readings were most difficult when the light was of high intensity, and in such cases their number was increased so as to give a fairly reliable mean. It was also difficult to match the intensities in the red, probably because in this region the dispersion is less, and the colour seen not so pure as in other parts.

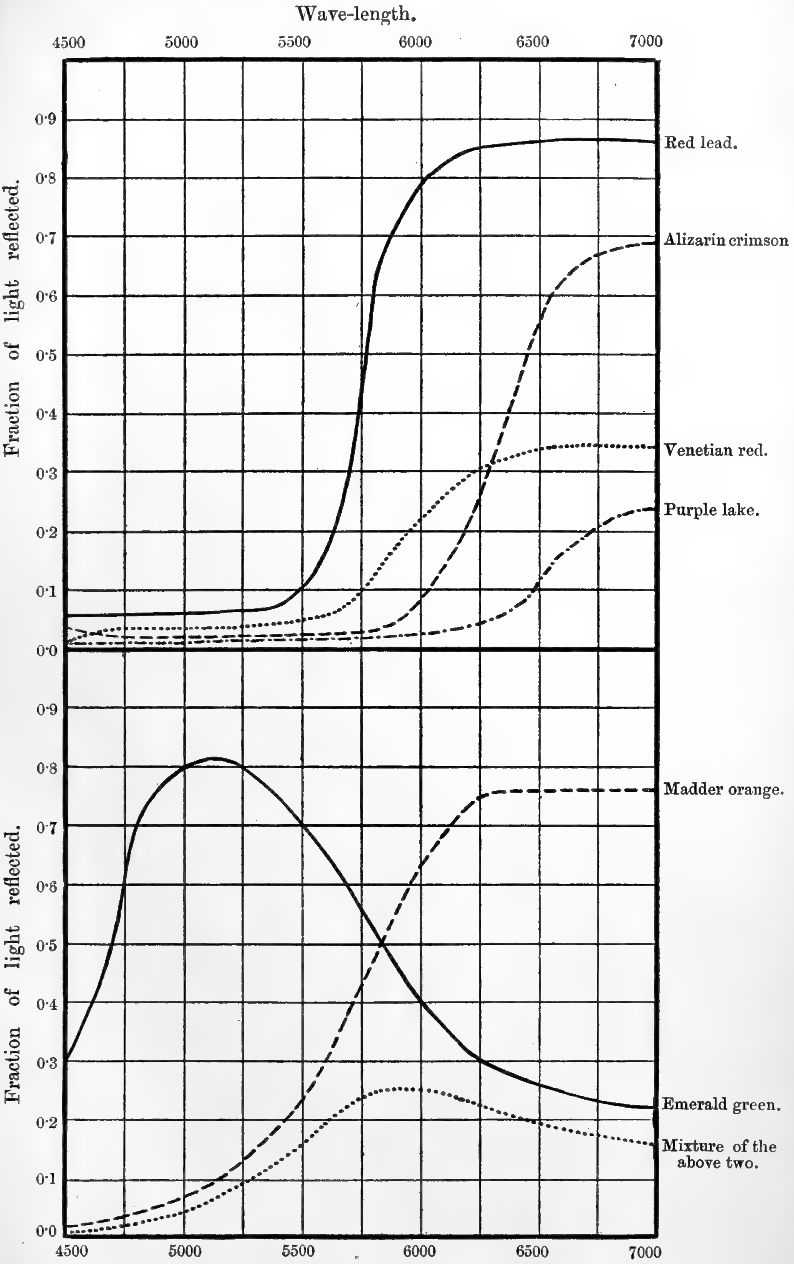
Some diagrams (pp. 732–33) are given showing the nature of the absorption. In them the fraction of the total light reflected by the paint is plotted against the wave-length. They show at a glance the true nature of the reflected light, and also the percentage of white light, this being given by the ordinate of the lowest point of the curve. It is also worthy of note that in all cases the region of maximum intensity extends over a considerable range of wave-length, that is to say, the apparent colour of a paint is never even approximately monochromatic, although to the eye it may appear to be so.

In addition to this, the effect of mixing one or more paints may be approximately obtained from the curves. Thus in the simplest case of a mixture of equal quantities of two paints, the absorption-curve of the resultant colour will be obtained by multiplying together the ordinates of the two curves for each wave-length, and joining the resultant points. An example of this is given for a mixture of emerald green and madder orange; these, although both very bright colours, will only combine to give a brownish-yellow of low intensity. This is of course only an approximation, but it helps to illustrate the fact that in order to obtain a bright colour from a mixture of others, it is necessary that these should have some part of the brightest portion of their spectra in common, and consequently the most efficient paints for producing bright colours, when mixed with others, are those possessing broad maxima of intensity.

In conclusion, I should like to express my best thanks to Sir William Ramsay for suggesting this work to me, and for his frequent help in it; and also to Dr. Mees for the loan of his spectrophotometer.

University College, London, January 1908.


Wave-length.
4500
5000
5500
6000
6500
7000
Fraction of light reflected.
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
Cobalt blue.
Malachite green.
Chromium green oxide.
Ceruleum.
Cadmium yellow.
Strontium yellow.
Naples yellow.
Raw umber.


Wave-length.
4500
5000
5500
6000
6500
7000
Fraction of light reflected.
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
Red lead.
Alizarin crimson
Venetian red.
Purple lake.
Madder orange.
Emerald green.
Mixture of the above two.

LXIII. *On the Resistance of a Conductor of Uniform Thickness whose Breadth suddenly changes, and on the Shapes of the Stream-Lines in the immediate neighbourhood.*

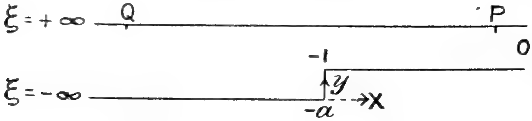
By CHARLES H. LEES, *D.Sc., F.R.S., Professor of Physics in the East London College, University of London* [*].

A KNOWLEDGE of the resistance of a conductor whose section suddenly changes is of considerable practical importance, but mathematical difficulties have prevented an exact solution of the problem. Lord Rayleigh [†] has given an approximate solution of the case in which a cylinder of circular section is joined at one end to the plane surface of a large conducting solid, and Professor Hicks [‡] has solved the case of a wire of small diameter ending in the surface of a conducting sphere [§].

The mathematical difficulties of the problem disappear if the conductors are of rectangular section and one dimension, *e.g.* the thickness, remains constant, while the other, the breadth, suddenly changes, and the two are joined together either with their axes or with two sides colinear. For a longitudinal flow through the conductors the former case becomes the latter by section through the common axis, which by symmetry is a line of flow.

Let the thickness of the conductor be t, the breadth of the wider part c, that of the narrower b, and let k be the conductivity of the material. Take the plane of the conductor as the z plane, fig. 1, and convert the outline of the conductor by means of the Schwarzian transformation

Fig. 1.—z plane.



$$\frac{dz}{d\zeta} = A\zeta^{-1}(\zeta+1)^{\frac{1}{2}}(\zeta+a)^{-\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (1)$$

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[*] Communicated by the Physical Society: read June 12, 1908.

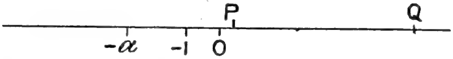
[†] Lord Rayleigh, Trans. Roy. Soc. London, lxi. p. 77, Nov. 1870; and 'Scientific Papers,' vol. i. p. 56. See also Phil. Mag. viii. p. 481 (1904).

[‡] Professor Hicks, Messenger of Mathematics, xii. p. 183 (1883).

[§] A list of cases which have been worked out will be found in Professor Auerbach's articles "Flächenströme" and "Körperliche Ströme" in Winkelmann's *Handbuch der Physik,* 2nd edit. iv.pp. 238, 246.

into the axis of ξ in the ζ plane fig. 2, the corresponding points being indicated by the lettering in the figures.

Fig. 2.—ζ plane.



In
$$z = \mathrm{A}\int \frac{1}{\zeta}\sqrt{\frac{\zeta+1}{\zeta+a}}\,d\zeta$$

write
$$\frac{\zeta+1}{\zeta+a}=\frac{1}{\theta^2},$$

and the integral becomes
$$z=2\mathrm{A}\int\frac{(a-1)\,d\theta}{(a-\theta^2)(1-\theta^2)}$$
$$=2\mathrm{A}\int\left(\frac{1}{1-\theta^2}-\frac{1}{a-\theta^2}\right)d\theta$$
$$= 2\mathrm{A}\left\{\arg\binom{\tanh}{\coth}\pm\sqrt{\frac{\zeta+a}{\zeta+1}}-\frac{1}{\sqrt{a}}\arg\binom{\tanh}{\coth}\pm\sqrt{\frac{\zeta+a}{a(\zeta+1)}}\right\};^{*}\quad(2)$$

where the origin in the z plane is taken at the point corresponding to $\xi=-a$, $\eta=0$ in the ζ plane, and tanh or coth is taken according to whether the quantity under the root sign is less than or greater than unity.

In order to show the connexion between the z and ζ planes graphically, we write
$$\zeta+a=r_a e^{i\theta_a},\qquad \zeta+1=r_1 e^{i\theta_1},$$

where r_a, θ_a, r_1, θ_1 are the coordinates of the point $\xi\eta$, with respect to the points $-a$ and -1 (fig. 2), and
$$r_a^2=r^2+2ar\cos\theta+a^2,\qquad \cot\theta_a=\frac{\cos\theta+\frac{a}{r}}{\sin\theta},$$
$$r_1=r^2+2r\cos\theta+1,\qquad \cot\theta_1=\frac{\cos\theta+\frac{1}{r}}{\sin\theta}.$$

Resolving each term of the above equation into its norm and

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* The form argtanh has been retained throughout because of the symmetry of the norm and amplitude when this is done.

amplitude, we obtain

$$z = A\left[\operatorname{argtanh}\left(\pm\frac{\cos\frac{\theta_a-\theta_1}{2}}{\cosh\log\sqrt{\frac{r_a}{r_1}}}\right) - i\arctan\left(\pm\frac{\sin\frac{\theta_a-\theta_1}{2}}{\sinh\log\sqrt{\frac{r_a}{r_1}}}\right)+im\pi\right.$$

$$\left.-\frac{1}{\sqrt{a}}\left\{\operatorname{argtanh}\left(\pm\frac{\cos\frac{\theta_a-\theta_1}{2}}{\cosh\log\sqrt{\frac{r_a}{ar_1}}}\right)-i\arctan\left(\pm\frac{\sin\frac{\theta_a-\theta_1}{2}}{\sinh\log\sqrt{\frac{r_a}{ar_1}}}\right)+in\pi\right\}\right]$$

where m and n are integers. The alternatives tanh and coth of equation (2) both lead to the same result.

On determining the values of the constants A and a so as to make $y=0$ from $\xi=-\infty$ to $\xi=-a$, $y=c-b$ from $\xi=-1$ to $\xi=0$, $y=c$ from $\xi=0$ to $\xi=\infty$, we find that the negative sign must be assigned to the term in the small brackets, that $A=c/\pi$, $\sqrt{a}=c/b$, and the equations become

$$z = x+iy = \frac{2b}{\pi}\arg\binom{\tanh}{\coth}\frac{c}{b}\sqrt{\frac{\zeta+1}{\zeta+c^2/b^2}} - \frac{2c}{\pi}\arg\binom{\tanh}{\coth}\sqrt{\frac{\zeta+1}{\zeta+c^2/b^2}}$$

$$=\frac{b}{\pi}\left\{\operatorname{argtanh}\frac{\cos\frac{\theta_1-\theta_a}{2}}{\cosh\log\frac{c}{b}\sqrt{\frac{r_1}{r_a}}} - i\arctan\frac{\sin\frac{\theta_1-\theta_a}{2}}{\sinh\log\frac{c}{b}\sqrt{\frac{r_1}{r_a}}}\right\}$$

$$-\frac{c}{\pi}\left\{\operatorname{argtanh}\frac{\cos\frac{\theta_1-\theta_a}{2}}{\cosh\log\sqrt{\frac{r_1}{r_a}}} - i\arctan\frac{\sin\frac{\theta_1-\theta_a}{2}}{\sinh\log\sqrt{\frac{r_1}{r_a}}}\right\},^{*} \quad (3)$$

where the arctan terms are to be taken within the limits 0 and π.

The curves in the z plane into which this equation converts the orthogonal system of circles $\theta_1-\theta_a=\text{constant}$, and $r_1/r_a=\text{constant}$, of the ζ plane, are shown in fig. 3 for the case $c/b=2$. They may be considered either as the potential and stream curves for a source at 1 and an equal sink at A,

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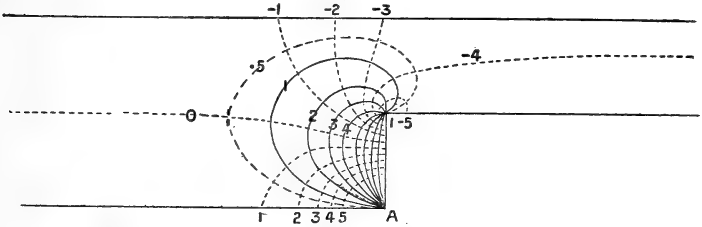
* The term argtanh $\dfrac{\cos\theta}{\cosh\log\rho}$ may be more familiar in the form

$$\tfrac{1}{2}\log\frac{\cosh\log\rho+\cos\theta}{\cosh\log\rho-\cos\theta}=\tfrac{1}{2}\log\frac{\rho^2+2\rho\cos\theta+1}{\rho^2-2\rho\cos\theta+1}.$$

or for the edge 1A kept at one potential and the whole of the remainder of the edges at another.

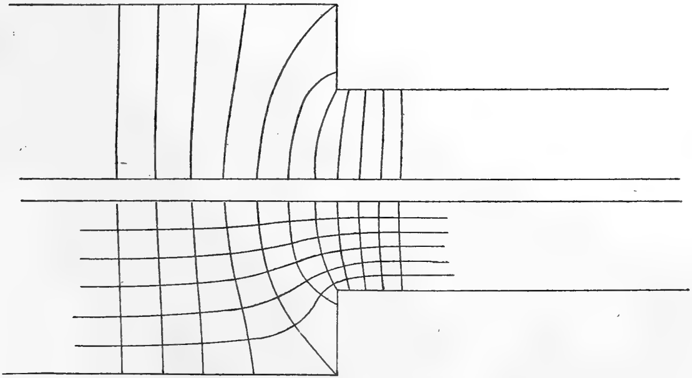
Fig. 3.



Full lines are equipotential lines, dotted lines are stream lines, when the end 1A is kept at potential 9, and the rest of the contour at 0. Ratio of breadths 1 : 2.

The curves in the z plane corresponding to $\log \zeta =$ constant in the ζ plane are shown in fig. 4 lower part, and represent the equipotential and stream lines for a current flowing along the two strips in series. The upper part shows the observed equipotential lines *.

Fig. 4.



Lower part equipotential and stream lines calculated; upper part equipotential lines observed. Ratio of breadths 1 : 2.

To determine the resistance of the compound conductor to the flow of current along its length, we find the distribution of the potential in the corresponding problem in the ζ plane. This is the case of a source at the point $\xi = \eta = 0$, sending a current C into the upper half of the plane.

* I have to thank my colleague Mr. W. H. White for making the observations on a thin strip of german silver transmitting an electric current, from which these curves have been drawn.

The vector function $w=u+iv$ for this case is given by the equation

$$w=\frac{C}{\pi kt}\log\zeta, \quad . \ . \ . \ . \ . \ . \ . \quad (4)$$

where t is the thickness of the conductors and k is the conductivity of the material of which they are composed.

If ξ_P, 0, are the coordinates of a point P near O in the ζ plane, and x_P is its X coordinate in the z plane (figs. 1 and 2), then by equation (3)

$$x_P=\frac{2b}{\pi}\operatorname{argcoth}\frac{c}{b}\sqrt{\frac{\xi_P+1}{\xi_P+c^2/b^2}}-\frac{2c}{\pi}\operatorname{argtang}\sqrt{\frac{\xi_P+1}{\xi_P+c^2/b^2}},$$

which since ξ_P is small reduces to

$$x_P=\frac{2b}{\pi}\operatorname{argcoth}\sqrt{1+\frac{c^2-b^2}{c^2}\xi_P}-\frac{2c}{\pi}\operatorname{argtanh}\frac{b}{c}.$$

$$=\frac{b}{\pi}\left\{\log\frac{4c^2}{c^2-b^2}-\frac{\pi kt}{C}\cdot u_P\right\}-\frac{c}{\pi}\log\frac{c+b}{c-b},$$

in virtue of equation (4).

Hence

$$\frac{\pi kt}{C}\cdot u_P=-\frac{\pi}{b}x_P-\log\frac{c^2-b^2}{4c^2}-\frac{c}{b}\log\frac{c+b}{c-b}.$$

Similarly if ξ_Q, 0, are the coordinates of a point Q near $+\infty$ in the ζ plane, and x_Q is its X coordinate in the z plane, then by equation (3)

$$x_Q=\frac{2b}{\pi}\operatorname{argcoth}\frac{c}{b}\sqrt{\frac{\xi_Q+1}{\xi_Q+c^2/b^2}}-\frac{2c}{\pi}\operatorname{argtanh}\sqrt{\frac{\xi_Q+1}{\xi_Q+c^2/b^2}},$$

which, since ξ_Q is large, reduces to

$$x_Q=\frac{2b}{\pi}\operatorname{argcoth}\frac{c}{b}-\frac{2c}{\pi}\operatorname{argtanh}\sqrt{1-\frac{c^2-b^2}{b^2\xi_Q}}$$

$$=\frac{b}{\pi}\log\frac{c+b}{c-b}-\frac{c}{\pi}\left\{\log\frac{4b^2}{c^2-b^2}+\frac{\pi kt}{C}\cdot u_Q\right\}$$

in virtue of equation (4).

Hence

$$\frac{\pi kt}{C}u_Q=-\frac{\pi}{c}x_Q-\log\frac{4b^2}{c^2-b^2}+\frac{b}{c}\log\frac{c+b}{c-b}.$$

Thus

$$\frac{kt}{C}(u_Q-u_P)=\frac{x_P}{b}-\frac{x_Q}{c}+\frac{1}{\pi}\left(2\log\frac{c^2-b^2}{4cb}+\frac{c^2+b^2}{cb}\log\frac{c+b}{c-b}\right)$$

Hence the resistance between two transverse sections of the conductors through the points P and Q situated at considerable distances from the change of section and on opposite sides of it, is equal to the sum of the resistances of the lengths of conductor on the two sides of the change of section, each considered as part of an infinite length, plus the resistance of a length of either conductor equal to

$$\frac{1}{\pi}\left\{2\log_\epsilon\frac{c^2-b^2}{4cb}+\frac{c^2+b^2}{cb}\log_\epsilon\frac{c+b}{c-b}\right\}$$

times the breadth of that conductor.

When the ratio of the breadths $c/b=n$ becomes large, the correction approximates to

$$\frac{2}{\pi}(\log_\epsilon n - \cdot 386),$$

and when very large to

$$\frac{2}{\pi}\log_\epsilon n.$$

When, on the other hand, the ratio n of the breadths becomes nearly unity the correction approximates to

$$\frac{(n-1)^2}{\pi}\left\{\frac{1}{2}+\frac{1}{n}\log_\epsilon\frac{2}{n-1}\right\},$$

and when it is very nearly unity to

$$\frac{(n-1)^2}{\pi}\left\{1\cdot 19-\log_\epsilon(n-1)\right\}.$$

In order to exhibit the character of this correction the following table has been calculated.

Correction to be added to the length of one conductor in terms of the breadth of that conductor, in order to make the total resistance equal to the sum of the resistances of the two conductors, each considered as part of a conductor of infinite length.

Ratio of breadths.	No. of breadths to be added to length.	Ratio of breadths.	No. of breadths to be added to length.
1·0	·0	3·0	·48
1·2	·032	4·0	·65
1·4	·080	6·0	·90
1·7	·17	10·0	1·24
2·0	·25	15·0	1·46
2·5	·37	20·0	1·65

LXIV. *The Specific Charge of the Ions emitted by Hot Bodies.* *By* O. W. Richardson, *Professor of Physics, Princeton University* *.

THE value of e/m, the specific charge or charge per unit mass of the negative ions from an incandescent carbon filament, was first measured by J. J. Thomson † in 1899. Since then the value of the same quantity for the negative ions emitted by other hot bodies has been determined by a number of different investigators, all of whom have found values approximating to 10^7 electromagnetic units, indicating that the ions in question are electrons and identical for all substances. The corresponding quantity for the positive ions from hot bodies has received comparatively little attention. The only experiments appear to be some by J. J. Thomson ‡, on an iron wire in an atmosphere of oxygen at a low pressure, which led to the value 400 for e/m. This is about what would be required if the ions were atoms of iron carrying a charge equal to that of the hydrogen ion in electrolysis.

The positive ionization produced by hot metals comprises a number of separate phenomena whose mutual relationships cannot be said, as yet, to be properly understood. A hot wire may give rise to positive ions under a variety of different circumstances. The most important of these conditions which have been investigated are (1) newness, (2) previous exposure to a luminous discharge, and (3) the presence of surrounding gas. A fresh wire, however carefully cleaned and handled, is found to give rise to a very large emission of positive ions when heated for the first time in a good vacuum. This property gradually disappears with continued heating, but may be restored to a certain extent, either by placing the wire near the cathode when a luminous discharge is made to pass in the tube or by heating the wire in an atmosphere of any of the commoner gases. The effect of the luminous discharge is of a temporary character like the property of freshness, whereas the admission of gas produces an effect which is permanent, the ionization at any given temperature being a definite function of the pressure of the gas. The connexion between these different manifestations is not at all well understood, so that it is difficult to discuss positive ionization as a general conception. In a recent

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* Communicated by the Author.

† Phil. Mag. [5] vol. xlviii. p. 547.

‡ Conduction of Electricity through Gases, 2nd ed. p. 148.

paper[*] the author has considered in detail the evidence bearing on the origin of the ionization caused by different gases, and has arrived at the conclusion that the ions arise from the gas absorbed by the metal and are not positive electrons. The argument is discussed particularly on p. 61 of the paper referred to. According to this view we should expect the mass of the positive ions to be comparable with that of the atoms or molecules of the gas surrounding the hot substance. It was felt at the time that most of the evidence adduced was rather indirect and that the case might be greatly strengthened by a direct investigation of the specific charge of the ions. The present investigation was commenced with that object in view, but the interest of the subject has been increased by the announcement by J. J. Thomson[†] of experiments in which he believes to have isolated positive corpuscles in the canal rays. Incidentally the specific charge of the negative ions for the substances experimented upon has also been measured.

§ 2. *The Method Employed.*

The method used by Thomson in measuring e/m for the positive ions emitted by an incandescent iron wire was to place the wire parallel to and 4 mms. distant from an insulated metal plate. The wire was positively charged and a magnetic field applied so that the lines of magnetic force were parallel to the plate. Under these circumstances the paths of the moving ions tend to curve round the lines of magnetic force, and if the magnetic field is strong enough the curvature will be such that none of them will ever reach the plate. If the plate were infinite in extent, if the electric and magnetic fields were uniform, and if all the ions were shot off from the hot body with zero velocity, this limiting value of the magnetic force would be the same for all of them. Under these conditions the current to the plate would be independent of the magnetic field until a certain value of this was reached, at which it would fall to zero and remain zero for all higher values of the field. From this limiting value of the magnetic field the value of e/m can be calculated.

The chief objections to this method, which has the merit of simplicity and quickness in practice, arise from the difficulty of satisfying the theoretical conditions with the large magnetic fields which it is necessary to employ. It is found that the current to the plate does not suddenly

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[*] Phil. Trans. A. vol. ccvii, p. 1.

[†] Phil. Mag. May & Sept. 1907.

disappear, but falls away gradually as the magnetic field is increased, and it is difficult, if not impossible, to tell how much of this effect arises from an actual variation in the specific charge of the ions and how much is to be attributed to the initial velocity of the ions, to the lack of uniformity of the two fields, and to causes of a like nature. For these reasons the author desired to adopt a method in which the theoretical conditions were more exactly fulfilled and where it would be possible also to directly test the uniformity of the character of the ions. The method finally selected, though much more laborious than that used by Thomson, appears to possess advantages in the directions indicated.

Stated briefly, the process used is a direct measurement of the deflexion of the path of the ions, moving in a uniform electric field, arising from the application of a transverse magnetic field. Imagine two infinite parallel conducting planes a few millimetres apart, each of which is divided by a narrow straight slit, the slits being parallel to each other. A narrow rectangular strip of hot metal theoretically infinite in length lies in the slit dividing the upper plane. The lower surface of the strip lies in the upper plane, and this part of the system is fixed. The lower planes and slit are rigidly connected and are movable in a direction lying in the plane and at right angles to the length of the slit. The upper plane and metal strip are charged positively, whilst each half of the lower plane is connected to one of the pairs of quadrants of an electrometer. Its potential is thus always approximately zero and there is a uniform electric field perpendicular to the two planes. The positive ions from the strip will be carried to the lower plane and will distribute themselves in a manner depending on the dimensions of the apparatus, the potential difference between the planes, and the distribution of velocity with which they are emitted from the strip. Each half of the lower plane will receive a positive charge, but in general one half will receive more than the other. Thus a deflexion of the electrometer will be observed, although both quadrants are receiving positive charges. There will be one position of the lower plane for which each half receives the same charge, and then no deflexion will be observed on separating the quadrants of the electrometer. In the absence of a magnetic field this will occur when the lower slit is symmetrically placed with respect to the strip. If we now apply a magnetic field in a direction parallel to the edges of the strip and the slits, the effect of this will be to superpose on the previous motions of the ions a displacement perpendicular to the slit. The lower plane will therefore have to be moved a certain distance in this direction before it will occupy a position such that no deflexion is observed on separating the quadrants of the electrometer. From the amount of this displacement, together with the strengths of the two fields and the distance between the planes, the value of e/m for the ions may be calculated.

The foregoing is an outline of the method which was used at the outset. It was found, however, with the apparatus used that the observed displacements were not strictly proportional to the applied magnetic force, as they should be according to the theory of the method. This discrepancy might arise in a variety of ways, but one of the possible explanations seemed so vital to the subject under investigation that it was essential to settle it definitely before proceeding further. It was evident that the observed absence of proportionality would occur if the ions, instead of being homogeneous, consisted of two or possibly more kinds. In order to settle this question and at the same time to measure the value of e/m the procedure was slightly modified. The two halves of the lower plane were metallically connected together, and an electrode was placed behind the lower slit so as to catch all the ions which passed through it. The quantity of electricity passing through the lower slit and the amount received by the planes were now measured simultaneously for different positions of the lower plane. Thus the fraction of the total quantity of electricity received by the lower plane which passed through the slit could be expressed as a function of the position of the latter. In this way the actual mode of distribution of the ions about the lower plane was obtained. By observing the way in which this is changed by applying a magnetic field in a direction parallel to the sides of the slit it is possible to find out whether the ions are homogeneous or not.

§ 3. *Description of Apparatus.*

The apparatus used in the second of these methods will now be described in detail. Any modifications necessary in changing to the first method are not sufficiently extensive to warrant separate description.

A number of different sections through the essential part of the apparatus are shown in fig. 1. The central figure represents a vertical section by the plane of symmetry of the apparatus. The same parts are denoted by the same letters in the different sections. The two conducting planes already alluded to were supported by an ebonite frame, *bb′ b′ b*.

The "upper" plane consisted of two brass plates *ff*, shown in plan in the top right-hand figure. The ends of these were slotted into ebonite pieces *tt*, which were screwed on to the main ebonite frame at *bb*. The line *bab* in the central

Fig. 1.

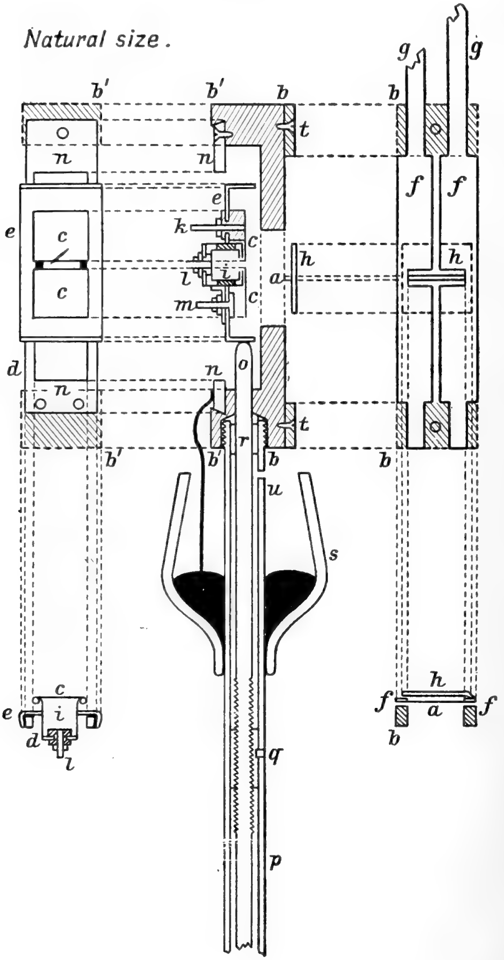
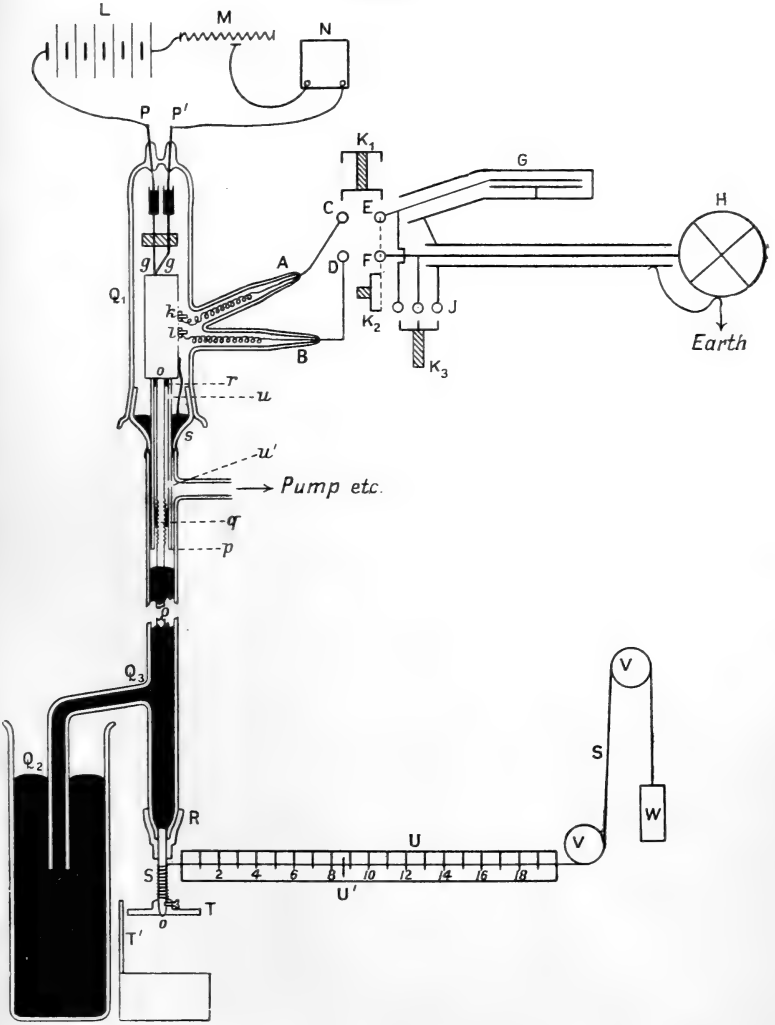


figure thus represents the section of the "upper" plane by the plane of the paper. The two plates *ff* were separated by a longitudinal slit somewhat exaggerated in the figure, and in addition were cut away at the centre so as to leave a narrow rectangular aperture. The platinum strip *a*, which was cut from foil ·0024 cm. thick, and was usually about ·03 cm. wide, was soldered to the inner side of the plates so as to stretch along this rectangular aperture. In order to eliminate as far as possible any lack of uniformity in the electric field caused by the rectangular aperture, an additional plate *h* was placed behind it and soldered to one of the plates *f*. A transverse section through the centre of the strip is shown below on the right. This shows the plates *f* and *h* and the ebonite support *b*. In both this and the next figure ebonite parts are indicated throughout by cross hatching. It will be observed that the only metallic connexion between the plates *ff* is by means of the metal strip. The terminals *gg* led to mercury cups, by means of which a current could be supplied which served to heat the metal strip.

The "lower" plane is represented by the plates *cc*, shown in plan on the left above. These were insulated from and supported by a brass carriage *e*, which slid on ways *d*, cut out of a brass plate *nn*. The edges of the topmost of the two plates *c*, which was fixed relatively to the carriage, were bent round and soldered to two stiff straight brass wires. The edges of the other plate *c* were similarly bent round but not soldered to the wires, so that this plate could be slid along the wires and the width of the slit thus adjusted. The top plate, *c*, had a brass wire, *k*, soldered to it, on which a thread was cut. This passed through to an ebonite button, which fitted into a hole in the carriage *e*, then through an ebonite washer, and was finally screwed tight by means of a brass nut. A wire soldered to this nut made connexion with the electrometer. It will be observed that in this way the plates *cc* were thoroughly insulated. The catching electrode behind the slit is shown at *i*. This consisted of an outer box in metallic connexion with the carriage, enclosing a [_] shaped electrode insulated from it. The method of fixing and insulating the inner electrode was identical with that for the plate *c*, with the addition that strips of ebonite were placed between its ends and the sides of the outer box, to prevent it from coming into contact with the latter. A metal bracket soldered to the outside of the box enabled it to be rigidly screwed into metallic connexion with the carriage at *m*, the sequence of nuts &c. being similar to *k* and *l*. The connexion of *l* to the electrometer was made by means of a wire soldered to its nut. A section near the slit showing the manner in which the carriage slid on the ways *d* is shown below on the left. The openings into the box and the electrode inside it were made considerably wider than the slit between *cc*, so as to allow for the curvature of the paths of the ions. The whole of the part of the apparatus comprised by $b' t t b'$ was surrounded by an earth-connected jacket of copper foil, not shown, so as to avoid creeping and induction effects as far as possible. This jacket was of course provided with suitable openings for the electrometer connexions *k* and *l*. The carriage was moved by a rod *o*, provided with a screw-thread which worked in a fixed nut *q*, held by a screw in the outer fixed tube *p*. It was kept pressed against the end of the rod by means of a rubber band passing over the upper end of the carriage *c*, and the lower end *b* of the ebonite frame. The rod was also guided by fixed rings at *r* and below *q*. The lower end of the ebonite frame screwed on to the outer tube *p*, so as always to be in a fixed position when mounted. The rest of the arrangements will be best understood by referring to fig. 2.

It is essential that the foregoing part of the apparatus should be in a very good vacuum. This was secured by placing it in the tube Q_1 which fitted on the ground-glass stopper *s*. The stopper was cemented on to the outside of the brass tube *p*. The rod *o* could be turned by means of the divided head T from outside the apparatus. In the first form of the apparatus the tube Q_1 was inverted and an air-tight joint was secured by simply slipping a thick-walled rubber tube over the tube *p* and the rod *o*, and drowning it with mercury. But this was found to be unsatisfactory owing to the mercury gradually forcing itself into the apparatus and settling in places where it was not wanted. The arrangement shown was therefore adopted in which the tube Q_1 and adjacent parts rest on the top of a barometer column. This was contained in the tube Q_3, which was cemented with sealing-wax to the brass tube *p*, just below the stopper *s*. A side tube near the top led to the pump, McLeod gauge, and pentoxide bulbs. The lower end of the glass tube was drawn down so that the rod could just comfortably turn in it, and the thick rubber tube R was slipped over the joint. The mercury entered from the vessel Q_2 by means of the side tube. The level of the mercury at Q_2 was always kept above R, so that there was no tendency for air to enter at the joint. An earth-connected wire, not shown, dipped permanently into Q_2. Another wire dipping into a small quantity of mercury placed in the stopper *s* ensured that the copper shield, the brass plate *n n*, and the carriage *e* (fig. 1) were kept at zero potential. To ensure satisfactory communication between Q_1 and the pump, the holes *u u'* were bored in the brass tube *p*. The micrometer head T was divided into twenty parts, so that fractions of a turn could be read by means of the stationary vertical index T′, supported on a fixed block. The whole turns were registered

Fig. 2.



by an index U′, carried by a cotton thread *s*, wound round *o*, and made to pass round pulleys VV by the weight W. The index U′ travelled over a scale U graduated in complete turns of the rod. One complete turn of the screw-head corresponded to a forward displacement of the rod of ·0635 cm. It is to be understood that fig. 2 is purely diagrammatic and does not represent the proportionate size of the different pieces of apparatus indicated.

The current used to heat the strip was admitted by the stout platinum wires PP′ fused into the tube Q_1. These dipped into mercury cups connected to the leads *gg* previously described. The current was supplied by the storage-battery L, regulated by the sliding rheostat M, and measured by the ammeter N. The whole circuit was insulated and could be maintained at any desired static potential by connecting the circuit to a battery not shown, the other terminal of which was connected with Q_2. The potential of the strip and plates was measured by a voltmeter, also not shown. One terminal of this was connected to Q_2, and the other could be switched either on to P or P′. The mean of the two readings was taken as the average potential of the strip and plates.

The nuts *k* and *l* connected respectively with the plates *cc*, and the electrode *i* (fig. 1) were each soldered to a narrow spiral of thin copper wire, which in turn was soldered to thin straight platinum wires. These were fused into the drawn-out glass tubes AB, and thence led to the mercury cups C and D. This arrangement was sufficiently flexible to admit of the upward and downward motion of the carriage to which *k* and *l* were rigidly attached. Wires passed from the mercury cups E and F to the condenser G and one pair of quadrants of the electrometer respectively. The other pair were connected to earth and the shielding arrangement indicated. The three mercury cups J were connected to the earth, the electrometer, and the condenser respectively. All the connexions and keys between *k* and *l* and the electrometer and condenser were surrounded by earthed metal shields, not all of which are shown. Before taking a reading the mercury cups J were connected together by the plug K_3, and the plug K_1 was placed in the key C D E F. Thus *k l* G and H were all connected to earth. At the beginning of an observation K_3 was taken out, leaving *k* connected with G and *l* connected with H. Thus the current to the plates all flowed into the condenser, whilst that passing through the slit flowed into the electrometer. After a certain interval of time, depending on the temperature of the strip, the plug K_1 was removed, both currents being thus interrupted simultaneously. The steady deflexion of the electrometer was then read; this measures the number of ions which pass through the slit. E and F were then connected together by inserting the plug K_2 and the charge in the condenser allowed to flow into the electrometer. The steady deflexion was again taken. This measures the total number of ions received by the slit and the plates together. This is only true of course if the capacity to the left of C is negligible compared with that to the right of E, and if that to the left of D is negligible compared with that to the right of F. This condition was always fulfilled. To compare the number of ions it is necessary to multiply the electrometer deflexions in the one case by the capacity of the electrometer and in the other by the combined capacity of the electrometer and the condenser. For most of the purposes of the present investigation, however, the ratio of the two deflexions for different positions of the slit was all that was required.

In an investigation of this kind it is important that the essential parts of the apparatus should be easily accessible, so that any desired changes may be readily effected. This condition was satisfied in the present instance. In order to get at the plates and strip air was first admitted into the apparatus by means of a glass tap connected with the pump. The glass tubes were cut at A and B as well as the wires. This could easily be done time after time, as these tubes were drawn out to a considerable length, much greater than that indicated in the diagram, at the ends. The tube Q could then be lifted off from the stopper, and the ebonite frame and parts that it supported unscrewed and taken away for alteration. The apparatus could be replaced with equal facility; in doing so it was necessary to pull the wires connected to k and l through the tubes A and B by means of thin wires previously threaded through these tubes.

It will be noticed that, with the device which has been described, the leaks to the plate and through the slit were always measured simultaneously. In this way errors arising from changes in the magnitude of the ionization were entirely avoided. This is a matter of great importance in dealing with an effect so sensitive to small changes as the ionization from hot bodies. Although it was not perhaps necessary, the temperature was kept as constant as possible by regulating the heating current to a constant value. This is a satisfactory method when the pressure of the gas is very low. Experiments were made at different times over most of the range from 750° C. to 1200° C.

The magnetic fields were furnished by a large electromagnet which was capable, with a gap of about 2 cms., of giving a very uniform field of up to 5000 lines, over an area of about 4 sq. cms. The field probably did not vary 5 per cent. from the mean value anywhere in the region where motion of the ions was investigated.

Care was taken that no iron was used in the construction of the apparatus. The strength of the magnetic field was determined by means of a bismuth spiral supplied and calibrated by Hartmann and Braun.

A Dolezalek electrometer was used. Its sensitiveness was made to vary from 80 to 900 divisions per volt, according to the magnitude of the currents to be measured. The capacity taken out of the condenser was always ·001 microfarad and the width of the slit between *cc* was usually about ·03 cm.

§ 4. *Theory of the Method.*

Let the two connecting planes be perpendicular to the axis of z, the plane which contains the strip being determined by $z=0$, and that containing the slit being determined by $z=z_1$. The electric force Z is everywhere constant and perpendicular to the two planes. Let the axis of y be taken parallel to the edges of the strip and slit. This is also the direction of the uniform magnetic force H. The equations of motion of an ion where mass is m and charge e, under the influence of the electric and magnetic fields, are

$$m\frac{d^2x}{dt^2}=\mathrm{H}e\frac{dz}{dt},\quad m\frac{d^2y}{dt^2}=0,\quad m\frac{d^2z}{dt^2}=\mathrm{Z}e-\mathrm{H}e\frac{dx}{dt}.$$

The solution of these equations is fully discussed in J. J. Thomson's 'Conduction of Electricity through Gases,' chapter iv. If the ion starts at the instant $t=0$ from the point $x_0\, y_0\, 0$, with velocity components $u_0\, v_0\, w_0$, the displacement $x\, y\, z$ at time t is given by

$$x-x_0=\frac{\mathrm{Z}}{\mathrm{H}}t-\left(\frac{\mathrm{Z}}{\mathrm{H}}-u_0\right)\frac{m}{\mathrm{H}e}\sin\frac{\mathrm{H}e}{m}t+\frac{w_0 m}{\mathrm{H}e}\left(1-\cos\frac{\mathrm{H}e}{m}t\right).$$

$$y-y_0=v_0t.$$

$$z=\left(\frac{\mathrm{Z}}{\mathrm{H}}-u_0\right)\frac{m}{\mathrm{H}e}\left(1-\cos\frac{\mathrm{H}e}{m}t\right)+\frac{w_0 m}{\mathrm{H}e}\sin\frac{\mathrm{H}e}{m}t.$$

The x and z displacements are independent of y. Since the object of the experiment is to determine the value of $x-x_0$ for given values of Z, H, and z_1, the y displacement is not required. As $\frac{\mathrm{H}e}{m}t$ was always less than unity, we may expand the sines and cosines in powers of t, obtaining

$$x-x_0=u_0t+\frac{1}{2}\frac{He}{m}w_0t^2+\left(\frac{Z}{H}-u_0\right)\frac{H^2e^2}{6m^2}t^3.$$

$$z=w_0t+\left(\frac{Z}{H}-u_0\right)\frac{He}{2m}t^2-\frac{H^2e^2}{6m^2}w_0t^3.$$

It is easy to show that with the values of the variables which occurred in the experiments the terms involving powers of t higher than the third introduced changes which were small compared with the errors of observation.

The problem now is to eliminate t between these two equations so as to obtain $x-x_0$ as a function of z &c. It is advisable at this stage to consider what further approximations are permissible. To do this we shall evaluate each of the terms in the above series, using the actual values of the quantities which occurred in a typical experiment. These were $Z=146\times 10^8$ E.M. units, $H=4670$ E.M. units, $z_1=\cdot534$ cm., $e/m=330$ E.M. units, and $\overline{u}_0=\overline{w}_0=6\times 10^4$ cms. per sec. approximately. The above mean value for u_0 and w_0 follows, assuming that the charge on a positive ion is equal to that carried by the hydrogen ion in electrolysis, from researches not yet published by Mr. F. C. Brown and by the author on the kinetic energy of the positive ions emitted by hot metals. We may write the expression for z_1

$$z_1=\underset{2\cdot76\times10^{-2}}{w_0t}+\underset{51\cdot1\times10^{-2}}{\frac{Ze}{2m}t^2}-\underset{\cdot98\times10^{-2}}{u_0\frac{He}{2m}t^2}-\underset{\cdot23\times10^{-2}}{\frac{H^2e^2w_0}{6m^2}t^3}.$$

The number underneath each term is the value of that term obtained by putting $t=4\cdot6\times10^{-7}$. This is the value which t, the time required by the ion to reach the lower plate, would have if there were no magnetic field. It will be observed that the term $\frac{1}{2}Ze/mt^2$ is by far the most important, and that both the terms involving H are comparatively small.

We shall see below that the measurements were made for those ions for which $u_0=0$, so that the third term vanishes in any case from the equation which represents the experimental conditions. The only term involving H which remains is the last and the omission of this term will only change the value of t by about ·2 per cent, a quantity small compared with the probable error of observation. Within this order of accuracy t will be given by solving the quadratic equation $\frac{Ze}{2m}t^2+w_0t=z_1$, and with practically the same degree of accuracy we may use

$$t = \left(\frac{2m}{Ze}\right)^{\frac{1}{2}} z_1^{\frac{1}{2}} - \frac{mw_0}{Ze}.$$

$$4{\cdot}71\times10^{-7} \qquad {\cdot}12\times10^{-7}$$

The values of the two terms, to the same degree of approximation, are written below them. The ratio is about 40 to 1.

Neglecting terms involving squares of this ratio we get

$$t^2 = \frac{2mz_1}{Ze} - \left(\frac{2m}{Ze}\right)^{\frac{3}{2}} w_0 z_1^{\frac{1}{2}},$$

and

$$t^3 = \left(\frac{2mz_1}{Ze}\right)^{\frac{3}{2}} - \frac{6m^2 w_0 z_1}{Z^2e^2}.$$

On substituting these values the equation for $x-x_0$ becomes

$$x-x_0 = \left(\frac{2mz_1}{Ze}\right)^{\frac{1}{2}} u_0 - \frac{mw_0}{Ze} u_0 + \frac{\mathrm{H}ez_1}{3m}\left(\frac{2mz_1}{Ze}\right)^{\frac{1}{2}} - \frac{\mathrm{H}w_0{}^2 z_1}{\mathrm{Z}}\left(\frac{2mz_1}{Ze}\right)^{\frac{1}{2}}$$
$$+ u_0 \frac{\mathrm{H}^2}{\mathrm{Z}^2} w_0 z_1 - u_0 \frac{\mathrm{H}^2 e^2}{6m^2}\left(\frac{2mz_1}{Ze}\right)^{\frac{3}{2}}.$$

The values of these terms taken in order from the left are $28{\cdot}26\times10^{-3}$, ${\cdot}72\times10^{-3}$, 129×10^{-3}, ${\cdot}29\times10^{-3}$, ${\cdot}194\times10^{-3}$, and $2{\cdot}48\times10^{-3}$.

It will be noticed that four of these terms contain u_0 as a factor. The method adopted in carrying out the experiments was to measure the ratio of the current through the slit to that received by the plates for different values of x, the position of the slit. This was first done in the absence of a magnetic field ($\mathrm{H}=0$), and the fraction of the total number of ions traversing the slit was plotted as a function of its displacement $x_1=x-x_0$. This curve had a sharp maximum opposite the centre of the strip. The maximum in this case was just opposite the centre of the strip, the shape of the curve being approximately that which would result if the distribution of velocity among the particles emitted by the strip was that given by Maxwell's law for a gas at the temperature of the metal. The position of this maximum therefore gave the position of those ions for which u_0, the original sideways velocity, was equal to zero. The experiment was then repeated with a magnetic field great enough to displace the particles, which reached the plates, a measurable distance. The effect of this was simply to displace the curve previously obtained a little to the right or left of its former position, the direction of the displacement depending on the direction of the magnetic field. This result might of course have been anticipated from the relative magnitude of the different terms in the last equation. It is clear, therefore, that the new position of the maximum will again represent the position of the particles for which $u_0=0$; so that by measuring the displacement of the maximum we obtain the value of x for the particles whose sideways component of initial velocity is equal to zero. The displacement x of this maximum will therefore be obtained if we put u_0 equal to zero in the last equation.

We thus get

$$x_1=\frac{\mathrm{H}ez_1}{3m}\left(\frac{2mz_1}{\mathrm{Z}e}\right)^{\frac{1}{2}}-\frac{\mathrm{H}w_0{}^2z_1}{\mathrm{Z}}\left(\frac{2mz_1}{\mathrm{Z}e}\right)^{\frac{1}{2}}.$$

The values of these two terms in the experiment cited are 129×10^{-3} and $\cdot29\times10^{-3}$ respectively; so that within an accuracy of about ·2 per cent. it will be sufficient to take

$$x_1=\frac{\mathrm{H}z_1{}^2}{3}\sqrt{\frac{2e}{m\mathrm{V}}},$$

where x is the displacement of the maximum and V is the potential-difference between the upper and lower plates.

The legitimacy of the approximations has been illustrated by means only of a single instance, but with all the values of the magnetic and electric fields which were used the quantities neglected were always of the order indicated and small compared with the experimental error. From the last equation the formula for e/m will be seen to be

$$\frac{e}{m}=\frac{9}{2}\frac{\mathrm{V}x_1{}^2}{\mathrm{H}^2z_1{}^4}.$$

The value of e/m is thus inversely proportional to the fourth power of z_1. In the experiments z_1 was always about 6 mm., and could, on paper, easily be measured to an accuracy of one per cent. But there was always a chance of something having gone wrong with this distance due to mechanical imperfections, a fact which probably gave rise to more trouble than anything else, particularly in the initial stages of the investigation. For this reason it is quite necessary to use apparatus as elaborate as that shown in fig. 1.

§ 5. *Results of the Experiments.*

In discussing the theory of these experiments we have assumed that the motion of the ions after leaving the metal is determined solely by the magnetic and electric fields. It is essential, therefore, that very few of them should collide with the atoms of the gas present in the apparatus during their passage from the strip to the plates. This condition will be satisfied if the mean free path of the ions is considerably greater than the distance between the two sets of plates. In nearly all the experiments the pressure was not allowed to rise above ·0005 mm. At this pressure the mean free path of a positive ion is approximately 20 cms., that of a negative electron being four times as great. The distance between the plates was always about ·5 cm., so that the required condition was evidently fulfilled.

It has been pointed out on pp. 742, 743 that the first experiments were made by a method different from that just described. The electrode behind the slit was not used, but the position of the slit was determined for which each of the plates *cc* (fig. 1) received equal charges. This was done for different values, both positive and negative, of the magnetic field. The apparatus used for this purpose was somewhat different from that figured. Each of the plates *cc* was separately mounted on the carriage and insulated, the lower of the two instead of 1 being connected to the mercury cup D (fig. 2). The cups E and F were connected by wires passing down a shielding tube to adjoining quadrants of the electrometer H which was insulated. The condenser G and plug K_2 were not used. C and D were connected respectively to E and F by means of the plug K_1, and the head T was turned until a position was found, such that the electrometer needle did not deflect on disconnecting the quadrants by taking out the plug K_3. It was very easy to find two points at a very short distance apart, such that the needle deflected strongly to the right for one and equally strongly to the left for the other. The means of two such points were taken. It was found that accurate and consistent results could be obtained in this way owing to the method being very sensitive to small displacements in the neighbourhood of the equilibrium position. The position was found first with the magnetic field equal to zero, then when it had a given value in one direction, then with zero again, and finally with the field reversed. The mean of the two deflexions was taken.

A series of measurements made in this way gave the following values :—

Magnetic Field H ...	0	1930	3440	4400	4900
Displacement. cms.	0	·105	·216	·292	·347

The distance z between the plates in these experiments was ·688 cm. and the potential-difference 55 volts.

If the deflexions produced by the magnetic field were sufficiently small and the geometrical conditions sufficiently near to those which obtain with infinite planes, the theory of this method would be the same as that already discussed. For the pattern formed by the ions on the slit plates, in the absence of a magnetic field, is symmetrical about the plane of symmetry of the strip, so that when the plates receive equal charges the centre of the slit will coincide with the position of the maximum in the other method. The same will be true after the magnetic field has been applied if the magnetic field simply shifts the pattern without altering its form. If these conditions are satisfied the displacement x will be given by the formula

$$x=\frac{1}{3}\sqrt{\frac{2e}{m\mathrm{V}}}z^2\mathrm{H}.$$

For V and z constant x should therefore be proportional to H. The numbers in the preceding table do not satisfy this relation. If the values of x are plotted against H the points lie very nearly on a smooth curve which curves away from the axis of H. On taking logarithms it is found that these points and the point $x=·0254$, $\mathrm{H}=500$, obtained by extrapolation, lie very nearly on the line corresponding to $x=k\mathrm{H}^{1·15}$, where k is a constant. The deviation from a straight line is therefore not very great but is nevertheless definite. This deviation might arise either from the positive ions not being homogeneous or from the theoretical conditions not being satisfied. It was felt that it was very important to settle the question as to whether there were more kinds than one of positive ions, and furthermore to be able to do this during any experiment at any time. For these reasons this zero deflexion method was discarded in favour of the method of exploring the actual distribution of the ions on the plates which has already been described.

If we assume that for small values of H the formula

$$x=\frac{1}{3}\sqrt{\frac{2e}{m\mathrm{V}}}z^2\mathrm{H}$$

may be applied to the results given by the zero method, we find $e/m=310$ E M. units. If each ion carries the same charge as an atom of hydrogen during electrolysis, the value of e/m for which is $9·66\times10^3$ E.M. units, the average mass of the ions is 31·2 times that of an atom of hydrogen.

Homogeneity of the Ions.

The type of curve obtained by the second method, showing the distribution of the ions on the plates when H=0, is shown by the central curve in fig. 4. If the ions were not homogeneous, if, for instance, they consisted of two groups having different values of e/m, then this figure would be made up of the superposition of those due to the two groups separately. Since the two groups have supposedly different values of e/m they would be differently deflected in a magnetic field, so that on this hypothesis the effect of the magnetic field would be to broaden out the pattern. If the magnetic field were great enough the separation should be sufficient to give rise to two groups, each similar to the first. In the intermediate stages the pattern would develop two humps separated by a hollow.

Humps of this character were looked for, and in the earlier stages of the investigation readily found. On further examination, however, these projections were found to be capable of division into two groups: (*a*) those which were permanent, and (*b*) those which only lasted through two or three sets of observations. The first group were not dependent on the magnetic field and so obviously arose from lack of symmetry in the mechanical arrangements, such as a slight bending or twisting of the strip, a point on the metal in its neighbourhood, &c. It is probable that the second class were of the same character, their temporary nature being determined by the heating of the strip. It is of course difficult to prove that they were not due to a short-lived emission of ions of another sort, due to impurities or what not, but it is a significant fact that the number of effects of this kind which were discovered diminished very rapidly when great care was taken in setting up the strip and the parts adjacent to it.

However this may be it is certain that in the majority of cases dealt with the positive ionization from platinum was homogeneous to a very high degree. This is well shown by the curves in figs. 3 & 4 which have been selected as typical of the experiments. In fig. 4, for which $z=\cdot534$ cm. and $V=78$ volts, the left-hand curve represents the distribution of the ions when $H=+4670$, the central curve when $H=0$, and the right-hand curve when $H=-4670$ lines per square centimetre. It will be seen that on the average the curves with a magnetic field have the same width as that with $H=0$, and there is no distinct evidence of separation by the magnetic field. The central curve shows on the left a small hump of the kind previously alluded to; these would often

Fig. 3.

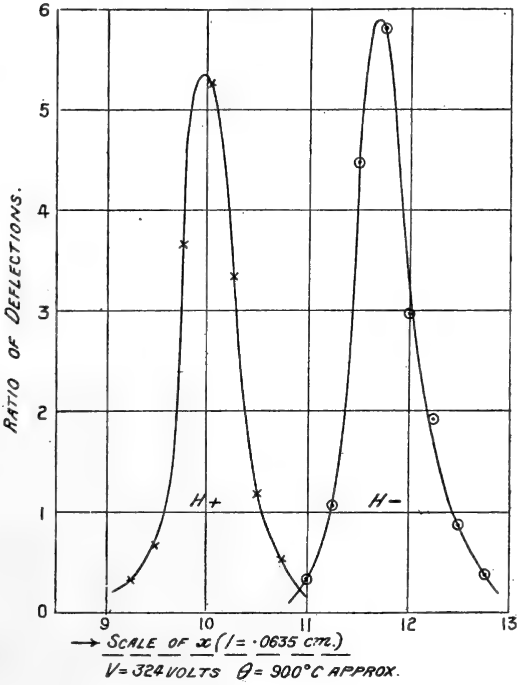
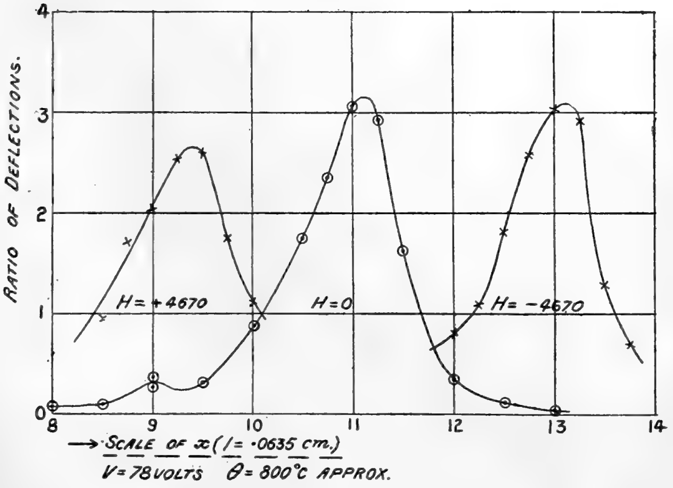

RATIO OF DEFLECTIONS.
0
1
2
3
4
5
6
9
10
11
12
13
H+
H−
→ SCALE OF x (1 = ·0635 cm.)
V = 324 VOLTS θ = 900°C APPROX.

Fig. 4.


RATIO OF DEFLECTIONS.
0
1
2
3
4
8
9
10
11
12
13
14
H = +4670
H = 0
H = −4670
→ SCALE OF x (1 = ·0635 cm.)
V = 78 VOLTS θ = 800°C APPROX.

exist through a number of experiments and then suddenly disappear. In fig. 3 z was also ·534 cm., whilst V was increased to 324 volts. The two curves correspond to $H = \pm 4670$ lines per square cm. respectively. Here again the curves give no indication of absence of homogeneity. The temperature during the experiment which fig. 3 represents was about 900°, and during fig. 4 about 800°. In the case of carbon inhomogeneity was not so definitely excluded. The patterns were so broad under all circumstances that a considerable broadening might have occurred in the magnetic field without being detected.

Kinetic Energy of the Ions.

The form of curves such as those in figs. 3 & 4 is determined by the kinetic energy of the emitted ions and the value of the electric field between the plates. From these curves important conclusions can be drawn as to the magnitude of this energy. This subject will be treated in a separate paper.

Positive Ionization from Platinum.

We have seen that the displacement x of the maximum point in the curves is given by the formula

$$x = \frac{1}{3}\sqrt{\frac{2e}{mV}}\, z^2 H,$$

so that for a constant value of z the quantity $\frac{x}{H}\sqrt{V}$ should remain constant. A series of determinations of x with different values of H and V, with z equal to ·534 cm., were made to test this question. The results are given in the subjoined table :—

V. (volts.)	$\sqrt{V}$.	H. (lines per cm.^{2})	x. ($1 = {\cdot}0635$ cm.)	$\frac{x}{H}\sqrt{V}$.
78	8·84	4670	1·85	35·0
78·1	8·85	4670	1·71	32·4
324	18·01	4670	0·97	37·3
78·5	8·87	3000	1·04	30·8

The constancy of the numbers in the last column is not all that might be desired, but the experimental error is considerable. The general character of the discrepancies was such as might arise if the orientation of the platinum strip was subject to slight changes produced by alternate heating and cooling. It seems probable that some such effect as this was the worst source of error to which the measurements were subject.

All the measurements of e/m for the positive ions from hot platinum which arrived at a satisfactory termination are represented in the following table. The first was that already described as obtained by the zero deflexion method; the others were all obtained by the maximum method. The values of the ratio m/H of the mass of the ions to that of an atom of hydrogen, on the assumption that both carry identical charges, is also given.

z (cm.).	H (lines per cm.^{2}).	V (volts).	x. (1 = ·0635 cm.)	e/m (E.M. units).	m/H.
·688	1200	55	1·00	310	31·2
·6165	4630	300	1·25	276	35·2
·640	4630	341	1·42	357	27·2
·534	4670	78	1·85	275	35·2
·534	4670	78·1	1·71	235	41·2
·534	4670	324	·97	317	30·6
·534	3000	78·5	1·04	211	45·8
·534	3000	78·3	·97	184	52·6
Mean values $e/m=271$, $m/\mathrm{H}=37{\cdot}4$					

The shape of the distribution curves obtained in the last experiment, and to a smaller extent in the one which preceded it, indicated that for some reason or another the mean kinetic energy of the ions had diminished very considerably (by a factor of about four in fact). This diminution may have been accompanied by a real change in the nature of the ions, so that the last two comparatively high values of m/H may be real and not due to experimental error. Leaving them out of account, the means of the first six determinations are $e/m=295$ and $m/\mathrm{H}=33{\cdot}4$. The greatest disagreement of any observation from this value is a little over 20 per cent., if we regard the last two measurements as exceptional.

Positive Ionization from Carbon.

Experiments similar to the above were carried out with carbon, except that the strip had to be replaced by a filament of circular section, ·0143 cm. in diameter. Owing doubtless to the strong radial electric field near the cylinder, the distribution curve was much broader than with the platinum strip, so that the position of the maximum was more difficult to determine. The results of the measurements are given in the following table :—

Z.	H.	V.	x.	e/m.	m/H.
·644	4700	330	1·275	257	37·6
568	4800	364	1·05	302	32·0
Mean : $e/m=280$, $m/\mathrm{H}=34{\cdot}8$.					

The units are the same as in the previous table. It will be observed that the value of e/m is the same within the limits of experimental error for carbon as for platinum.

Classification of the Ionization dealt with.

The experiments in the positive ionization from hot platinum were all made with specimens which had only been heated for comparatively short periods. The temperatures used were also rather low, the highest being estimated as about 950°–1000°. When the low pressure (5×10^{-4} mm. at most) which prevailed is taken into account it is clear that the ionization under investigation is that which has been referred to as the initial ionization. Under the conditions of the experiments the ionization caused by the gas itself would form only a negligible proportion of the whole.

Similar conditions held in the first of the two measurements with carbon. In the second, however, the temperature was considerably higher, and frequent pumping did not prevent the pressure from rising to about ·01 mm. In this case a considerable proportion of the ionization may have been due to the action of the gas. The agreement between the two experiments with carbon would seem to show that with the kind of vacua used the positive ions due to the gas have about the same value of e/m as those due to the initial leak. Both carbon filaments were taken from old lamps which had been lying about the laboratory for some time.

Both had therefore been strongly heated at some time during their history.

It will be difficult to make experiments on the value of e/m for ions produced by different gases, since the low pressures which are rendered necessary to eliminate the effects of collisions make the proportion of the ionization due to the effect of the gas very small.

Method of Checking the Measurements.

It was felt that with previously untried methods like those which have been employed it would be a great advantage if they could be tested by using ions for which the value of e/m is known. This is the case with the negative ions from hot substances. These are known to be negative electrons, and the value of e/m for them at low speeds has been estimated by Kaufmann * to be very near $1{\cdot}88 \times 10^7$ E.M. units. The value of e/m for the negative ions from both platinum and carbon was therefore determined with this apparatus, by the method of finding the deflexion of the maximum point. In order to do this of course much smaller magnetic fields had to be employed. This was furnished by a pair of coils whose outer diameter was 17 cms. These were bolted together at the distance apart required to give the most uniform field and were supported so that this field was parallel to the edge of the strip. It was found by calculation that 1 amp. through the coil gave 13·5 lines per cm.², and this result was confirmed by experiments with the fluxmeter.

The first experiments on the negative ionization were made with the carbon filament to test whether the product $V^{\frac{1}{2}}\frac{x}{H}$ was constant. The apparatus broke down after two sets of observations had been made, but these were considered satisfactory. The numbers are given in the next table.

V. (volts.)	$\sqrt{V}$.	H. (lines per cm.²)	x. (1 = ·0635 cm.)	$\frac{x}{H}\sqrt{V}$.
129	11·36	13·5	1·6	1·346
366	19·13	24·3	1·54	1·213

It was found to be very difficult to make measurements on the negative ionization when potentials greater than about

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* *Ann. der Phys.* (4) vol. xix. p. 551 (1906).

40 volts were used. This was apparently due to secondary rays or scattered primary rays being emitted by the electrode behind the slit, so that this did not appear to absorb its full proportion of the negative electrons which reached it.

The temperature during the experiments on the negative ions was higher than in the case of the positive ions, most of the observations being made between 1100° and 1200° C.

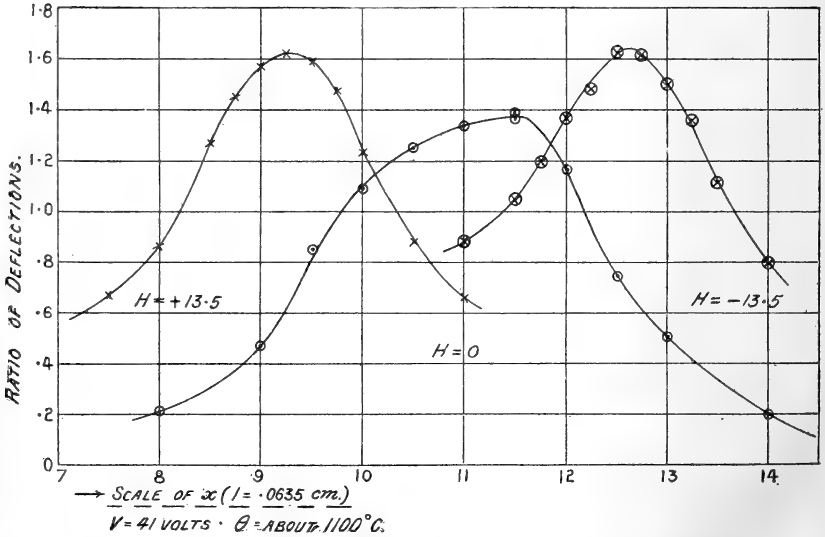
e/m *for the Negative Ions.*

The results of all the complete experiments which led to values of e/m for the negative ions from carbon are given in the next table.

V. (volts.)	H. (lines per cm.^{2})	Z. (cms.)	x. (1 = ·0635 cm.)	e/m. E.M. units.
129	13·5	·677	1·60	$1·57 \times 10^7$
366	24·3	·677	1·54	$1·27 \times 10^7$
34·5	9·45	·568	1·56	$1·64 \times 10^7$

Mean $e/m = 1·49 \times 10^7$.

Fig. 5.



The curves obtained in one of the experiments which determined the value of e/m for the negative ions from hot platinum are shown in fig. 5. The central curve is for a potential-difference of 10·6 volts. For the curves with the magnetic field on the potential-difference was 41 volts. The ions are, of course, more spread out the lower the potential-difference.

The numbers which were obtained in the two determinations of e/m for the negative ions from hot platinum are given in the next table.

V.	H.	z.	x.	e/m.
40·8	13·5	·534	1·7	$1{\cdot}46 \times 10^7$
41	13·5	·534	1·69	$1{\cdot}44^3 \times 10^7$
Mean $e/m = 1{\cdot}45 \times 10^7$.				

The mean value of e/m for the negative ions is thus almost the same for both carbon and platinum. It is significant that not only the mean but each individual value of e/m is distinctly smaller than the best value, which is $1{\cdot}88 \times 10^7$, with some uncertainty as to the last figure.

A Possible Correction.

It seems likely that some of this difference is due to the electric field, in the immediate neighbourhood of the strip of filament, not being the same as if the hot body were a portion of an infinite plane. Both strip and filament are narrow conductors stretched across a much wider gap. It is difficult to know exactly what difference this will make in the electric field. In the case of the filament it would seem reasonable to suppose that the deviation of the field from uniformity would be smaller than, but comparable with, what would occur if the filament were a cylinder of equal radius a, and the slit plates formed part of a concentric cylinder of radius b, where the shortest distance between the filament and slit plates is equal to $b-a$.

To illustrate the question consider the motion of an ion projected perpendicularly from the surface of the inner cylinder whose radius is a. Let the direction of projection be the axis of z, and let a difference of potential V be maintained between the two cylinders. Since the electric force is radial the ion will always remain on the axis of z. Now suppose there is a uniform magnetic force H parallel to the axis of the cylinder; let us calculate the sideways displacement x of the moving ion due to the action of the magnetic force, whose direction is taken to be that of the y axis.

The radial electric force at a distance v from the axis is

$$Z=V/z \log b/a.$$

The equations of motion of the ions are

$$m\frac{d^2z}{dt^2}=Ze-He\frac{dx}{dt},$$

and

$$m\frac{d^2x}{dt^2}=He\frac{dz}{dt}.$$

Integrating the last subject to the condition $\frac{dx}{dt}=0$, when $z=a$ we have

$$\frac{dx}{dt}=\frac{He}{m}(z-a),$$

so that

$$m\frac{d^2z}{dt^2}=\frac{Ve}{Z\log b/a}-\frac{H^2e^2}{m}(z-a).$$

Integrating this subject to the condition that when $Z=a$, $\frac{dz}{dt}=w$, we obtain

$$\left(\frac{dz}{dt}\right)^2=w^2+\frac{2Ve\log z/a}{m\log b/a}-\frac{H^2e^2}{m^2}(z-a)^2.$$

Since

$$He(z-a)=m\frac{dx}{dt}=m\frac{dx}{dz}\frac{dz}{dt},$$

we have finally, the sideways displacement

$$x_1=\frac{He}{m}\int_a^b\frac{(z-a)dz}{\left\{w^2+\frac{2Ve\log z/a}{m\log b/a}-\frac{H^2e^2}{m^2}(z-a)^2\right\}^{\frac{1}{2}}}.$$

The corresponding expression for planes, distance $b-a$ apart, is

$$x_1=\frac{He}{m}\int_0^{b-a}\frac{z\,dz}{\left(w^2+\frac{2Vez}{m(b-a)}-\frac{H^2e^2}{m^2}z^2\right)^{\frac{1}{2}}}.$$

To compare with the experimental results these integrals have been determined graphically and their values compared for the following series of values of the constants:—$a = \cdot 006$ cm., $b = \cdot 606$ cm., $V = 3\cdot 65 \times 10^{10}$ E.M. units, $H = 4800$, $u^2 = 8 \times 10^8$ cm.^{2}/sec.^{2}, $e/m = 250$ E.M. units. The ratio of the two values of x is found to be 1·25, that for the plates being the greater.

In working out our results we have assumed that the conditions for parallel plates held; whereas the actual conditions are probably somewhere between the two cases. The actual displacements are smaller than they should be according to the simple theory of parallel planes, so that the values of e/m calculated from the measurements will be too small. Since e/m varies very nearly as $x_1{}^2$ it follows from the calculations first given that the values which have been obtained will have to be increased by a factor lying between 1 and 1·625. We may use the experiments on the negative ions, for which e/m is known, to determine this factor, approximately at any rate. Using $1\cdot 88 \times 10^7$ as the correct value of e/m for the electrons we get for the correction factor α: for platinum $\alpha = 1\cdot 30$, and for carbon $\alpha = 1\cdot 26$, both of which lie between the assigned limits. Using these values to correct the numbers previously given for e/m and m/H for the positive ions we find the mean values

For Platinum... $e/m = 384$, $m/H = 25\cdot 7$.
,, Carbon ... $e/m = 353$, $m/H = 27\cdot 6$.

This method of applying the correction is somewhat unsatisfactory on account of the great disparity between the values of e/m for the positive and negative ions. It is clear, however, from the nature of the two integrals, that with the values of the constants which were used the corrections will be about the same for both kinds of ions.

§ 6. *Conclusion.*

The constitution or material structure of the positive ions given out by hot bodies is a matter of great interest. It is a significant fact that the mean corrected ratio of the mass to that of the hydrogen atom is so nearly the same for the ions from both carbon and platinum, and so nearly equal to the corresponding quantity found by J. J. Thomson for iron. The values under consideration are: for platinum $m/H = 25\cdot 7$, for carbon $m/H = 27\cdot 6$, and for iron $m/H =$ about 24. It is difficult to say what the ions are, but it is evident that the values which have been found enable certain definite assertions to be made as to what they are not. They are not, for instance: (1) Atoms of the metal. This would have involved a great variation in the value of m for the above elements whose atomic weights are: carbon 12, platinum 195, and iron 56. (2) Atoms or molecules of absorbed hydrogen. The value of m/H is far too high for this. (3) The positive electrons which Thomson has found in the canal rays and which other physicists have suggested the α rays might be. These have to be eliminated for the same reason as hydrogen.

It has been pointed out that the ions appeared to be quite homogeneous, and that the patterns did not show any definite broadening out in a magnetic field. These experiments show quite definitely, not only that the majority of the ions were comparatively heavy, but also that there were no ions (no measurable number, that is) which were light enough to fall under headings (2) and (3).

The experiments do not seem to indicate that the value of e/m depends on the temperature of the hot body in any definite way. There was some slight evidence that m tended to increase with continued heating of the substance, but this point cannot be regarded as definitely established. It is to be observed that the stated values of m would be doubled, if we were to assume that the positive ions carried twice the charge of an electrolytic hydrogen ion, as Townsend [*] has recently found to be the case for the positive ions produced by Röntgen rays in air.

The values of m/H are near to the molecular weights of N_2, CO, and O_2, but there appears to be no very convincing reason why all the substances investigated should evolve one or more of these gases when heated. The current evidence indicates that the bulk of the gas given off by metals when heated is hydrogen. It is possible that the ions arise from some impurity which is common to all the materials which have been examined. The most likely one to occur would appear to be sodium or its salts, and if positively charged sodium atoms were emitted they would furnish a value of e/m sufficiently near to that which has been observed.

There does not appear to be any evidence of the occurrence of light positive ions, even after the metal has been heated for a long time, so that the greater part of the initial positive ionization has been got rid of. The absence of ions of this kind is consistent with the view which the author [†] has previously expressed that the positive ions produced by hot

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[*] Roy. Soc. Proc. A, vol. lxxx. p. 207 (1908).

[†] Phil. Trans. A. vol. ccvii. p. 1 (1906).

platinum in different gases are atoms or molecules of the gas and not positive electrons out of the metal.

It is possible that the positive ionization in a vacuum is due to a real constituent which is common to the different elements examined, as opposed to some foreign substance whose presence is accidental. In this case it would be necessary to assume that the ions carry a charge which is smaller than the (at present) fundamental electronic charge e. This would follow from the fact that the value of m/H for these ions is greater than the atomic weight of carbon, one of the substances from which they are produced. There is no other evidence, as yet, of the existence of fractions of this natural unit of electric charge.

It is proposed to extend the list of elements included in the investigation, and to institute other experiments which will decide between the preceding alternatives.

In conclusion the author wishes to thank Mr. P. Thomas, Instructor in the Laboratory, for his assistance during part of the investigation, and also Mr. F. Fisher, University Mechanician, for the care which he bestowed on the construction of the apparatus shown in fig. 1.

Princeton, N.J.
22nd June, 1908.

LXV. *On the Corpuscular Theory of the Thermoelectric Forces.* *By* JAKOB KUNZ, *Dr. phil., Privatdozent für Physik am eidg. Polytechnikum in Zürich* [*].

CONTENTS.

THE theoretical laws of the thermoelectric phenomena have been derived from two different theories. The electromotive force, the Peltier effect, and the Thomson effect are related to one another by thermodynamic formulas, which were given first by Clausius [†] and Lord Kelvin [‡].

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[*] Communicated by the Author.

[†] Clausius, Pogg. *Ann.* xc. p. 513 (1853).

[‡] W. Thomson, Edinburgh Roy. Soc. 'Transactions,' xxi. (1854).

Lord Kelvin even predicted the last of the three phenomena, showing that in some metals an electric current carries heat from the hot to the cold parts of the metal, while in other metals the transference of the heat is in the opposite direction. The experiments proved in a very satisfactory way the existence of this effect first derived from theoretical considerations.

After an interval of about half a century, the corpuscular theory of metallic conduction has been applied to the thermoelectric phenomena by Riecke[*], Drude[†], H. A. Lorentz[‡], and J. J. Thomson[§]. The results of the kinetic theory, developed by Lorentz and J. J. Thomson, agree completely with those of the thermodynamic theory, while there is a disagreement between the results of Drude and Lorentz, which is not to be ascribed only to the different suppositions of the calculations, Drude assuming two or more different kinds of free corpuscles, while Lorentz and J. J. Thomson admit only one kind of free corpuscles, in agreement with the fact, that we know only one kind of these minute particles. The agreement of the results derived from two quite different theories is the more remarkable as it is not what we should expect. Indeed, according to the corpuscular theory, the thermoelectric phenomena are very closely connected with the conduction of heat, taking place in the circuit, while in the thermodynamic theory, we are obliged to leave aside this conduction, as an irreversible process. Therefore the question arises, how the above-stated agreement between the results of the two theories is possible. An attempt will be made to answer this question in the following paper.

According to the corpuscular theory of electric conduction, developed by Riecke, Drude, and Lorentz, the currents of electricity and heat are carried by negatively charged corpuscles, diffused as a very light gas throughout the metal, having a mean free path and a mean velocity, and exerting a definite pressure. J. J. Thomson has lately shown that the theory in its usual form requires the presence of so many corpuscles that the specific heat would exceed by far the actual specific heat of the metal. J. J. Thomson has in addition proposed a modification of the theory which is not

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[*] Riecke, *Annalen der Physik,* lxvi. pp. 353, 545, 1199 (1898).

[†] Drude, *Annalen der Physik,* i. p. 566 (1900); iii. p. 369 (1900).

[‡] Lorentz, 'Proceedings' Acad. of Amsterdam, pp. 438, 585, 684 (1904-05).

[§] J. J. Thomson, 'The Corpuscular Theory of Matter,' pp. 73, 97 (1907).

open to this objection, which makes the ratio of the conductivities for heat and electricity of the right magnitude, and gives an account of the radiation of heat and of the different effects called after Hall, Peltier, and Thomson. I shall, however, begin with the first method, supposing the corpuscles to be free and in temperature equilibrium with their surroundings like a very rarefied gas in a porous body. The following considerations apply to the first as well as to the second theory.

§ 1. *Potential-Differences between Metals in Contact.*

When two metals A and B at the same temperature are placed in perfect contact, if the number N_1 of corpuscles in unit volume in the metal A is greater than that in B, then corpuscles will flow from A to B. There is evaporation of negative electricity in the first metal and condensation in the second. After a very short time, however, this distillation will be stopped, the metal A getting charged positively and the metal B negatively. These charges produce an electric force X directed from A to B. The attraction of the positive electricity in A will tend to prevent the corpuscles escaping from it, and the flow will cease, when the attraction of the positive electricity in A and the repulsion of the negative in B just balances the effect of the difference in pressure. The positive electrification in A and the negative in B will be close to the surface of separation, and these two electrifications will produce a difference in electric potential between A and B, which we can calculate in the following way.

Let N be the number of corpuscles per unit volume in A at a point distant x from the boundary between the two metals. Then the number of corpuscles crossing unit surface at x in unit time according to the law of diffusion is equal to $\frac{1}{3} vl \,.\, \partial N/\partial x$, where v denotes the mean velocity and l the mean free path of the corpuscles at the temperature T. Let e be the negative charge of a corpuscle and X the electric force at the point x, then the number of corpuscles acted on by the force X, passing through unit surface in unit time, is equal to $NelvX/4\alpha T$, α being the universal constant of the kinetic theory of gases. The number of corpuscles, flowing in unit time through unit surface from A to B, is equal to

$$\frac{1}{3} vl \frac{\partial N}{\partial x} - \frac{NelvX}{4\alpha T}:$$

in the case of equilibrium this flux must vanish. Therefore

$$X = \frac{4}{3} \frac{\alpha}{e} T \frac{\partial N}{\partial x} \frac{1}{N}.$$

Let us suppose that there is a thin layer between the substances A, B in which the transition from A to B takes place gradually, and let us reckon the abscissa x from one of the boundaries of this layer.

$$\mathrm{X}dx = \frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial \log \mathrm{N}}{\partial x}dx$$

$$\int_{\mathrm{A}}^{\mathrm{B}} \mathrm{X}dx = \mathrm{V}_a - \mathrm{V}_b = \frac{4}{3}\frac{\alpha}{e}\mathrm{T}\log\frac{\mathrm{N}_2}{\mathrm{N}_1}.$$

V_a and V_b denote the potentials in the metals A and B, N_1 the number of free corpuscles in the metal A, N_2 that in metal B.

The potential-differences which arise in this way are not comparable with the Volta differences of potential between metals in contact. The experimental results, however, cannot be in accord with this theoretical calculation for well known reasons. Let us remark, in addition, that we have assumed a perfect metallic contact; if this condition is not satisfied quite different phenomena take place, when an electric force is acting between two metals or even between two pieces of the same metal.

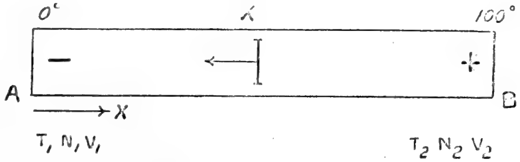
These new phenomena occur in the coherer, which we shall consider later on in the light of the second theory of metallic conduction due to J. J. Thomson.

§ 2. *Thermoelectric Force in an unequally heated Metallic Bar.*

Let AB be a bar of metal, and let the temperature increase from A to B. If we assume the number of corpuscles to be independent of the temperature, there is a diffusion of corpuscles with a large amount of kinetic energy from the hotter parts of the metal to the colder ones. In consequence of the collisions which the corpuscles make with the atoms of the metal, resulting in alterations in the energy, the corpuscles will carry heat from the hot to the cold parts of the metal. This transference of heat takes place without a change in the number of corpuscles in unit volume, without a transference of the electric charges, and therefore without the production of an electromotive force. This process is a completely irreversible one, like the diffusion of two volumes of a gas of different temperatures but of the same number of molecules per unit volume. No mechanical work can be produced by such a process. If the number of corpuscles per unit volume in a metal does not depend on the temperature, there can be no electromotive force along the bar to keep the corpuscles from drifting under the pressure differences. Let us now suppose that the number of corpuscles per unit volume depends on the temperature, so that at 100° C. one c.cm. contains a larger number of these particles than one c.cm. at 0° C.

Let the temperature increase from A to B. If we consider in a distance x from A a cross-section of unit surface, a larger number of corpuscles will drift in unit time from right to left than in the opposite direction. An accumulation of negative charges will take place in A at the colder end of the bar and of positive charges at the hotter end B. These charges produce a certain electromotive force X at a point distant x from A, tending to move the corpuscles from A to B. The attraction of the positive electricity in B will tend to prevent the corpuscles escaping from it, and the flow will cease when the attraction of the positive electricity in B and the repulsion of the negative in A just balance the effect of the difference in the number of corpuscles per unit volume due to the difference of the temperature. The same considerations as in the first paragraph, applied to this case, lead to the expression of the electric force X

Fig. 1.



$$X = \frac{4}{3}\frac{\alpha}{e} T \frac{\partial \log N}{\partial x}.$$

N is the number of corpuscles in unit volume at x, and T the corresponding temperature, thus

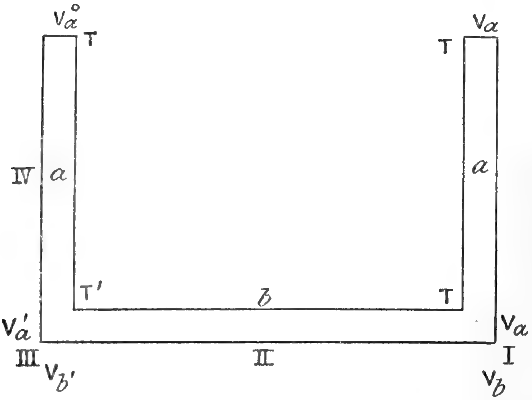
$$V_1 - V_2 = \frac{4}{3}\frac{\alpha}{e}\int_{N_1}^{N_2} T \frac{\partial \log N}{\partial x}\, dx.$$

A potential-difference of this amount will be found between the two ends of the metallic bar. The electric force X will account for the Thomson effect and for one part of the electric forces of thermoelectric couples. These forces X may be used for the performance of mechanical work, which again could be transformed into heat, so that the process under consideration is a reversible one.

§ 3. *The Electromotive Force of Thermo-elements.*

Let us combine two metals *a* and *b* in a way indicated by fig. 2. By this arrangement four different differences of electric potential will occur, according to the two contacts

Fig. 2.



I. and III. at the temperatures T and T′, and according to the differences of temperature in the two metals *a* and *b*.

$$\text{I.} \ldots\ V_a - V_b = \frac{4}{3}\frac{\alpha}{e} T \log \frac{N_b}{N_a},$$

$$\text{II.} \ldots\ V_b - V_{b'} = \frac{4}{3}\frac{\alpha}{e}\int_T^{T'} T \frac{\partial \log N_b}{\partial T}\, dT,$$

$$\text{III.} \ldots\ V_{b'} - V_{a'} = \frac{4}{3}\frac{\alpha}{e} T' \log \frac{N_{a'}}{N_{b'}},$$

$$\text{IV.} \ldots\ V_{a'} - V_{a_0} = \frac{4}{3}\frac{\alpha}{e}\int_{T'}^{T} T \frac{\partial \log N_a}{\partial T}\, dT.$$

The thermoelectromotive force $E = V_a - V_{a_0}$ is therefore

$$E = \frac{4}{3}\frac{\alpha}{e}\left\{ T' \log\frac{N_{a'}}{N_{b'}} - T \log\frac{N_a}{N_b} \right\}$$

$$-\frac{4}{3}\frac{\alpha}{e}\left[T \log \frac{N_a}{N_b} \right]_T^{T'} - \int_T^{T'} \log\frac{N_b}{N_a}\, dT \cdot \frac{4}{3}\frac{\alpha}{e},$$

$$E = \frac{4}{3}\frac{\alpha}{e}\int_T^{T'} \log\frac{N_a}{N_b}\, dT.$$

Suppose N_a/N_b to be independent of the temperature, then

$$E=\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}(T'-T),$$

$$Ee=\frac{4}{3}\log\frac{N_a}{N_b}\Big[\alpha T'-\alpha T\Big],$$

the thermoelectromotive force would be proportional to the difference of temperature, and would only depend on the potential-differences of contact at the temperatures T' and T. If one single corpuscle passes round about the thermoelectric circuit, the force E will perform an amount of electric work equal to $E\,.\,e$. Neglecting a certain factor this work is equal to the difference of the values which the quantity αT possesses at the temperatures T and T'. The difference $\alpha T'-\alpha T$ is the increase in the mean kinetic energy of a molecule of gas, which is heated from the temperature T to the temperature T'.

If we study the electromotive force produced by a standard metal, for instance lead combined with any other metal a, we may represent the electromotive force as a function of the temperature difference in the following way:

$$E=\alpha_a t+\frac{\beta_a}{2}t^2,$$

α_a and β_a are the temperature coefficients of the metal a; combining the standard metal with any other metal b we find:

$$E=\alpha_b t+\frac{\beta_b}{2}t^2,$$

α_b and β_b are the first and second coefficients of temperature of the metal b. If two metals a and b form a thermo-element, one junction of which is at the temperature t, the other at 0° C., the thermoelectric force will be found to be:

$$E=(\alpha_a-\alpha_b)t+\left(\frac{\beta_a-\beta_b}{2}\right)t^2, \quad \text{or}$$

$$E=(\alpha_a-\alpha_b)(T-273)+\left(\frac{\beta_a-\beta_b}{2}\right)(T-273)^2,$$

T being the absolute temperature.

$$\frac{dE}{dT}=\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}=\alpha_a-\alpha_b+(\beta_a-\beta_b)(T-273)$$

$$\frac{N_a}{N_b}=\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a-\alpha_b+(\beta_a-\beta_b)(T-273)]}.$$

This formula is symmetrical with regard to the coefficients of the metals a and b. The two metals playing the same part, we may conclude from this symmetry that the numbers of free corpuscles in the two metals are the following functions of the temperature:

$$N_a = C\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a+\beta_a(T-273)]},$$

$$N_b = C\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_b+\beta_b(T-273)]}.$$

The last step is of course not conclusive. For suppose

$$N_a = C\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a+\beta_a(T-273)+\gamma T^2]},$$

and
$$N_b = C\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_b+\beta_b(T-273)+\gamma T^2]},$$

we should find again

$$\frac{N_a}{N_b} = \epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a-\alpha_b+(\beta_a-\beta_b)(T-273)]},$$

$$N_a = C_1 + C_1\frac{3}{4}\frac{e}{\alpha}\beta_a T + \ldots\ldots$$

The number of free corpuscles will vary approximately as the absolute temperature. β_a for some metals and for certain intervals of temperature of other metals being negative, we see that in these cases the number N_a will decrease with increasing temperature. The electric conductivity is proportional to $\frac{Nlv}{T}$, and by experiment it has been shown to be proportional to T^{-1}; thus, N being approximately proportional to T, and v proportional to $T^{1/2}$, l the mean free path of the corpuscles must vary approximately as $T^{-3/2}$. The variation of the number of free corpuscles with the temperature involves a still more rapid variation of the mean free path. Thus the effects which depend on the free path, such as the effect of magnetic force on electrical resistance or the absorption of light by the metal, would be greatly influenced by the lowering of the temperature.

§ 4. *The Peltier Effect.*

Returning to the suppositions of § 1, we find an electric force acting at the junction of two metals, produced by the different number of corpuscles per unit volume in the two substances. The potential-difference arising in this way is equal to

$$V_a - V_b = \frac{4}{3}\frac{\alpha}{e}T \log \frac{N_2}{N_1}.$$

If a current i is flowing through the metals in a direction opposite to the electric force

$$X = \frac{4}{3}\frac{\alpha}{e}\frac{\partial \log N}{\partial x},$$

a corpuscle in travelling from B to A, and acted on by the force Xe, will increase its kinetic energy, and therefore abstract from the metal an amount of heat whose mechanical equivalent is $Xe\,dx$. If the current i is flowing in the direction opposite to X, the number of corpuscles which cross unit area in unit time is $\frac{i}{e}$, and the mechanical equivalent of the heat they abstract from the metals passing through the junction is

$$Q' = \frac{i}{e}.\int_B^A Xe\,dx = i(V_b - V_a) = i.\frac{\alpha}{e}\frac{4}{3}T \log \frac{N_1}{N_2}.$$

The heat absorbed in unit time and per unit current, *i. e.* the Peltier effect, will be:

$$Q = \frac{4}{3}\frac{\alpha}{e}T \log \frac{N_1}{N_2} = V_b - V_a.$$

If the current were to flow in the opposite direction the same amount of heat would be communicated to the metal. The Peltier effect is a real measure of the potential-differences between metals in contact. From the Peltier effect we may derive the ratio of the number of corpuscles in two metals. Thus to take the case of antimony and bismuth, whose Peltier effect is exceptionally large,

$$\log \frac{N_1}{N_2} = 1{\cdot}33 \quad \text{or} \quad \frac{N_1}{N_2} = 3{\cdot}8.$$

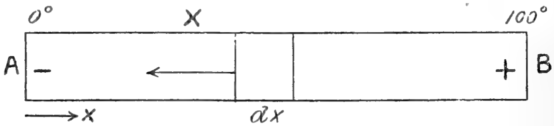
Thus, if the number of corpuscles in the unit volume of antimony were about four times that in bismuth we should, on this theory, get Peltier effects of about the right amount. The Peltier effect for antimony and bismuth being very much larger than that for most pairs of metals, we see that the theory indicates that the number of free corpuscles per unit volume does not vary much from one metal to another.

Now Professor J. J. Thomson *, by a comparison of the numbers of free corpuscles and the mean free path in different metals, came to the conclusion that the mechanism by which, according to this first corpuscular theory, the electric current is supposed to be conveyed, is at most only a part and not the whole of the process of metallic conduction.

§ 5. *The Thomson Effect.*

If the number of corpuscles in unit volume of a metal increases with increasing temperature, there must be electric forces X along the bar, which, following the notation of § 2, are found to be equal to

Fig. 3.



$$X = \frac{4}{3}\frac{\alpha}{e}T\frac{\partial \log N}{\partial x},$$

and tend to move the corpuscles from left to right. Hence a corpuscle in travelling from $x+dx$ to x, will abstract from the metal an amount of heat whose mechanical equivalent is $Xe\,dx$, or

$$\frac{4}{3}\alpha T\frac{\partial \log N}{\partial x}dx = \frac{4}{3}\alpha T\frac{\partial \log N}{\partial T}dT.$$

The corpuscle when at $x+dx$ has an amount of kinetic energy equal to $\alpha\left(T+\frac{\partial T}{\partial x}dx\right)$, while at x its kinetic energy is equal to αT; hence between $x+dx$ and x the corpuscle will lose a part of its kinetic energy equal to $\alpha\frac{\partial T}{\partial x}dx$, which is communicated to the metal in the form of heat. The transference of this amount of heat is an irreversible process. Thus the total amount of heat communicated by the corpuscle to the metal is:

$$\alpha\frac{\partial T}{\partial x}dx - \frac{4}{3}\alpha T\frac{\partial \log N}{\partial T}dT, \quad \text{or}$$

$$\alpha\left(1-\frac{4}{3}T\frac{\partial \log N}{\partial T}\right)dT.$$

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* J. J. Thomson, 'Corpuscular Theory of Matter,' p. 75 (1907).

If the current i is flowing in the direction from A to B, *i. e.* in the direction of increasing temperature, the number of corpuscles which cross unit area in unit time in the direction from B to A is i/e, and the mechanical equivalent of the heat they communicate to the metal between the places where the temperatures are respectively T and $\mathrm{T}+d\mathrm{T}$ is equal to

$$i\frac{\alpha}{e}\left(1-\frac{4}{3}\mathrm{T}\frac{\partial\log\mathrm{N}}{\partial\mathrm{T}}\right)d\mathrm{T}.$$

But if σ is the specific heat of electricity in the metal, this amount of heat is by definition equal to

$$-i\sigma\, d\mathrm{T},$$

the sign minus being applied because the electric current is flowing from the cold to the hot part of the metal; hence

$$\sigma=-\frac{\alpha}{e}\left(1-\frac{4}{3}\mathrm{T}\frac{\partial\log\mathrm{N}}{\partial\mathrm{T}}\right).$$

As lead has no Thomson effect, its σ is zero. If the current is flowing in the direction of decreasing temperature, and if in this case heat is developed, we consider σ as positive; thus σ would be positive in the metals Cu commercial, Sb commercial, Cd, Zn, Ag. On the other hand, σ is negative in the metals: Fe, Hg, Sn, Al, Pt, Sb pure, Bi pure.

In these metals heat will be absorbed when an electric current flows from hot to cold parts. When the specific heat σ in the lead disappears we see that the corpuscle passing from $\mathrm{T}+d\mathrm{T}$ to T loses the same amount of kinetic energy in consequence of the decreasing temperature as it gains in consequence of the acceleration produced by the pressure difference due to the increasing number of corpuscles with increasing temperature. Consider two metals a and b, containing at the same temperature T the numbers N_a and N_b of free corpuscles, the corresponding specific heat of electricity will be

$$\sigma_a=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial\log\mathrm{N}_a}{\partial\mathrm{T}}-\frac{\alpha}{e},$$

$$\sigma_b=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial\log\mathrm{N}_b}{\partial\mathrm{T}}-\frac{\alpha}{e},$$

$$\sigma_a-\sigma_b=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial\log\frac{\mathrm{N}_a}{\mathrm{N}_b}}{\partial\mathrm{T}}.$$

§ 6. *Connexion between the different Effects.*

The results hitherto arrived at are as follows :—

If the number of free corpuscles increases with increasing temperature there is an electric force along an unequally heated metallic bar, given by the expression

$$X=\frac{4}{3}\frac{\alpha}{e}T\frac{\partial \log N}{\partial T}\frac{\partial T}{\partial x}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The electromotive force of a thermoelement is equal to

$$E=\frac{4}{3}\frac{\alpha}{e}\int_{T}^{T'}\log\frac{N_a}{N_b}\,dT. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The Peltier effect between two metals at the temperature T is equal to

$$Q=\frac{4}{3}\frac{\alpha}{e}T\log\frac{N_a}{N_b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The Thomson effect of a metal is equal to:

$$\sigma=\frac{4}{3}\frac{\alpha}{e}T\frac{\partial \log N_a}{\partial T}-\frac{\alpha}{e}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\frac{dE}{dT}=\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

$$\frac{d^2E}{dT^2}=\frac{4}{3}\frac{\alpha}{e}\frac{\partial \log\frac{N_a}{N_b}}{\partial T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2'')$$

Comparing the equations 3 and 2′ we get

$$Q=T\frac{dE}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\sigma_a-\sigma_b=\frac{4}{3}\frac{\alpha}{e}T\frac{\partial \log\frac{N_a}{N_b}}{\partial T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

Comparing the equations 4′ and 2″ we get

$$\sigma_a-\sigma_b=T\frac{d^2E}{dT^2}=T\frac{d}{dT}\left(\frac{Q}{T}\right). \quad . \quad . \quad . \quad . \quad (6)$$

Lord Kelvin has from thermodynamic principles derived the equations 5 and 6. The results of the thermodynamic theory agree with those of the corpuscular theory of metals. We see immediately why we are allowed in the thermodynamic theory to neglect the irreversible process of thermal conduction. In the corpuscular theory of the laws of thermoelectricity too we do not consider the predominant part of the heat conduction, but take into account only the small reversible part of the conduction, which depends on the variation in the number of free corpuscles in unit volume. This variation gives rise to an electric force along an unequally heated bar of metal. All the phenomena connected with this force are reversible. According to this theory, a current of heat is to a small extent connected with a reversible process, able to perform mechanical work. This is, I think, the reason for the agreement of the two theories, whose assumptions are quite different. The corpuscular theory, however, affords a deeper insight into the nature of the physical processes, and gives expressions for the electric force X and for the electromotive force E, depending on the number of free corpuscles. According to the experimental law:

$$\frac{dE}{dT}=\alpha_a-\alpha_b+(\beta_a-\beta_b)(T-273),$$

$$Q=T\frac{dE}{dT}=(\alpha_a-\alpha_b)T+(\beta_a-\beta_b)(T-273)T.$$

If we keep the temperature of a junction between two different metals *a* and *b* constant at 0° C. the Peltier effect will be

$$Q_0=(\alpha_a-\alpha_b)273.$$

If a current of 1 ampere is flowing from copper to the other metal in the following table, the heat developed or absorbed in an hour, measured in calories, will have the values indicated as follows:—

	Calculated from numbers of Riecke.	Calculated from numbers of Clemencic.	Observed by Jahn *.
Cu—Pt	+0·292	+0·327	+0·320
Cu—Ag	−0·183	−0·495	−0·413
Cu—Fe	−3·762	−2·64	−3·163
Cu—Zn	−0·207	−0·353	−0·585
Cu—Cd	−0·306	−0·617	−0·616
Cu—Ni	+4·37	+4·68	+4·362

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* Jahn, Wiedemann's *Annalen*, Bd. xxxiv. p. 763 (1888).

$$\sigma_a - \sigma_b = \mathrm{T}\frac{d^2\mathrm{E}}{d\mathrm{T}^2},$$

but
$$\frac{d^2\mathrm{E}}{d\mathrm{T}^2} = \beta_a - \beta_b,$$

hence,
$$\sigma_a - \sigma_b = \mathrm{T}(\beta_a - \beta_b)\,;$$

therefore
$$\sigma_a = \mathrm{T}\,.\,\beta_a - \frac{\alpha}{e}, \quad \sigma_b = \mathrm{T}\,.\,\beta_b - \frac{\alpha}{e}.$$

Admitting the number of free corpuscles to be the simple function of the temperature as indicated by the formula

$$\mathrm{N}_a = \mathrm{C}\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a + \beta_a(\mathrm{T}-273)]},$$

we get
$$\log \mathrm{N}_a = \mathrm{C} + \frac{3}{4}\frac{e}{\alpha}(\alpha_a + \beta_a \mathrm{T})$$

$$\frac{\partial \log \mathrm{N}_a}{\partial \mathrm{T}} = \frac{3}{4}\frac{e}{\alpha}\beta_a,$$

but
$$\sigma_a = \frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial \log \mathrm{N}_a}{\partial \mathrm{T}} - \frac{\alpha}{e},$$

hence
$$\sigma_a = \mathrm{T}\beta_a - \frac{\alpha}{e}.$$

This second deduction of the value of σ_a is only possible if N_a is of the form indicated above, and not of the form

$$\mathrm{N}_a = \mathrm{C}\epsilon^{\frac{3}{4}\frac{e}{\alpha}[\alpha_a + \beta_a(\mathrm{T}-273) + \gamma\mathrm{T}^2]}.$$

If a current of 10 amperes is flowing through bismuth in the direction of decreasing temperature, the heat developed between two cross-sections, whose temperature differences are 1° C., in unit time will be $\sigma = 24{\cdot}5\,.\,10^{-6}$ gr. cal.

For Hg the Thomson effect would be $-6{\cdot}9\,.\,10^{-6}$ gr. cal.* Combining these results of absolute measurements with a series of relative observations, we shall find the observed values of the Thomson effect united in the following table, which contains moreover the values of the quantity $\mathrm{T}\beta_a$ and $\mathrm{T}\beta_a - \alpha/e$. $\mathrm{T}=273$, $\mathrm{A}=4{\cdot}2\,.\,10^7$ mechanical equivalent of 1 calory, $e=1{\cdot}2\,.\,10^{-20}$, $\alpha=1{\cdot}5\,.\,10^{-16}$, $\frac{\alpha}{e}\frac{1}{\mathrm{A}}=0{\cdot}3\,.\,10^{-3}$.

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* Hagen, Wied. *Ann.* Bd. xxviii. p. 199 (1886).

	$\sigma_a \,.\, 10^6$ observed.	$T\beta_a \,.\, 10^6$.	$\left(T\beta_a - \frac{\alpha}{eA}\right) . \, 10^6$.
Bi ord.	+24·5		
Sb ord.	+21·6		
Cd ord.	+10·2	+28·1	−272
Zn	+ 3·6	+15·68	−284
Ag	+ 1·8	+ 9·8	−290
Cu	+ 0·6	+ 6·21	−294
Pb	0	0	
Sn	− 0·04	+ 3·59	−296
Al	− 0·04	+ 2·55	−297
Pt	− 6·0	− 6·0	−306
Hg	− 6·9		
Sb pure	− 7·8		
Bi pure	−10·2		

Only the values of commercial bismuth and of mercury correspond to absolute measurements, and for these two metals the second coefficient β_a of the thermoelectric force is unknown. A larger number of absolute determinations of the Thomson effect in the same time as the exact measurements of β_a are very necessary. The value $T\beta_a$ is not much greater than the specific heat of electricity, being at any rate of the same order of magnitude as σ_a. The theoretical value $T\beta_a - \frac{\alpha}{eA}$, however, is not even of the same order of magnitude as the observed value of the specific heat of electricity. There is a serious disagreement between the theory and the experimental result.

We assumed in paragraph 5 that a corpuscle, moving from $x+dx$ to x or from $T+dT$ to T, will lose a part of its kinetic energy equal to αdT which is communicated to the metal in the form of heat. This transference of heat would take place if the corpuscles were drifting, but under the action of the difference of temperature. The heat motion of the corpuscles not being much affected by electric forces which we are able to apply on conductors, the heat communicated by the corpuscles to the metal in the interval of temperature dT as consequence of the electric force, is not αdT, but $\alpha dT \,.\, C$, where C denotes a certain constant, smaller than unity. Thus we find σ to be equal to

$$\sigma = -\frac{\alpha}{e}\left(C - \frac{4}{3} T \frac{\partial \log \bar{N}}{\partial T}\right).$$

From the numbers of the last table we derived the following values of C, which, however, are not to be considered as definite figures.

	C.
Cd	0·0604
Zn	0·0404
Ag	0·0207
Cu	0·0186
Sn	0·0119

If C had really different values for various metals $\sigma_a-\sigma_b$ would be equal to

$$\frac{4}{3}\frac{\alpha}{e}\left(\mathrm{T}\frac{\partial \log \frac{\mathrm{N}_a}{\mathrm{N}_b}}{\partial \mathrm{T}}\right)-\frac{\alpha}{e}(\mathrm{C}_a-\mathrm{C}_b),$$

and there would be no more agreement between the thermodynamical and corpuscular theory of the Thomson effect.

§ 7. *On the Electric Force* X *and Pyroelectricity.*

We found
$$\sigma=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial \log \mathrm{N}_a}{\partial \mathrm{T}}-\frac{\alpha}{e},$$

$$\sigma=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial \log \mathrm{N}_a}{\partial x}\frac{\partial x}{\partial \mathrm{T}}-\frac{\alpha}{e},$$

$$\mathrm{X}=\frac{4}{3}\frac{\alpha}{e}\mathrm{T}\frac{\partial \log \mathrm{N}_a}{\partial x};$$

hence
$$\sigma=\mathrm{X}\frac{\partial x}{\partial \mathrm{T}}-\frac{\alpha}{e},$$

$$\mathrm{X}dx=\left(\sigma+\frac{\alpha}{e}\right)d\mathrm{T}$$

$$\int_{\mathrm{A}}^{\mathrm{B}}\mathrm{X}dx=\mathrm{V}_1-\mathrm{V}_2=\frac{\alpha}{e}(\mathrm{T}_2-\mathrm{T}_1)+\int_{\mathrm{T}_1}^{\mathrm{T}_2}\sigma d\mathrm{T}.$$

But
$$\sigma=\mathrm{T}\beta_a-\frac{\alpha}{e},$$

hence
$$\mathrm{V}_1-\mathrm{V}_2=\frac{\beta_a}{2}(\mathrm{T}_2^2-\mathrm{T}_1^2).$$

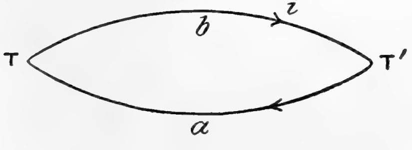
From this corpuscular theory of thermoelectricity we should expect a potential-difference between the ends of a metallic bar whose temperature varies from T_2 to T_1. This potential-difference has never been measured, but it ought to be measurable by means of an electrometric method. For iron β_a is equal to $-4{\cdot}87$; if we put $T_2=373°$, $T=273$ we find $V_1-V_2=4{\cdot}87 \, . \, 6{\cdot}46 \, . \, 10^4 \, . \, 10^{-8}=0{\cdot}0031$ volt. Since the actual value of the specific heat of electricity does not agree with the theoretical value, we cannot predict exactly the value of the electric force. If we suppose σ_a to be independent of the temperature, and if, in order to get a better agreement between the actual and the theoretical value of σ_a, we neglect the term α/e, we find for a bar of bismuth whose difference of temperature is 100° C., a potential-difference of 0·00102 volt, in the case of iron 0·00030 volt.

Though the forces X have not yet been detected we might suspect them to exist not only in metals of different temperatures, but even in other bodies, whose temperature varies from point to point. Thus the phenomena known under the name of pyroelectricity may to a certain extent be ascribed to forces of the same origin as the forces X, a difference of temperature being connected with a difference of electric potential. The phenomena of pyroelectricity, occurring in crystals of every crystallographic system, depend, however, in a very complicated way on the structure of the crystal. It is interesting to remark, that even crystals of bismuth exhibit these phenomena. If electric poles in the crystals are to be found not only by differences of temperature, but also under the influence of pressure and of rays of light, these latter effects may be reduced to the former ones.

§ 8. *Conservation of Energy.*

Let us consider a thermoelectric circuit made up of two metals *a* and *b*, whose junctions are at the constant temperatures T and T′. Then the thermoelectromotive force E will give rise to an electric current *i*; and the amount of heat absorbed in unit time by the Peltier and Thomson effects

Fig. 4.



will be :

$$W=i(Q'-Q)+i\int_{T}^{T'}(\sigma_b-\sigma_a)dT$$

$$=i\frac{4}{3}\frac{\alpha}{e}\left\{T'\log\left(\frac{N_a}{N_b}\right)_{T'}-T\log\left(\frac{N_a}{N_b}\right)_{T}\right\}$$

$$+i\frac{4}{3}\frac{\alpha}{e}\int_{T'}^{T}T\frac{\partial\log\frac{N_a}{N_b}}{\partial T}dT$$

$$=i\frac{4}{3}\frac{\alpha}{e}\left\{T'\log\left(\frac{N_a}{N_b}\right)_{T'}-T\log\left(\frac{N_a}{N_b}\right)_{T}\right\}$$

$$+i\frac{4}{3}\frac{\alpha}{e}\left[T\log\frac{N_a}{N_b}\right]_{T'}^{T}+i\frac{4}{3}\frac{\alpha}{e}\int_{T}^{T'}\log\frac{N_a}{N_b}dT,$$

but $$E=\frac{4}{3}\frac{\alpha}{e}\int_{T}^{T'}\log\frac{N_a}{N_b}dT,$$

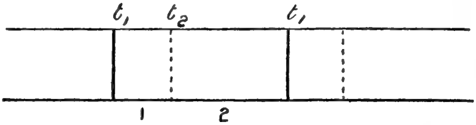
hence $W=iE$.

The work done by the current i under the influence of the electromotive force E in unit time is equal to the heat absorbed in the circuit in the same time.

§ 9. *Resistance of Alloys.*

Lord Rayleigh[*] has pointed out that in the case of a mixture of metals there is, owing to their thermoelectric properties, something which cannot be distinguished by experiments from resistance, and which is absent when the metals are pure. Let us suppose that the mixed metals are arranged in thin layers, the adjacent layers being of different metals, and that the current passes through the body at right angles to the faces of the layer. When a current passes across the junction of two metals there is absorption or production of heat, proportional to the current passing across

Fig. 5.



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[*] Lord Rayleigh, Collected Works, vol. iv. p. 232.

the junction. Thus, when the current passes through the system of alternate layers of the two metals, one face of each layer will be cooled and the other heated, and thus in the pile of layers differences of temperature proportional to the current will be established. This will give rise to a thermoelectric force tending to oppose the current. Such a force would produce exactly the same effect as a resistance.

If Δt is the difference of temperature between two junctions, the electromotive force of an elementary couple will be equal to

$$e=\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\Delta t.$$

The amount of heat developed in unit time and per unit area of the cross-section in each couple is equal to

$$iQ_1+i\sigma_1\Delta t.$$

This amount is to be equated to the heat conducted per second towards the cold junctions on the two sides. Let k_1, k_2 be the conductivities for heat of the two metals, l_1 and l_2 the corresponding lengths; the heat conducted per second towards the cold junctions is

$$\frac{\Delta t}{l_1}k_1+\frac{\Delta t}{l_2}k_2=\Delta t\left(\frac{k_1}{l_1}+\frac{k_2}{l_2}\right)\frac{1}{\left(\frac{l_1+l_2}{l_1+l_2}\right)}=\Delta t\,.\,n\,.\left(\frac{k_1}{p_1}+\frac{k_2}{p_2}\right),$$

if there are n similar couples per unit of length,

$$n(l_1+l_2)=1,$$

and if we put

$$\frac{l_1}{l_1+l_2}=p_1 \quad\text{and}\quad \frac{l_2}{l_1+l_2}=p_2,$$

when a stationary state is reached,

$$i(Q_1\pm\sigma_1\Delta t)=n\Delta t\left(\frac{k_1}{p_1}+\frac{k_2}{p_2}\right).$$

The whole electromotive force per unit of length is equal to

$$ne=\omega' i=\omega'\frac{n\Delta t\left(\frac{k_1}{p_1}+\frac{k_2}{p_2}\right)}{Q_1\pm\sigma_1\Delta t},$$

ω' denoting the false resistance due to thermoelectric causes,

$$\omega' = \frac{e(Q_1 \pm \sigma_a \Delta t)}{\Delta t\left(\frac{k_1}{p_1} + \frac{k_2}{p_2}\right)} \qquad T_1 = t_1 + 273$$

$$= \frac{\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\Delta t\left(\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}T \pm \sigma_1 \Delta t\right)}{\Delta t\left(\frac{k_1}{p_1} + \frac{k_2}{p_2}\right)}$$

$$= \frac{\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\left(\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}T_1 \pm \sigma_1 \Delta t\right)}{\frac{k_1}{p_1} + \frac{k_2}{p_2}}.$$

In the stationary state $\Delta t = 0$ and we get

$$\omega' = \frac{T_1\left(\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\right)^2}{\frac{k_1}{p_1} + \frac{k_2}{p_2}}.$$

This false resistance superposed on the other resistance makes the electrical resistance of alloys greater than the value expected from the simple view of mixture. If we suppose the molecules of an alloy to be distributed in every direction in the same way, then only the third part of the doublets will oppose the current flowing in a certain direction. Therefore

$$\omega' = \frac{T_1}{3}\frac{\left(\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\right)^2}{\frac{k_1}{p_1} + \frac{k_2}{p_2}}.$$

Let p_1 be so small in comparison with p_2 that we may neglect $\frac{k_2}{p_2}$ beside $\frac{k_1}{p_1}$.

We get

$$\omega' = \frac{1}{3}T_1\left(\frac{4}{3}\frac{\alpha}{e}\log\frac{N_a}{N_b}\right)^2\frac{p_1}{k_1}.$$

The false additional resistance is a reversible proportional to the thermal conductivity of the impurity. Since

$$Q = \frac{4}{3}\frac{\alpha}{e}T_1\log\frac{N_a}{N_b},$$

we get

$$\omega' = \frac{1}{3\mathrm{T}_1}(\mathrm{Q}_1)^2 \frac{p_1}{k_1};$$

in the general case:

$$\omega' = \frac{1}{3\mathrm{T}_1} \frac{\mathrm{Q}_1^2}{\frac{k_1}{p_1} + \frac{k_2}{p_2}}.$$

Let us take the metals copper and zinc. The thermal conductivity of copper $k_2 = 0{\cdot}94$ cm. gr. sec. cal.; the thermal conductivity of zinc $k_1 = 0{\cdot}26$. Let us consider an alloy of these two metals containing 40 gr. zinc and 60 gr. copper. The density of copper being 8·8, that of zinc 7·1, we shall have 45 cm.^{3} zinc and 55 cm.^{3} copper, therefore

$$p_1 = 0{\cdot}45, \quad p_2 = 0{\cdot}55,$$

$$\frac{k_1}{p_1} = \frac{0{\cdot}26}{0{\cdot}45} = 0{\cdot}58, \quad \frac{k_2}{p_2} = \frac{0{\cdot}94}{0{\cdot}55} = 1{\cdot}71,$$

$$\frac{k_1}{p_1} + \frac{k_2}{p_2} = 2{\cdot}29.$$

The Peltier effect between copper and zinc is

$$\frac{5{\cdot}85}{36.10^2} = 1{\cdot}62 \,.\, 10^{-3} = \mathrm{Q}_1; \quad \mathrm{Q}_1^2 = 2{\cdot}62 \,.\, 10^{-6},$$

the false resistance at 0° C. would be

$$\omega' = \frac{2{\cdot}62 \,.\, 10^{-6}}{3 \,.\, 273 \,.\, 2{\cdot}29} = 1{\cdot}4 \,.\, 10^{-9} \,.\, 4{\cdot}2 \,.\, 10^7,$$

$$\omega' = 5{\cdot}9 \,.\, 10^{-2} \text{ absolute unit.}$$

$$\omega' = 5{\cdot}9 \,.\, 10^{-11} \text{ ohm.}$$

The electric conductivity of copper is $60 \,.\, 10^4$, its specific resistance $\frac{1}{60} \,.\, 10^{-4} = 1{\cdot}6 \,.\, 10^{-6}$; the electric conductivity of zinc is $16 \,.\, 10^4$ per cm.^{3}, its specific resistance

$$\frac{1}{16} \,.\, 10^{-4} = 6{\cdot}2 \,.\, 10^{-6}.$$

If the resistance of the alloy copper and zinc were to be found as the property of a simple mixture, we should get:

$$\frac{(1{\cdot}6 \,.\, 55 + 45 \,.\, 6{\cdot}2)}{100} \,.\, 10^6 = 3{\cdot}67 \,.\, 10^{-6}.$$

The actual electric conductivity of the alloy considered is equal to $13{\cdot}58 \,.\, 10^4$, its specific resistance therefore $7{\cdot}4 \,.\, 10^{-6}$; thus, the actual resistance is very nearly twice as large as that calculated from the mixture formula. The false resistance $\omega' = 5{\cdot}5 \,.\, 10^{-11}$ is exceedingly small in comparison with the difference between the actual and the calculated resistance.

We shall now consider an alloy made up of 99·3 gr. copper and 0·7 gr. zinc. Using the same notation as before we get

$$p_1 = 0{\cdot}01, \qquad \frac{k_1}{p_1} + \frac{k_2}{p_2} = 26 + 0{\cdot}95,$$
$$p_2 = 0{\cdot}99,$$

$$\omega' = \frac{1}{3.273} \cdot \frac{2{\cdot}62 \,.\, 10^{-6}}{26{\cdot}95} = 1{\cdot}19 \,.\, 10^{-10},$$
$$\omega' = 1{\cdot}19 \,.\, 10^{-10} \,.\, 4{\cdot}2 \,.\, 10^7,$$
$$\omega' = 5 \,.\, 10^{-3} \text{ absolute unit},$$
$$\omega' = 5 \,.\, 10^{-3} \,.\, 10^{-9} = 5 \,.\, 10^{-12} \text{ ohm}.$$

The mean resistance would be:

$$10^{-6} (1{\cdot}6 \,.\, 0{\cdot}99 + 6{\cdot}2 \,.\, 0{\cdot}01) = 1{\cdot}64 \,.\, 10^{-6}.$$

But the actual conductivity is equal to $54{\cdot}56 \,.\, 10^4$; therefore the actual specific resistance is equal to $1{\cdot}84 \,.\, 10^{-6}$. Here again the actual resistance is found to be larger than the calculated one, by an amount of quite a different order of magnitude from the false resistance.

The last example may be an alloy composed of equal volumes of copper and platinum. The thermal conductivity of platinum k_1 is equal to 0·17, the electric conductivity $9{\cdot}2 \,.\, 10^4$, the specific resistance $10{\cdot}8 \,.\, 10^{-6}$. The Peltier effect between the two metals is equal to $Q_1 = 8{\cdot}9 \,.\, 10^{-4}$.

$$Q_1{}^2 = 79 \,.\, 10^{-8}$$

$$\frac{k_1}{p_1} + \frac{k_2}{p_2} = 0{\cdot}17 \,.\, 2 + 0{\cdot}94 \,.\, 2 = 2{\cdot}22.$$

The false resistance would be equal to

$$\omega' = \frac{1}{3} \cdot \frac{79 \,.\, 10^{-8}}{3 \,.\, 273 \,.\, 2{\cdot}22} = 4{\cdot}35 \,.\, 10^{-10},$$
$$\omega' = 4{\cdot}35 \,.\, 10^{-10} \,.\, 4{\cdot}2 \,.\, 10^7 = 1{\cdot}82 \,.\, 10^{-2},$$
$$\omega' = 1{\cdot}82 \,.\, 10^{-11} \text{ ohm}.$$

In this case we shall calculate this false resistance from the first formula given by Lord Rayleigh:

$$\omega' = 273\, e^2 \left(\frac{k_1}{p_1} + \frac{k_2}{p_2}\right)^{-1},$$

e is the thermoelectric force of the element copper-platinum for a difference of temperature of 1 degree.

$$e = 0{\cdot}72 \,.\, 10^{-5} \,.\, 10^{8} \text{ absolute units.}$$
$$e^2 = 0{\cdot}52 \,.\, 10^{6},$$
$$\omega' = \frac{273 \,.\, 0{\cdot}52 \,.\, 10^{6}}{2{\cdot}22 \,.\, 4{\cdot}2 \,.\, 10^{7}} = 15{\cdot}2 \,.\, 10^{-1} \text{ absolute unit,}$$
$$\omega' = 1{\cdot}52 \,.\, 10^{-9} \text{ ohm.}$$

The mean electric conductivity of the alloy is found to be* $3{\cdot}09 \,.\, 10^4$; the specific electric resistance would be

$$\omega = 0{\cdot}323 \,.\, 10^{-4}.$$

Considering the alloy as a single mixture we should find

$$\tfrac{1}{2}(10{\cdot}8 + 1{\cdot}6) \,.\, 10^{-6} = 0{\cdot}062 \,.\, 10^{-4}$$

The false resistance is in these cases far too small to explain the difference between the observed and the calculated value of the resistance of the alloys. This result may partly explain why Dr. R. S. Willows † could detect no difference between the apparent resistances of alloys with direct current and with alternating current.

An alloy of equal volumes of copper and iron has a false resistance amounting to 1·5 per cent. of that of copper.

Cambridge, April 6th, 1908.

LXVI. *A Recalculation of the Vapour Pressure of Mercury.*

By T. H. Laby, *B.A.*, *Exhibition of* 1851 *Research Scholar*, *Joule Student of the Royal Society*, *Emmanuel College*, *Cambridge*‡.

THE vapour-pressure of mercury is intrinsically important: it has been determined for a wider range of temperatures than that of any other substance; and Professor Nernst hopes to be able to find the integration constant of the equation of the reaction isochore "by continuing the vapour-pressure curves as far as possible in the direction of very small pressures, for example to ·001 mm." § Yet the greatest—and it should be added, unnecessary—disagreement is to be found in the current values of this vapour-pressure, nor is there any table

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* *Landolt-Börnstein Physikalish-chemische Tabellen*, 3 Auflage, p. 721*a*.

† R. S. Willows, 'Proceedings of the Physical Society of London,' vol. xx. p. 427 (1907).

‡ Communicated by the Author.

§ Nernst, 'Thermodynamics and Chemistry,' New York, 1907, p. 60.

combining all the existing observations. It appeared, then, that a reduction of these numerous observations would be of value.

The existing Data.

The results of the following observers, which are quoted in Table II. after their initial letters, have been obtained by varied methods as indicated below:—

H.—Hertz (Wied. *Ann.* 1882, xvii. p. 193): Statical method and mercury in glass thermometer corrected by a Joly air-thermometer.

RY.—Ramsay & Young (Trans. 1886, xlix. p. 37); Young (Trans. 1891, lix. p. 629): Dynamical method, temperatures obtained by vapour-jackets of aniline, quinoline, &c. boiling at known pressures.

CG.—Callendar & Griffiths (Phil. Trans. 1891, clxxxii. p. 151): Boiling-point of mercury by platinum thermometers in terms of constant-pressure air-thermometer.

P.—Pfaundler (Wied. *Ann.* 1897, lxiii. p. 36): Absorption (by silver) of mercury from a stream of air saturated with it.

M.—E. W. Morley (Phil. Mag. [6] vii. p. 662, June 1904): Loss of weight of mercury saturator on passing carbon dioxide through it.

G.—A. Gebhardt (*Verhand. Deut. Phys. Ges.* 1905, viii. pp. 184–188, and *Diss. Univ. Erlanger*, 1904): Dynamical method, lower pressures measured with a McLeod gauge.

C.—Cailletet, Colardeau, & Rivière (*Compt.-rend.* 1900, cxxx. p. 1585): Static method, thermojunction, and metallic manometer calibrated by open-air manometer.

Few of the observers are explicit as to their unit of pressure, and no mention of the value of g for the place of observation has been found. The latter omission is unimportant as few of the observations are correct to 1 in 1000; but it is more important to know that mm. of mercury means mercury at 0° C.

Regnault's observations have not been used, as he distinctly states they are only approximate, and Ramsay & Young (*loc. cit.*) have given reasons for doubting their accuracy. Nor have I used the results of the elaborate experiments of Van der Plaats [*], who was the first to absorb mercury from a stream of gas saturated with mercury vapour, nor those of Hagen [†] and of McLeod [‡], which differ widely from the values deduced from the concordant observations of Hertz, Pfaundler, and Morley. This want of agreement is shown in Table I.

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[*] *Rec. Trav. Chim.* 1886, v. pp. 149–182.

[†] Wied. *Ann.* 1882, xvi. p. 610.

[‡] Brit. Assoc. Rep. 1883, p. 443.

TABLE I.

Temp.	Pressure of Mercury Vapour in mms. according to			
	Van der Plaats.	Hagen.	McLeod.	Hertz, Pfaundler, Morley.
10°	·008	—	—	·00042
20	·013	—	·00574	·00109
50	—	·042	—	·0122

In order that the experiments of each observer should contribute about equally to the final result of my reduction, some of the numerically fewer observations of Ramsay & Young, and Young alone have have been given 2 †, 3, or 4 times the weight of the other observations, according to the accuracy the writer attached to the measurement of the temperature concerned.

TABLE II.

Observed Vapour-Pressures of Mercury.

	Temp. ° C.	Pressure, in mm.		Temp. ° C.	Pressure, in mm.		Temp. ° C.	Pressure, in mm.
P.	15	·00081	RY.	183·4*	9·87	G.	268	122·9
M.	16	·0010	H.	184·7	11·04	RY.	270·3	124·35
M.	30	·0027	G.	188	12·51	G.	271·5	126·11
M.	40	·0052	H.	190·4	12·89	G.	277·5	150·8
M.	50	·0113	H.	203	20·35	G.	278·5	147·5
P.	56·3	·01801	H.	206·9	22·58	RY.	280·2	157·15
M.	60	·0214	G.	207	21·07	G.	286·5	185·0
M.	70	·0404	RY.	222·15	34·4	G.	295·5	224·9
H.	89·4	·16	G.	224·5	38·82	G.	302·5	263·9
P.	98·8	·26305	G.	230·5	46·49	G.	309·5	308·1
H.	117	·71	G.	236	51·58	G.	315·0	360·2
G.	129	1·0	RY.	236·95	51·85	CG.	356·7	760
H.	154·2	3·49	G.	245	68·42	C.	400	1596
G.	157·5	3·93	G.	248	71·39	Y.	403·15	2896·9
H.	165·8	5·52	G.	255	87·87	Y.	403·9	2904·5
G.	176·5	8·22	G.	256	94·4	C.	450	3230
H.	177·4	8·2	G.	264	105·69			

* Taking the boiling-point of aniline as 184°·1.

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† See Table III., under Δ: this weight is indicated by ×2, &c.

Reduction of Observations.

The logarithms of the observed pressures of the last table were plotted against the temperatures on squared paper 600 by 300 mm., and a $(\log p, t)$ curve was drawn through the points. The final curve, or rather formulæ, were then obtained by the following successive approximations.

The most probable values for p at 50° and 250° were found from the above diagram, and a Kirchhoff-Rankine-Dupré formula (B) of the form

$$\log p = \mathrm{A} + \mathrm{B}/\theta + \mathrm{C} \log \theta \quad (\theta = t + 273)$$

was deduced from these values, and the boiling-point 356°·7. The observed values of t and $\log p$ were replotted (diagram B) on a larger scale, giving a curve about 1100 mm. long when the graph of formula B was drawn in. This figure enabled (as is described below) six points to be found from which a three-constants Kirchhoff formula was calculated by the method of least squares.

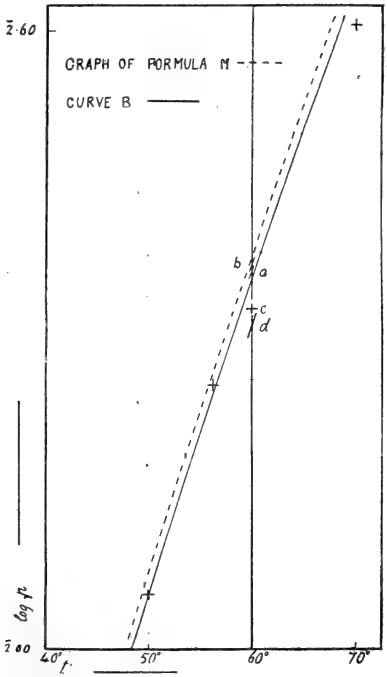
The 46 observations from 15° to the boiling-point, at the following temperatures, were arranged thus:—

15°, 16°, 30°, 40° (reduced to 16°);
50°, 56°·3, 60°, 70° (reduced to 60°);
89°·4, 98°·8, 117°, 129° (reduced to 120°);
154°·2, ... to 224°·5 (reduced to 190°);
230°·5, 236°, . . . to 315° (reduced to 270°);
B.P. 356°·7.

One value of p was deduced for each group (namely, the values of p at 16°, 60°, 120°, 190°, 270°) by the process indicated in fig. 1, in which so much of the curve B (one-eighteenth) is drawn as the second group covers. Lines parallel to B were drawn through the observed points 50°, 56°·3, 60°, 70° to cut the isotherm 60° in *a, b, c, d*. The mean position of these four points gave the value of p at 60°. The other groups were similarly treated, and it was found that $\log p$ for the different groups is:—

16°	$\bar{4}\cdot994$	60°	$\bar{2}\cdot333$	120°	$\bar{1}\cdot875$
190°	1·1072	270°	2·0965	356°·7	2·8808

But the $\log p = \mathrm{A} + \mathrm{B}/\theta + \mathrm{C} \log \theta$ formula, calculated by the method of least squares from these observations, gave too much weight to the fewer and less accurate low-temperature observations; and it was clear that one three-constants formula would not fit all the observations as closely as was desirable. The graph of the last formula, however, showed



that two Kirchhoff formulæ could be found, which would fit the observations as closely as was required by the concordance and accuracy of the experiments concerned. These formulæ are :—

$$\log p = 15{\cdot}24431 - 3623{\cdot}932/\theta - 2{\cdot}367233 \log \theta, \quad \text{(M)}$$

derived from

$$41^\circ{\cdot}7,\ \log p = \bar{3}{\cdot}8157\ ;\quad 190^\circ,\ 1{\cdot}1072\ ;\quad 270^\circ,\ 2{\cdot}0965\ ;$$

and $\log p = 10{\cdot}04087 - 3271{\cdot}245/\theta - {\cdot}7020537 \log \theta,$ (L)

derived from

$$16,\ \bar{4}{\cdot}994\ ;\quad 270^\circ,\ 2{\cdot}0965\ ;\quad 356^\circ{\cdot}7,\ 2{\cdot}8808.$$

The following Table shows how closely these formulæ fit the observations. M is used from 15° to 270°, and L from 270° to 450°, to calculate $\log p$. Under Δ is given ($\log p$ observed) − ($\log p$ calculated), and under $\Sigma\Delta$ is given the sum of the Δ's for each group.

TABLE III.

Closeness of fit of formulæ (L and M) to observations.

	t°.	Δ.	ΣΔ.
P.	15	·0687	−·0247 ΣΔ/n =−·0021
M.	16	·1213	
M.	30	·0214	
M.	40	−·0427	
M.	50	−·0318	
P.	56·3	−·0237	
M.	60	−·0604	
M.	70	−·0713	
H.	89·4	·0180	
P.	98·8	·0075	
H.	117	·0328	
G.	129	−·0645	
H.	154·2	·0092	−·0059 ΣΔ/n =−·0004
G.	157·5	·0032	
H.	165·8	·0114	
G.	176·5	·0127	
H.	177·4	−·0023	
RY.	183·4	−·0142×4	
H.	184·7	·0147	
G.	188·0	·0198	
H.	190·4	−·0027	
H.	203	·0164	
H.	206·9	·0079	
G.	207	−·0236	
RY.	222·15	−·0096×3	
G.	224·5	·0130	

	t°.	Δ.	ΣΔ.
G.	230·5	·0169	−·0042 ΣΔ/n =−·0002
G.	236	−·0046	
G.	245	·0124	
RY.	236·95	−·0137×4	
G.	248	−·0035	
G.	255	·0081	
G.	256	·0284	
G.	264	−·0092	
G.	268	·0140	
RY.	270·3	−·0050×2	
G.	271·5	−·0114	
G.	277·5	·0040	
G.	278·5	−·0157	
RY.	280·2	−·0056×2	
G.	286·5	·0023	
G.	295·5	−·0008	
G.	302·5	·0026	
G.	309·5	·0051	
G.	315·0	·0232	
CG.	356·7	·0000	ΣΔ=0
C.	400	·0083	
Y.	443·9*	−·0084	
C.	450	·0001	

If the formulæ L and M fitted the observations perfectly, ΣΔ would be zero, while actually ΣΔ/n (where n is the number of observations in each group) has the values −·0021, −·0004, −·0002, and 0. Are these sufficiently small? When it is noticed that the average value of Δ is ·0215, it will be seen that no real gain is made by decreasing ΣΔ/n: the accuracy of the observations does not warrant any efforts to obtain more closely-fitting formulæ.

It is worthy of remark that the formula L, whose constants were determined from p at 16°, 270°, and 356°·7, was afterwards found to fit the existing observations to 450°; and it does not differ from them as much as they differ from one another between 16° and 700°, which shows how well a

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* Young's two observations, 443°·15 2896·9 mm. and 443°·9 2904·5 mm., give 443°·9 2916·2 mm. on combining them; this mean is used here.

Kirchhoff formula will express vapour-pressures. Thus, for temperatures above 450° we have:—

Temp.	Formula L.	Cailletet, Colardeau, and Rivière.
450°	3,229 mm.	3,230 mm.
500	6,107 „	6,080 „
550	10,456 „	10,488 „
600	16,943 „	16,948 „
700	38,109 „	38,000 „

Table IV.

Vapour-Pressure of Mercury (in mm. of mercury at 0°).

Temp. ° C.	Pressure.	Temp. ° C.	Pressure.	Temp. ° C.	Pressure.	Temp. ° C.	Pressure.
15	·000691	135	1·52	255	86·24	370	959·2
20	·00109	140	1·89	260	97·82	380	1135
25	·00168	145	2·34	265	110·7	390	1337
30	·00257	**150**	2·88	270	124·8	**400**	1566
35	·00387	155	3·53	275	140·8	**450**	3229
40	·00574	160	4·30	280	158·4		
45	·00840	165	5·218	285	177·9		
50	·0122	170	6·298	290	199·3		
55	·0174	175	7·567	295	222·8		
60	·0246	180	9·054	**300**	248·6		
65	·0344	185	10·78	305	276·9		
70	·0476	190	12·80	310	307·7		
75	·0652	195	15·12	315	341·4		
80	·0885	**200**	17·81	320	378·1		
85	·1191	205	20·89	325	418·0		
90	·1589	210	24·42	330	461·3		
95	·210	215	28·46	335	508·3		
100	·276	220	33·03	340	559·1		
105	·360	225	38·23	345	614·1		
110	·465	230	44·10	**350**	673·3		
115	·597	235	50·73	355	737·2		
120	·761	240	58·16	356·7	760 *		
125	·965	245	66·50	360	805·9		
130	1·215	**250**	75·83	365	879·8		

Cailletet, Colardeau, & Rivière Observations.

Atmospheres.	
500	8
550	13·8
600	22·3
650	34
700	50
750	72
800	102
850	137·5
880	162

* $\delta p/\delta t$ at the boiling-point = 13·6 mm. per degree.

Extrapolated by formula M:

10° ·00043, 5° ·00026, 0° ·00016.

Interpolation.

The vapour-pressure may be found for temperatures between those given in the Table by the linear interpolation of log p against t; this is accurate for 5° intervals. Between 365° and 450°, formula L will give p for temperatures not given.

Density and Pressure.

It should be remembered that the vapour-pressure of mercury has not been observed below 89°·4. Pfaundler and Morley observed the density (for they measured the mass per unit volume) of mercury-vapour in gases saturated with it at different temperatures, and calculated the pressure assuming that the vapour obeys the gas laws and has a density of 100 ($H_2=1$). This is justified at higher temperatures; for Gebhardt, using these assumptions, has calculated the vapour-pressure from the densities of mercury-vapour as observed by Jewett *. The agreement of his results with the actual pressures (see Table V.) is interesting, for it shows that the saturated vapour of mercury is wholly monatomic at nearly half-an-atmosphere pressure.

TABLE V.

Temperature...	140°.	160°.	180°.	200°.	220°.	240°.	260°.	280°.	300°.	310°.
Pressure calc. from density.	1·84	4·23	9·1	24·2	32·2	62·3	100·6	155	250	311 mm.
Pressure from Table IV. ...	1·89	4·30	9·05	17·8	33·0	58·2	97·8	158	249	308 mm.

It does not appear that the critical point of mercury has been reached: it must be at an exceptionally high temperature, apparently above 850°.

LXVII. *Telescopic Vision.*

By G. JOHNSTONE STONEY, *M.A.*, *Sc.D.*, *F.R.S.*†

PART II.—DETERMINATION OF THE KIND OF IMAGE WHICH CAN BE OBTAINED.

[Plate XII.]

CHAPTER 3.

The elementary parts of which an image consists.

32. IN the First Part of this Memoir, in the August number of the Phil. Mag., we have described an apparatus (represented in Plate XII., which is reproduced in the present number) with which the astronomer can make experiments that will disclose to him the imperfections

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* Phil. Mag. [6] vol. iv. 1902, p. 546.

† Communicated by the Author.

which of necessity * exist in the images which his astronomical telescopes are competent to furnish ; which will tell him how to mitigate these imperfections and how to guard against being misled by them ; and, above all, which will reveal to him the causes of all these imperfections.

In this second part of the Memoir, we propose to investigate by its aid, of what kind the images will be ; reserving for the third part which is to follow the most important part of our inquiry by which the causes of the observed defects will be made fully known to us.

33. An image, whether formed by an optical instrument or upon the retina, is found to consist of parts distinguishable from one another, which are of such a kind that within each of these units there is either no detail to be seen or at least none that can be made out satisfactorily. Each such elementary part of an image may be called a spile or blur (σπῖλος, a blot or blur), since it is the outcome of light emitted from an immense amount of molecular and other events going on upon the object, all parts of which with all the activities in or between minutiæ being in the image blurred into a single spile, with, in some cases, an admixture of light that has strayed on to this spile from other parts of the object.

Of spiles there are varieties, and a somewhat full study of them is required in order to understand the images seen in microscopes; but only two or three kinds present themselves in the telescopic images of celestial objects, and among these the plateo-spile or surface-blur is that with which we have most to do. The images formed on the retina by a grape, a cherry, a sheet of white paper, or a whitewashed ceiling are examples of plateo-spiles. In the astronomical telescope this description of spile may be the full size of the image of the planet, or it may be of any smaller size down to the smallest speck which in any degree exhibits the shape of the detail upon the planet which has occasioned it. Specks smaller than this or more shapeless are spiles of another kind. Most, however, of the features visible in the image of a planet are plateo-spiles.

34. Plateo-spiles in many cases have a well defined outline, and then become perigrapho-spiles or silhouette blurs. The leaves of a tree viewed from a suitable distance are good examples of objects of which the images formed on the retina are silhouette-blurs. A leaf may retain a markedly distinct

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* By the expression "imperfections which *of necessity* exist" is meant, which would continue to exist if his telescope could be made perfect as an optical instrument, and if "seeing" through our atmosphere were also perfect.

outline even when the spectator has retreated to such a distance that all appearance of detail upon the surface of the leaf ceases to be seen. It indeed seems marvellous, when we come to think of it, that the boundary of each leaf can continue to be so distinctly seen, when perhaps detail upon the leaf has become unseen or so confusedly seen as to indicate that light from one part of the leaf is able to stray to other parts on the image, while, at the same time, no light from any part of the leaf is allowed outside the boundary of the image of the whole leaf, nor is any of the light from the background against which the leaf is seen allowed to trespass within that barrier. The green of the leaf seems to stop abruptly at the boundary of the image ; and the light from the background stops there as abruptly. *We shall be able to discover by our experimental apparatus, the conditions which have to be fulfilled in the process by which the image is formed in order to secure these results.*

35. An object may of course furnish very different images when viewed under different conditions. Thus a ruling upon a sheet of paper of equidistant parallel lines at intervals of a millimetre, when well illuminated, and when looked at by a spectator whose eyesight is good from a distance exceeding 12 feet, will present a mere uniform appearance, *i. e.* the image upon the retina will be a simple plateo-spile ; while from distances less than 11 feet the image will be quite different, since the ruling itself will then come into view. The limit between the two appearances will usually be found when the eye is somewhere between 11 and 12 feet from the ruling (see Phil. Mag. for March 1894, p. 317).

36. Two quite similar objects upon a planet, but of different sizes, may be such that the larger of them will furnish an image which is a silhouette-blur, retaining the shape of the object with its outline well defined ; while the image of the smaller one may be hazy in outline and distorted in shape, representing the object as too large in some places and too small in others, and sometimes introducing features that do not exist upon the object.

So, again, things that appear to be streaks in the image may in some cases be the kind of spile which may be called rhabdo-spiles, *i. e.* rod-like blurs occasioned by features upon the planet which are not streaks.

The causes of all these and of many other effects will be satisfactorily exposed to our view by the experiments of which we shall be able to give examples.

37. The part of the planet or other object which corresponds in position, shape and size to a spile in the images, may be

called its anti-spile. Under some conditions the light seen in the spile is the same as the light received by the telescope from its anti-spile; but this is by no means always the case.

CHAPTER 4.

The kind of image that will be formed.

38. When some feature, z', upon a planet is to be made visible by looking at it through a telescope, then, if what we see in the telescope corresponding to that part of the planet, is the kind of image which we have called a spile, *i. e.* if it is some one of the elementary parts of which the image of the whole planet is seen to consist;—if, for example, it is one of the white polar caps seen upon the image of Mars, or one of those extensive regions which are bounded by whatever on the planet corresponds to the faint streaks in its image which have been called Canals "upon Mars"—in such cases the outline of this spile is often tolerably well seen in the image, although the immense amount of detail which really exists upon its anti-spile (an extensive region upon the planet) is so blurred together that it is unseen or but imperfectly seen. Even the image of an entire planet may present this appearance. This happens with our best telescopes when the planet is Uranus or Neptune; and with telescopes of insufficient aperture, however good in other respects, all the planets will present this appearance. Under such circumstances no detail except the mere outline of the planet is well seen.

39. Let us take the case of Neptune, which when in opposition subtends at the earth an angle of about $1\frac{1}{3}\ \epsilon$, where ϵ is the angle $2''\cdot062648$ which in circular measure is $0\cdot00001$; or of Uranus which subtends nearly 2ϵ. These are objects which appear simply as round disks of nearly uniform light in the telescope; that is to say, the image of the planet is the kind of plateo-spile or surface-blur which we have distinguished by the name of silhouette-blur. Its outline only is seen; and we represent it in our experimental apparatus by light coming through a round hole in copper-foil at z'. To do this satisfactorily we must adjust the size of the round hole at z', which is our pro-planet, and the aperture A′ of the iris-diaphragm at C, so as correctly to represent the size of the planet and the aperture of the astronomical telescope whose performance upon it we want to investigate. This may be done in any one of the ways described in

the footnote [*]; and having got his adjustments made the observer should note the position at C (see Plate XII.) of the handle of the iris-diaphragm, and the direction in which he moved it into position, in order that he may be able to restore it to that position, if he should have occasion to increase or diminish the opening. He may then freely vary that opening, and thus see how the image of the planet will be affected by differences in the aperture of his astronomical

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[*] When making experiments the observer often finds it convenient to have more than one way of bringing his apparatus into accordance with the conditions that have to be complied with. And in the present instance, where we want to reproduce in our pro-telescope the appearance which Neptune will have in the astronomical telescope, we have the choice of several ways of doing so. The simplest in principle is to give to the hole at z', which is to represent the planet, a diameter of $1\frac{1}{3}$ mm., and to contract the aperture of the pro-telescope by the iris-diaphragm at C until it becomes one-hundredth part of the aperture of the astronomical telescope. But we may proceed otherwise: we may assign any other size, if more convenient, to the opening of z', provided that we increase or diminish the aperture of the pro-telescope inversely as we have altered the size of the opening at z'.

A third, and often the most convenient method of making the adjustment, depends upon the mode of observing which we shall have to adopt in Part III. of this Memoir. We shall there find that if we make a round opening at z', and illuminate it by light from the pro-star s', it will furnish a very remarkable concentration image upon plane Y'; which the observer will see by removing the pro-telescope and looking through the Steinheil lens when placed at B. This concentration image will consist of a central boss of light surrounded by coloured rings, which the observer can make to present itself centrally in the field of view, by adjusting the B end of the board BE, which he has the means of doing. Now, it can be proved that the condition to be fulfilled in order that the aperture of the pro-telescope shall correspond to that of the astronomical telescope is that the iris-diaphragm at C shall be closed until a definite amount of this concentration image shall remain visible, which amount can be calculated by a known formula. Thus, if we want to investigate the performance of a 12-inch telescope used in examining a planet subtending the angle $1\frac{1}{3}\,\epsilon$, it is found that the iris-diaphragm has to be closed until only the central boss of the concentration image, the whole of the first appendage ring, and nearly but not quite the whole of the second appendage ring, remain visible. Accordingly, as it is the visibility of this amount of the concentration image which is the condition to be secured, the observer is at liberty to make the round hole at z' of any size that he finds convenient, provided that he then adjusts the iris-diaphragm at C to allow him to see this portion of the concentration image. He has then only to illuminate z' by diffused light, instead of by light from the pro-star, in order to see it through his pro-telescope under the same optical conditions as those under which a 12-inch astronomical telescope would show the disk of the planet Neptune when in opposition.

This last method of adjusting has the practical advantage that it dispenses with the necessity of accurately making the round hole at z' of a prescribed size, and that what the observer has to do in making the adjustment is easily performed.

telescope. Let us suppose that he begins by making the adjustments which correspond to a 12-inch telescope employed upon Neptune; and that he illuminates the pro-planet z' with diffused light. To provide diffused light with a sufficient maximum intensity, and with this intensity easily regulated, the author reflected a sunbeam horizontally towards z' by the heliostat H, having removed out of its path all obstructions—viz., lens G and the apparatus at F. He then introduced into its path a plano-convex lens of tolerably long focus (about 70 cm.) which happened to be at hand, and by it formed an image of the sun at a distance of some five or six centimetres to the right of z'. This image of the sun was the source of the diffused light which is to illuminate object z'. For some observations this light is too bright, and to moderate it, pieces of the kind of neutral dark glass which is made in large panes for export to India, were introduced—one, two, or three of them as required—at E, between screen Z′ and lens L′. These provided four degrees of intensity, which were found sufficient for the experiments.

40. Using two of these dark shades, the observer sees satisfactorily[*] the image of the pro-planet z' in the pro-telescope, and can measure the apparent diameter of the pro-planet by employing on the pro-telescope the eyepiece provided with an eyepiece micrometer scale—see § 28, p. 335 of the August number of this magazine. If now he opens the iris diaphragm at C, he will see how the planet would appear in a telescope of larger aperture, and to make the comparison satisfactory it is well to reduce the intensity of the incident light by interposing all three of the pieces of dark glass in the path of the light. With these precautions the observer will see that the outline of the planet will be perceptibly smaller with the larger aperture, and at the same time markedly more sharply defined, and that this improvement goes on increasing until the aperture has been increased beyond that which corresponds to the aperture of the largest existing telescope.

41. He has next to learn what the effect of using smaller apertures will be. This is done by gradually closing the iris-diaphragm at C, whereupon the image of the pro-planet dilates and ceases to be uniformly bright, becoming less bright towards its edge: it now shades off gradually all

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[*] If too much light is admitted the eye is dazzled by false light, and the image is spoiled. Perhaps this false light is occasioned by reflexions and refractions within the eye, due to the fibrous texture of the cornea and crystalline lens.

round. If this process is carried far enough the planet will be seen to behave more and more like a star, until it at length furnishes in great perfection the kind of image produced by a star and which we have called a star-burst, consisting of a central boss of light (which by that time will have become much larger than the geometrical image of the planet) surrounded by coloured appendage rings. These rings, as seen in the pro-telescope, are apt to be irregularly broken up if we have limited the aperture of the pro-telescope by an iris-diaphragm, owing to the circumstance that the opening in an iris-diaphragm is not bounded by a circle but by a polygon. This, however, is a defect which can be satisfactorily gotten rid of by dispensing with the iris-diaphragm and limiting the aperture of the pro-telescope by a clean round hole in copper-foil. With a hole of half a millimetre in diameter, which corresponded to using a $1\frac{1}{2}$-inch telescope upon Neptune, the phenomenon was found to be splendidly seen with its central boss of light much larger than the geometrical image of the planet, and with five of the appendage-rings visible ; but then, all the dark glasses at E had been removed and the brightness of the pro-planet was much greater than that of the real planet. However, it is only increased brightness which the planet Neptune would need, to enable it to exhibit the same appearance ; it would, however, be seen in the astronomical telescope on a smaller scale, since we can with advantage use upon the pro-telescope the power 12, which corresponds to a power of 1200 upon the astronomical telescope, and this it would be impracticable to use on a $1\frac{1}{2}$-inch telescope.

It is noteworthy that the star-burst which the image of a small bright object can be made to present, may be obtained either by contracting A' (the aperture of the pro-telescope) or by diminishing the size of z' (which represents either a planet or some spot upon a planet). It is also noteworthy that in whichever of these ways the appearance is produced, it comes on gradually when we diminish the aperture of the pro-telescope. In its earlier stages it manifests itself first by a very slight enlargement of the disk in the image accompanied by an appearance of clumsiness in its outline, and at a somewhat later stage by some luminosity at a little distance from the principal light, where at a subsequent stage appendage-rings will be formed. This intermediate stage is interesting, because of its presenting an appearance noticed by some exceptionally skilful observers of the images made by the polar caps of Mars. Between the principal light and the faint luminosity, there appears at this stage a *conspicuously* dark streak, like a dark border to the principal light.

The round form of the object z' is not necessary for this phenomenon. It presents itself when that object has any other shape, provided that it is sufficiently narrow and sufficiently bright. It is beautifully seen by using as object a slit at z', or a row of holes (which in the image will be seen as a rhabdo-spile, *i. e.*, run together into the appearance of a rod); and it may be exhibited conveniently by placing at z' the adjustable slit of a spectroscope, which can be gradually narrowed, whereupon all the phases of the phenomenon will successively present themselves. And, of course, the observer can induce the same succession of appearances without changing the slit, by altering the aperture of his pro-telescope. The astronomer would do well to familiarize himself with several other details of this phenomenon, which cannot be included in so brief an account of it as that to which we must confine ourselves here. Our aim in the present Memoir is to go far enough into detail to indicate the value of the work which can be done with an Observatory-experiments apparatus, rather than to attempt to describe what has been accomplished by it—an adequate account of which would be too voluminous.

42. What has been already described has an obvious bearing upon the interpretation to be put on some of the appearances detected at Flagstaff, when we bear in mind that the 12- and the 24-inch telescopes employed in Professor Lowell's observatory (and we might indeed add, all existing astronomical telescopes) belong essentially to the class of instruments whose apertures are vastly too small for dealing *adequately* with the details upon Mars. The experiments made with the OE apparatus suggest that the dusky band filled with blue light, which has sometimes been seen to border the image of a polar cap upon Mars, may prove to be produced in the way described in the last two paragraphs. Any object of the kind seen with a telescope of insufficient aperture will if bright enough exhibit an image consisting of a principal patch of light near to which, though separated from it by a conspicuous dark band, will be a detached field of milder luminosity. If, therefore, the polar cap upon Mars is bright enough and if the albedo of the neighbouring regions is sufficiently low, this dark interval will appear very dark, and may sometimes be so dark that its faint luminosity (which will be whatever is the intrinsic luminosity of that part of Mars) shall not suffice to prevent colour being there seen due to the blue and violet

colour which surrounds the image of every bright object in an achromatic telescope. I ought here to mention that this explanation of the blue colour by the familiar semblance of a blue atmosphere which surrounds every bright image in an achromatic telescope, was suggested to me in conversation by Professor Simon Newcomb. Presumably, the blue coloration would disappear if the object were examined with a reflecting telescope, and if the observer takes care not to employ an eyepiece which can produce it.

43. A bright object seen in a telescope projected upon a darker background will present the succession of appearances described above in §§ 40 and 41, if we progressively make the object smaller without changing its shape. We shall here give a synopsis of this succession of appearances. While the object is large enough, its shape and size will be correctly seen and its outline will be sharply defined; when somewhat smaller, its image becomes slightly too large for the size of the object, and its outline gets a kind of rounded appearance, as if the boundary were the kind of spile called a rhabdo-spile (*i. e.* a rod-like marking in the image). At the next stage the central boss of light will have become a little larger compared with the size of the object, and will be surrounded at a little distance by a field of vague luminosity, which is separated from the brighter light by a narrow and *conspicuous* dark interval. At the more advanced stages, if the bright object is made progressively smaller, the vague luminosity will gradually develop into the coloured spectra of an image of the same kind as that which a star produces in a telescope. Such is an account of the successive appearances which a sufficiently bright object would have if its size could be made to dwindle, or if viewed from different distances.

44. A dark object seen upon a bright background will, if made progressively smaller, present a series of stages which can be shown to be closely related to the above, but which would appear to our eyes materially different. This is because faint additions or subtractions of light at situations upon the surrounding brighter background may exist unseen by us, under conditions such that similar additions of light upon a surrounding dusky background would be conspicuous. A familiar and in some degree analogous phenomenon, is the less visibility of the Newton's rings seen by refracted light, than of those seen by reflected light; where a part of the faintness of their appearance is due to their being superposed upon a bright field. When the image of a dark object in a telescope is surrounded by a bright background, we have usually

to make special arrangements to enable appendage spectra (corresponding to the coloured rings round the image of a star) to be at all visible. Moreover as the object becomes small the phenomenon which corresponds to the dilatation of the central boss of light in the image of a bright object will be an enlargement of the size and lessening of the darkness of the image of the dark object. This lessening of its darkness will prevail all over the enlarged image, but will tell with most effect on its marginal portions, so that what is usually perceived is that the surrounding brightness encroaches upon the image and causes the central portions of the dark image to be alone visible, and that these central portions, especially in the later stages, become fainter and ultimately cease to be seen. The dark spot upon the planet has now become so dim that its image is no longer visible to us, being, as it were, swallowed up in the surrounding brightness.

45. It need hardly be pointed out that while this necessary succession of events is in accordance with the recorded appearance of most of the dusky patches entered upon maps of Mars, it is inconsistent with the appearance recorded of those smallest and darkest specks upon the image which have been supposed to represent oases upon the planet. This raises the presumption that these nearly black specks are almost certainly not alētho-spiles, that is are not markings on the image which have been caused by anything like what they suggest to the beholder as existing upon the planet, but on the contrary are probably phenāko-spiles *—*misleading*

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* It may make this clearer to give a possible instance. In June 1903 (see Annals of the Lowell Observatory, vol. iii. p. 156) Mars was receding from the earth. On the 28th of that month the double streaks in the image called Euphrates and Phison (longitude 333° on maps "of Mars") were seen with dark appendages, called carets by Professor Lowell, at their southern ends. These had not been seen when Mars was less remote; which Professor Lowell attributes to a seasonal change having taken place. But may not the intrusion of these triangular specks into the image have been simply because the planet had by that time got to be sufficiently far from the telescope? Experiment shows that the appearance is one which will necessarily present itself *so soon as the inefficiency of the telescope reaches a certain point*, and the inefficiency of the telescope went on gradually increasing according as the planet receded. How considerable it had become at the time of the observation will appear from the following considerations.

On that night the distance of Mars from the observer was 437 times the average distance of the Moon when full, from which we learn that Professor Lowell's 24-inch objective was—even if objective and atmosphere were optically perfect—only as efficient as an aperture of 1·4 mm. employed upon the full Moon; and that the 12-inch objective was no more efficient than 0·7 mm. employed upon the Moon. These apertures details such as under some circumstances intrude into the image and seem to the observer to betoken, although not really indicating, that there is something more or less like themselves upon the object. We shall have occasion to return to this subject farther on.

46. The ordinary experience of every man all through his life is almost exclusively taken up in dealing with objects of such a kind and at such distances, that he can see their size and their outline; which means that they are such that an optical apparatus with an aperture so moderate as the pupil of the eye* *can form an adequate image* of them. It is by this abundant and unfortunately one-sided experience that our judgments as to how we are to interpret visual objects has been trained. We must therefore be prepared to find ourselves filled by it with prepossessions, which become embarrassing whenever we have occasion, like the astronomer, to deal with an entirely new field of exploration *which lies outside that ordinary experience.* The astronomer will therefore do well to lose no opportunity of acquiring effectual experience within this new field, so as thus to do what he can to counteract the misapprehensions in the interpretation of astronomical images into which his (common sense), which here means the misapplication of ordinary experience, tends to lead him with an insistance that is too often successful.

47. A valuable opportunity of acquiring experience which will help to correct these errors is open to the student of

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may be taken to be about half and a quarter of what we employ when we look at the Moon with the naked eye, so that the vision of Mars which Professor Lowell had at his disposal was immensely inferior to that which we obtain when we look at the full Moon with one eye.

Any trained astronomer can easily take steps which will enable him to appreciate with some exactness what Professor Lowell's telescope could succeed in substituting for Mars on that night, if the state of the atmosphere was at its best. He has only to make holes 0·7 mm. and 1·4 mm. in diameter with sufficiently fine needles, in a piece of card, and then to see for himself the deterioration which the image of the full Moon undergoes when examined with the naked eye restricted to looking through one or other of these holes.

It seems wonderful that Professor Lowell could succeed in securing the remarkable observations he made under such difficult circumstances; and the question arises, What can these "carets" mean? It is to this inquiry that experiments give an answer. The control observations only go so far as to show that their presence in the image *does not betoken* that anything like them exists upon the planet.

* The reader will find an inquiry as to the ways in which vision with the naked eye is limited in Section 1 of a paper on Insect Vision in the Phil. Mag. for March 1894, p. 317.

Mars, if he will with sufficient diligence make, in connexion with his observations upon the planet, control observations upon the Moon when nearly full, by examining it as often as weather permits on the day it is full and the day before and the day after: and under optical conditions *the same as those to which he is obliged to confine himself* in his observations upon Mars while at the distance from the Earth at which it happens to be at that time. To facilitate his own observations of this kind, the author found a table such as the following useful, in which D is the distance of Mars from the Earth, L is the estimated mean distance of Full-Moon from the observer, and ϵ is our standard angle which is $2''{\cdot}062648$, or in circular measure 0·00001. The table furnishes the values of α, the aperture of the telescope to be used upon the Moon, and of μ the maximum magnifying power to be applied to it—this latter being the power which produces the same effect upon the Moon as 400 does when employed upon Mars.

Diameter of Mars.	Semi-Diameter of Mars.	D. Distance of Mars.	α. Aperture to be used on Moon.	μ. Maximum magnifying power to be used on Moon.
$12\ \epsilon$	$12''{\cdot}38$	150 L	2 mm.	2·67
$10\frac{1}{2}\ \epsilon$	$10''{\cdot}82$	171 L	$1\frac{3}{4}$ mm.	2·34
$9\ \epsilon$	$9''{\cdot}28$	200 L	$1\frac{1}{2}$ mm.	2
$7\frac{1}{2}\ \epsilon$	$7''{\cdot}73$	240 L	$1\frac{1}{4}$ mm.	1·40
$6\ \epsilon$	$6''{\cdot}19$	300 L	1 mm.	1·23
$4\frac{1}{2}\ \epsilon$	$4''{\cdot}64$	400 L	$\frac{3}{4}$ mm.	1
$3\ \epsilon$	$3''{\cdot}09$	600 L	$\frac{1}{2}$ mm.	0·67
$2\ \epsilon$	$2''{\cdot}06$	900 L	$\frac{1}{3}$ mm.	0·44

This table is somewhat more convenient when thrown into the form of a diagram, to be hung up in the Observatory. If we use the numbers of the first column as abscissas and the distances of Mars as ordinates, the latter will terminate in a hyperbola. Again keeping the same abscissas, and using the values of α as ordinates, they will terminate in a straight line. And, finally, with the same abscissas and the values of μ as ordinates, they also terminate in a straight line. Of course the two straight lines and the hyperbola can be plotted down upon one diagram, and then we can read off on it any required intermediate values of D, α, or μ*.

48. Quite a small telescope is sufficient for use in the control experiments. The author's was a small pocket telescope with an objective of 2 cm. aperture and ten-inch focal length. The erecting apparatus and eyepiece were removed, and simple plano-convex lenses took their place as eyepieces. These, when the convex side is turned towards the eye, are sufficiently good eyepieces of the low powers indicated in column 5 of the table. Each of these lenses should be mounted in a tube with an eyestop, to keep the eye in the right position, that is, where the plano-convex lens can form its image of the objective. To limit the aperture of the telescope, a hole a few mm.'s in diameter may be made in the cover which is usually sold with such telescopes for keeping dust off the objective, and thin disks of brass may be provided like those used for microscope stops, with central holes of the sizes entered in column 4 of the table. Any one of these when fitted inside the dust-cover will, when the cover is slipped on to the objective, limit its aperture in one of the required degrees. This formed the entire outfit: and it may for convenience be strapped on to an equatoreal stand. The whole was adapted for comparisons with the performance of an astronomical telescope of 12-inch aperture. To fit it for the minority of occasions when the state of our atmosphere allows an 18-inch or a 24-inch aperture to be used with more advantage upon Mars, the numbers in columns 4 and 5 will need to be increased in the same ratio as the astronomical aperture is increased. This will necessitate a small addition to the stock of eyepieces and of disks of brass with holes in them, which will have to be provided; and it will be convenient to add to the diagram described in § 47 the straight lines which will indicate which of these is to be used on each occasion. It will of course be understood that the observer will when observing carefully make allowance

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* D, the distance of Mars, has been computed from the assumption that when its distance from the earth is 7 metro-tens (10^{10} metres) its apparent semi-diameter is 10″, which is a sufficiently close approximation. L was deduced from the assumption that the mean distance of the Moon is 384,000 kilometres, by applying two corrections to this value—1°, by subtracting from it 1/180 part to allow for the effect of the perturbation known as Variation upon the Moon when in syzygy; and 2°, by further subtracting 3/4 of the length of the earth's radius to allow roughly for the observations being made from the surface of the earth and not from its centre. Of course, if these approximations are not thought sufficient, the observer can make a separate calculation for each day of observation, using the exact values for that day: but the author did not think it necessary to take this trouble.

for the circumstance that his control apparatus shows the Moon better than his astronomical telescope can show Mars, and better in a greater degree the larger the objective of the astronomical telescope, the control apparatus being very much less affected by the state of the atmosphere.

49. The author intended to have given here an account of observations made with this simple apparatus and of the lessons they teach the astronomer, but finds that to do so would occupy too much space. If, however, any reader of this paper is willing to make the observations for himself, being careful to make them only when the Moon is nearly full, he will receive in this way far more instruction than could reach him by merely reading about them. No one who sees and appreciates the significance of these observations can again fall into the error of supposing that the astronomers of our day have even so much knowledge of what exists upon Mars, as the astronomers of old before the telescope was invented could have of what exists upon the Moon. In fact they have not nearly so much. It is easy for us now when we look at the Moon with the naked eye to read into what we then see, some of the details with which the telescope has made us familiar; but those old astronomers had no such help, *nor has any man that kind of help now in reference to Mars.*

50. A distinct advance would be made if scientific men would desist from talking about what can be seen "upon Mars." Nobody has as yet seen what is on Mars nor anything like what is upon Mars. What the astronomer has had presented to him has really been an eidolon, that is a model such as a sculptor could make and which would present to the sculptor's eye precisely the same appearance as the telescope presents to the astronomer. It is not upon what is on Mars that the astronomer is enabled by his telescope to look. He sees whatever finds a legitimate place upon this model *and nothing more*; and our control experiments show that what he sees would amount to being an effective disguise thrown over what is really upon the planet. How utterly unlike it must be to what is really upon the planet is forced upon his attention when making the control experiments, if he is acquainted with the details which an adequate telescope reveals upon the Moon, and compares these with what is substituted for them when a full moon is viewed through telescopes as inefficient upon the Moon as our best astronomical telescopes are upon Mars.

51. Nor, unfortunately, do we seem entitled to expect much better results from employing very much larger telescopes than those hitherto brought to bear. Will the optical

state of our atmosphere permit? In early life the author had the privilege of spending some years as Astronomical Assistant to the then Earl of Rosse, and in the experience he had while in charge of his Observatory, he did not come across even one night in which the seeing seemed to him sufficiently good to enable a planet to be better or even as well seen in the Great Telescope (except perhaps for some small portion of a second at a time), as it would on that same night be seen, and much more continuously, in smaller instruments if optically as perfect. He had opportunities of making comparisons between apertures of 6 feet, 3 feet, and 20 inches. And on almost every trial the state of the air was such that the best vision *upon a planet* was with the instrument of smaller aperture.

52. The cause of this was made impressively evident by an observation he had occasion to make in 1849 or 1850. Lord Rosse had two specula for the Great Telescope, with one of which he continued his experiments on figuring immense mirrors, while the other was in use in the telescope. At the time referred to the mirrors had been exchanged, and the new one had to be tested. A most suitable object was available at the time—the companion of γ Andromedæ, itself a very close double star ($0''\cdot 5$ separation) of two nearly equal constituents and not too bright; and it was besides singularly well situated as it crossed the meridian not far from the zenith. An exceptionally good night was selected, and special arrangements were made by which the mirrors of the telescope came almost accurately into adjustment when the telescope was pointed towards the star. The constituents of this excessively close double were then (but never for more than a small fraction of a second) exquisitely seen like the light of a flame seen through two minute holes made with a fine needle in a piece of card, and with a lane of sky between them wider I think, than each of the star images. This appearance every now and again presented itself like a flash, but was almost immediately swallowed up by the two images boiling together into a single larger mass of light which seemed in a state of intense commotion. This was the usual appearance, even on so good a night; and the moments of real definition were only occasional. The distance between the two stars was at that time only half a second of angle according to Professor See who has studied this binary system. The two stars are sensibly equal and were of a remarkably intense blue as seen in the Great Telescope. The powers employed upon the telescope were 750 and 1300, and the object was exquisitely seen with them both, perhaps most pleasingly with the higher power, as it

was in that year so very close a double star. The lower of these powers was the usual working power used upon the Great Telescope, as it is not far from the lowest power which enables the whole pencil of light to enter the pupil of the observer's eye.

53. Such being the state of things, I have little doubt that on that night, although it was an exceptionally good night, the small telescopes used by Professor Lowell, if equally good as optical instruments, would have shown Mars better than Lord Rosse's enormous telescope with its exquisite defining power. So that I have not much hope of good results from the use upon Mars of any such immense aperture. No doubt the instantaneous vision obtained now and then would do something, but I fear not much. We are therefore confronted by two limitations in examining an object such as Mars. We cannot use really large apertures* on account of the imperfections of our atmosphere, and with such apertures as we can avail ourselves of, the image of the planet is remote from representing what is really upon the planet. It behoves us then to avoid confident assertions as to what exists or does not exist upon Mars, and to refrain from guesses as to what is going on there. The necessity for this caution in the interests of correct thinking, in no degree detracts from the merit of the great achievements of those astronomers who have secured for science a knowledge of important details, before unknown, but which they have shown the insufficient telescopes that man can employ to be competent to reach, and which they have ascertained *did truly exist upon the* eidolons or *substitutes for Mars* which those telescopes exhibited, when Mars was at the various distances from us at which it was on the nights upon which the observations were made.

In the present chapter we have aimed only at ascertaining facts. We have sought to discover what that appearance is *into which an insufficient telescope will seem to transform an object* containing certain definite details. But this is not enough. We have still to learn the precise process by which nature produces this imperfect image, which will lead to our discovering its true nature and the cause of its imperfections. This, the most important branch of our inquiry, will occupy our attention in the next and final part of this memoir.

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* Lord Rosse's marvellous instrument if used upon Mars when nearest to us would, even if the imperfections of our atmosphere could be removed, only have shown Mars as well as a half-inch objective will show the Moon when full.

[To be continued.]

LXVIII. *The Action of the Radium Emanation upon Water. By* Prof. E. Rutherford, *F.R.S., and* T. Royds, *M.Sc., 1851 Exhibition Science Scholar*[*].

SINCE the initial experiments of Ramsay and Soddy in 1903, the production of helium from radium and its emanation have been completely substantiated by a number of independent observers. On the view that the α particle is a helium atom, the appearance of helium from radioactive matter in general receives a simple and satisfactory explanation.

Recently Mr. Cameron and Sir William Ramsay have attacked the important question as to whether the radiations from a large quantity of radium emanation are effective in transforming the atoms of ordinary matter. They have published results to prove that under the influence of the radium emanation, copper is transformed into lithium and possibly into sodium and potassium. In addition they have given evidence that in the presence of copper solutions the emanation disintegrates into argon, and in the presence of water into neon. A complete and satisfactory proof of these transformations is attended by great experimental difficulty. In a recent paper[†], Cameron and Ramsay sum up the results of their experiments as follows:—"In carrying out such work it is extremely difficult to prevent traces of air leaking into the apparatus during the considerable length of time which must elapse before an experiment is completed. Since 0·1 c.c. of atmospheric nitrogen contains sufficient argon to be detected spectroscopically after the nitrogen has been removed by sparking, the proof that the presence of argon is due to some other cause is rendered extremely difficult. Similarly, it is far from easy to free copper solutions completely from traces of lithium, and to prove convincingly that lithium did not pre-exist in such solution treated with emanation. The detection of neon is open to no such objection. The only possible source, other than transmutation, is the aluminium of the electrodes. The vacuum-tube had been previously run a great number of times at different pressures, washed out with air, and finally showed traces of hydrogen, and hydrogen alone. It is inconceivable that neon can have resulted thus by chance from two experiments with water, where in each case the residues were tested between those from numerous similar experiments with other solutions in which no neon was detected. We must regard

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[*] Communicated by the Authors.

[†] Journ. Chem. Soc. June 1908, p. 992.

the transformation of emanation into neon, in presence of water, as indisputably proved, and, if a transformation be defined as a transformation brought about at will, by change of conditions, then *this is the first case of transmutation of which conclusive evidence is put forward.*"

Mme. Curie and Mlle. Gleditsch[*] have recently repeated the experiments of Cameron and Ramsay with reference to the transformation of copper into lithium, and have obtained no certain evidence of the production of lithium.

With the aid of the radium loaned by the Vienna Academy of Sciences, we have made experiments to see whether neon is produced when the radium emanation disintegrates in the presence of water. Thanks to the use of the absorbing properties of charcoal, the detection of a minute quantity of neon is now a comparatively simple matter. Coconut charcoal at the temperature of liquid air absorbs all gases except neon and helium. The spectroscopic test of the presence of neon is unmistakable on account of its very characteristic spectrum of a bright line in the yellow and a group of bright lines in the red. Since there could be no possible doubt that neon was present in the experiments of Cameron and Ramsay, the question arose whether the neon observed could have been derived from the air; for Strutt[†] has recently shown that the presence of neon can be spectroscopically detected in $\frac{1}{10}$ c.c. of atmospheric air. Cameron and Ramsay state that in their experiments it was impossible to avoid a small leakage of air into their apparatus during the week or more that an experiment was in progress.

Before beginning the main investigation, a number of experiments were made to determine the amount of neon that could be detected spectroscopically. The apparatus, already described for the purification of the emanation[‡], was used for this purpose. The arrangement will be clearly seen from fig. 1.

The whole apparatus was first completely exhausted by means of a mercury-pump. A known volume of air contained in a small burette over mercury was introduced into the reservoir R by means of the mercury trough. The stopcocks A and B were closed and C opened, and the mercury raised to the level D by raising the reservoir S. The stopcock A was opened to allow the gas to expand into the reservoir E of capacity about 30 c.c. and then closed. To the top of E was attached a small spectrum-tube F, of length about 7 cms.,

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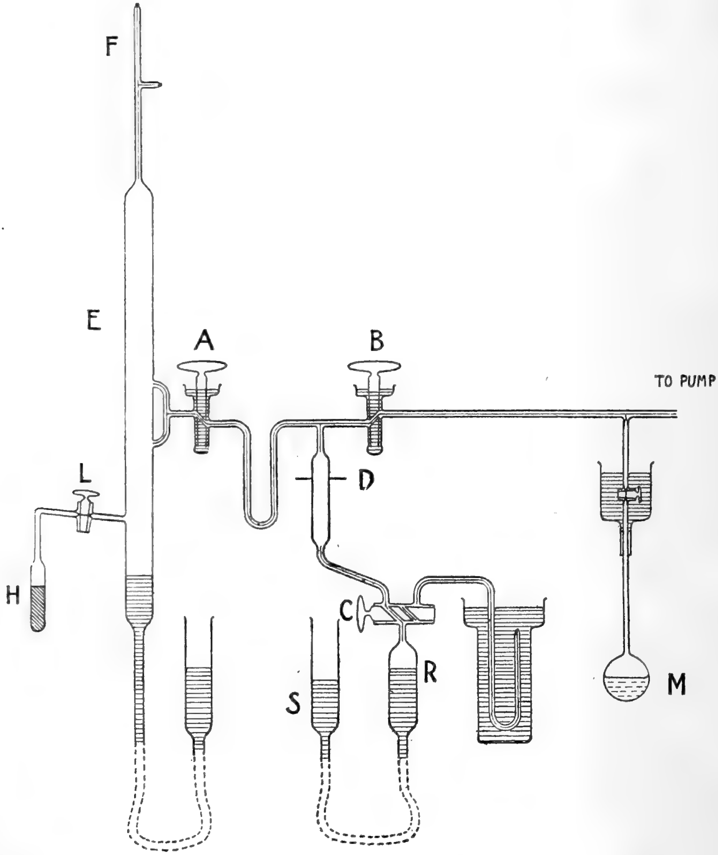
[*] Acad. Sciences, Aug. 10, 1908.

[†] Proc. Roy. Soc. A. lxxx. p. 572 (1908).

[‡] Rutherford, Phil. Mag. Aug. 1908.

and of diameter 1 mm., provided with thin platinum electrodes. A tube H containing a small quantity of coconut charcoal was attached to the side tube through a stopcock L. Before the experiment the charcoal tube was thoroughly heated and exhausted. On surrounding the tube H by liquid air, all the gases present in the air except neon and helium were absorbed. The stopcock L was then closed, and by raising the mercury reservoir the gases remaining in E were compressed into the vacuum-tube. On passing a discharge, the hydrogen and mercury lines were usually prominent, the former probably due to a trace of water vapour present. A pad of cotton-wool was then wrapped round the spectrum-tube just above the level of the mercury and was soaked with liquid air.

Fig. 1.



The spectrum of hydrogen and mercury disappeared, and the tube became very hard and showed only the neon spectrum.

Proceeding in this way, we were able to detect easily the neon yellow line when $\frac{1}{15}$ c.c. was introduced into the reservoir E. The conditions to bring out the spectrum most clearly could readily be tested by passing a discharge at short intervals through the tube as it slowly warmed up from evaporation of the liquid air. At a certain stage, the neon yellow line and the stronger reds flashed out clearly. With $\frac{2}{15}$ c.c. of air the red lines of neon were clearly visible, and with $\frac{1}{5}$ c.c. a brilliant spectrum of neon was obtained, showing most of the lines. These experiments were repeated on several occasions, the vacuum-tube being changed between each experiment, and in every case the same results were obtained.

According to the measurements of Ramsay neon is present in air in about one part in 100,000 by volume. The experiments thus show that one can readily detect the presence of neon in amount less than one millionth of a cubic centimetre. It is quite probable that with a still better choice of conditions, a still smaller quantity could be spectroscopically detected.

A Watts binocular grating spectroscope was found very convenient for a rapid examination of the spectra; measurements of wave-lengths were carried out by means of a Hilger direct-reading spectroscope.

Experiments with the Emanation.

In order to collect the gases formed by the action of radium emanation on water, we employed a method very similar to that used by Cameron and Ramsay. For clearness, we shall describe with some detail the progress of a complete experiment. A glass bulb of about 4 c.c. capacity, provided with a stopcock, was half filled with distilled water and then placed in an evaporation-bath to expel the air from the bulb and the water. The stopcock was then closed, and the bulb sealed on to a side-tube connected with the mercury-pump, as shown at M. The water in the bulb was frozen by surrounding it with liquid air and the last trace of air then pumped out. In the meantime the emanation, corresponding to the equilibrium amount from 150 mg. of radium, was carefully purified after the manner described in a previous paper and stored in the U-tube. By opening the stopcock B the emanation was then all condensed in the frozen bulb. The stopcock was thereupon closed and surrounded by a mercury seal, to prevent any possible leakage of air into the bulb. At the end of three days, when it was judged that the pressure of hydrogen and oxygen formed by the emanation from the water was about an atmosphere, the bulb was again frozen in liquid air and the non-condensable gases pumped out and collected. About 4 c.c. of mixed gases * were obtained, consisting mainly of hydrogen and oxygen. The gases were then introduced into a separate burette and exploded. A small quantity of pure electrolytic oxygen was then added, and the gases again exploded to remove any excess of hydrogen. The residual gases (about 0·2 c.c.) were not further treated, but passed directly into the receiver E in the manner already described, and the gases not absorbed by the charcoal were compressed into the vacuum-tube and spectroscopically examined. A complete and brilliant spectrum of helium was observed, but not a trace of the neon spectrum.

The greater part of the emanation had remained condensed in the bulb when the mixed gases were pumped out. The stopcock was closed and the seal again placed in position and the liquid air removed. The bulb was allowed to stand for six days, when about 4 c.c. of the mixed gases were again pumped out. As it might be possible that any neon formed would be dissolved in the water, the bulb was allowed to warm up to atmospheric temperature and then connected with the pump. The rapid evaporation of the water then gave a chance for removal of any absorbed gases into the pump. The small quantity of gas thus obtained was pumped out and added to the first quantity. The mixed gases were treated as before. A complete spectrum of helium was obtained but again no sign of the neon lines.

It might be thought that the presence of the helium in the discharge-tube would interfere with the detection of a small quantity of neon. A special experiment was made to test this point. At the end of the last experiment, the mercury was lowered below the level of the carbon tube and $\frac{1}{10}$ c.c. of air passed into the reservoir. After absorption by the charcoal, the residual gases were tested spectroscopically as before. The neon spectrum was now clearly seen in addition to that of helium. When the lower part of the vacuum-tube was cooled to the temperature of liquid air by the pad of

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* This amount of mixed gases is one third of that experimented with by Cameron and Ramsay, but the amount of neon to be expected from their results could have easily been detected with the smaller quantity. In experiments recorded later in the paper 30 c.c. of mixed gases were used.

cotton-wool, the yellow line of helium was distinctly brighter than the yellow line of neon, but at a certain stage of the warming up, the neon and helium spectra were about equal in brilliancy.

In all five experiments were made by this method, but in only one case was the presence of neon observed. This was in the first experiment of the series. In order to see whether the presence of neon in this experiment could be ascribed to a leak of air into the apparatus, the charcoal was warmed up and the gases again pumped out and collected in a burette. The oxygen present was removed by melted phosphorus. About $\frac{1}{15}$ c.c. of gas remained, consisting mainly of nitrogen. Now $\frac{1}{15}$ c.c. of nitrogen corresponds to a leakage of about $\frac{1}{10}$ c.c. of air. The brightness of the neon yellow line compared with that of helium in the experiment was about that to be expected if this quantity of air had been added. This was confirmed by the observation that when an additional $\frac{1}{10}$ c.c. of air was added, the neon spectrum was increased notably in brightness.

Experiments with the Gases produced from the Radium Solution.

Cameron and Ramsay point out that if the emanation produces neon in the presence of water, neon should be found in the water solution of the radium salt from which the emanation is pumped off, and they state that they have observed the spectrum of neon from the gases thus obtained from the radium solution. We have made experiments to test this point. The radium salt containing over 200 mgrs. of radium was dissolved in water to which a small quantity of hydrochloric acid had been added. The emanation was allowed to collect for about five days, and was then pumped off with about 30 c.cs. of hydrogen and oxygen. These gases were treated as before, and the emanation removed by condensation. The residual gas, mostly oxygen, was tested, by the method described, for neon. We have made four experiments in all, but in no case have we found a trace of neon, although a brilliant spectrum of helium was always observed.

Conclusions.

From the rate of production of helium by radium recently measured by Sir James Dewar*, the quantity of helium produced by a known quantity of emanation can be readily estimated. In most of the experiments with water a quantity of emanation corresponding to the equilibrium amount from

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* Proc. Roy. Soc. A. lxxxi. p. 280 (1908).

about 150 mgr. of radium was introduced and left for three days. This should lead to the production of about $\frac{1}{10}$ c.mm. of helium. We have seen that in these experiments we could detect with certainty a quantity of neon less than $\frac{1}{1000}$ c.mm. Consequently, even supposing that the emanation does change into neon, the amount so produced cannot be more than one per cent. of the helium which is also formed. Cameron and Ramsay were apparently not aware of the delicacy of the spectroscopic detection of neon in small quantities of air. In the experiment described in their last paper, they state that they were unable to avoid a leakage of air into their apparatus, and working with 12·6 c.c. of mixed gases, they found after the removal of hydrogen and oxygen that the residue consisted of ·292 c.c. of nitrogen and carbon dioxide. Assuming that this residue consisted mainly of nitrogen, it would show that there was a leakage of air of about ·36 c.c. In our experience, the admission of such a quantity of air into the apparatus gives a brilliant spectrum of neon comparable in brightness with the companion helium spectrum. Consequently, the experiment described by Cameron and Ramsay is quite inadequate as a proof of the production of neon from the emanation.

University of Manchester,
Oct. 6, 1908.

LXVIII. *On the Equilibrium of Heterogeneous Substances* (1876). *By the late* Prof. J. Clerk Maxwell, *F.R.S.*

[The paper here reprinted is the report of an Address delivered by Prof. Clerk Maxwell on May 24, 1876, at the South Kensington Conferences in connexion with the Special Loan Collection of Scientific Apparatus. It is contained (pp. 144–150) in the official volume of reports of the Conferences, which has long ago dropped out of notice. An earlier and less complete version of this summary of Prof. Willard Gibbs's developments of the doctrine of available energy, on the basis of his new concept of the chemical potentials of the constituent substances, was communicated to the Cambridge Philosophical Society on March 8, 1876, and appeared in abstract in vol. ii. of their Proceedings, pp. 427–430: it was reprinted in Maxwell's 'Collected Papers,' vol. ii. pp. 498–500. The fact that the energy associated with any constituent substance is proportional jointly to the mass of that constituent and to another factor representing energy per unit mass, is of course involved in the very notion of conservation of energy; but the general factorization into magnitudes (or quantities) and intensities (such as the potentials of Gibbs) is, it would seem, here set forth formally and explicitly for the first time, though it is thoroughly implied throughout Gibbs's work. This paper reviews only the first portion of that work, Proc. Connecticut Academy, Oct. 1875–May 1876; the second part of it, mainly special applications, did not appear in the same Proceedings until May 1877–July 1878. The principle, as restated in less guarded terms by G. Helm (1887), that each type of (available) energy strives to pass from positions of higher to positions of lower intensity, has been supposed sometimes to mark a new departure in physical ideas: *cf.* Prof. W. Ostwald, *Die Energie* (1908) p. 103, whose regret, expressed in this connexion, that he has not had access to Maxwell's paper, has revived the project of reprinting it. Some years before this time, in a paper "On the Mathematical Classification of Physical Quantities," Proc. Lond. Math. Soc. vol. iii., Maxwell had pointed out, in connexion with Rankine's idea of factors of energy, that this conception loses most of its definiteness and efficacy when applied to kinetic phenomena. It is only for static or steady material transformations that it is effective; and it became so, in development of the general Kelvin doctrine of available energy, only by virtue of the fundamental step involved in Gibbs's recognition of the existence of quantitative chemical potentials for the independent constituent substances of a mixture or solution,—involving the formulation of the general criterion of chemical coexistence of complex substances in contact, that the potential of each constituent should be the same in both of them, and of the trend of chemical change, towards positions of lower aggregate potential.

Most interesting also as regards this evolution of ideas is the postscript of a letter from Maxwell to Stokes of an earlier date, August 3, 1875, in which, in connexion with Andrews's experiments on the condensation of mixed gases, Maxwell sends a tentative sketch of the whole theory, using a provisional term *reaction*, printed between inverted commas, for the quantity which his friend Gibbs soon afterwards named chemical *potential*: see 'Memoir and Scientific Correspondence of Sir G. G. Stokes,' vol. ii. pp. 33–35 (Cambridge, 1907).—J. Larmor.]

THE warning which Comte addressed to his disciples, not to apply dynamical or physical ideas to chemical phenomena, may be taken, like several other warnings of his, as an indication of the direction in which science was threatening to advance.

We can already distinguish two lines along which dynamical science is working its way to undermine at least the outworks of Chemistry, and the chemists of the present day, instead of upholding the mystery of their craft, are doing all they can to open their gates to the enemy.

Of these two lines of advance one is conducted by the help of the hypothesis that bodies consist of molecules in motion, and it seeks to determine the structure of the molecules and the nature of their motion from the phenomena of portions of matter of sensible size.

The other line of advance, that of Thermodynamics, makes no hypothesis about the ultimate structure of bodies, but deduces relations among observed phenomena by means of two general principles—the conservation of energy and its tendency towards diffusion. The thermodynamical problem of the equilibrium of heterogeneous substances was attacked by Kirchhoff in 1855, when the science was yet in its infancy, and his method has been lately followed by C. Neumann. But the methods introduced by Professor J. Willard Gibbs, of Yale College, Connecticut *, seem to me to be more likely than any others to enable us, without any lengthy calculations, to comprehend the relations between the different physical and chemical states of bodies, and it is to these that I now wish to direct your attention.

In studying the properties of a homogeneous mass of fluid, consisting of n component substances, Professor Gibbs takes as his principal function the energy of the fluid, as depending on its volume and entropy together with the masses, m_1, m_2, ... m_n of its n components, these $n+2$ variables being regarded as independent. Each of these variables is such that its value for any material system is the sum of its values for the different parts of the system.

By differentiating the energy with respect to each of these variables we obtain $n+2$ other quantities, each of which has a physical significance which is related to that of the variable to which it corresponds.

Thus, by differentiating with respect to the volume, we obtain the pressure of the fluid with its sign reversed; by differentiating with respect to the entropy, we obtain the temperature on the thermodynamic scale; and by differentiating with respect to the mass of any one of the component substances, we obtain what Professor Gibbs calls the potential of that substance in the mass considered.

As this conception of the potential of a substance in a

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* Transactions of the Academy of Sciences of Connecticut, vol. iii.

given homogeneous mass is a new one, and likely to become very important in the theory of chemistry, I shall give Professor Gibbs's definition of it.

"If to any homogeneous mass we suppose an infinitesimal quantity of any substance added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass, divided by the mass of the substance added, is the potential of that substance in the mass considered."

These $n+2$ new quantities, the pressure, the temperature, and the n potentials of the component substances, form a class differing in kind from the first set of variables. They are not quantities capable of combination by addition, but denote the intensity of certain physical properties of the substance. Thus the pressure is the intensity of the tendency of the body to expand, the temperature is the intensity of its tendency to part with heat; and the potential of any component substance is the intensity with which it tends to expel that substance from its mass.

We may therefore distinguish between these two classes of variables by calling the volume, the entropy, and the component masses the *magnitudes*, and the pressure, the temperature, and the potentials the *intensities* of the system.

The problem before us may be stated thus:—Given a homogeneous mass in a certain phase, will it remain in that phase, or will the whole or part of it pass into some other phase?

The criterion of stability may be expressed thus in Professor Gibbs's words:—"For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

"The condition may also be expressed by saying that for all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be negative."

Professor Gibbs has made a most important contribution to science by giving us a mathematical expression for the stability of any given phase (A) of matter with respect to any other phase (B).

If this expression for the stability (which we may denote by the letter K) is positive, the phase A will not of itself pass into the phase B, but if it is negative the phase A will of itself pass into the phase B, unless prevented by passive resistances.

The stability (K) of any given phase (A) with respect to any other phase (B), is expressed in the following form :—

$$K = \epsilon - vp + \eta t - m_1\mu_1 - \&c. - m_n\mu_n,$$

where ϵ is the energy, v the volume, η the entropy, and m_1, m_2, &c. the components corresponding to the second phase (B), while p is the pressure, t the temperature, and μ_1, μ_2, &c. the potentials corresponding to the given phase (A). The intensities therefore are those belonging to the given phase (A), while the magnitudes are those corresponding to the other phase (B).

We may interpret this expression for the stability by saying that it is measured by the excess of the energy in the phase (B), above what it would have been if the magnitudes had increased from zero to the values corresponding to the phase B, while the values of the intensities were those belonging to the phase (A).

If the phase (B) is in all respects except that of absolute quantity of matter the same as the phase (A), K is zero ; but when the phase (B) differs from the phase (A), a portion of the matter in the phase (A) will tend to pass into the phase (B) if K is negative, but not if it is zero or positive.

If the given phase (A) of the mass is such that the value of K is positive or zero with respect to every other phase (B), then the phase (A) is absolutely stable, and will not of itself pass into any other phase.

If, however, K is positive with respect to all phases which differ from the phase (A) only by infinitesimal variations of the magnitudes, while for a certain other phase, B, in which the magnitudes differ by finite quantities from those of the phase (A), K is negative, then the question whether the mass will pass from the phase (A) to the phase (B) will depend on whether it can do so without any transportation of matter through a finite distance, or, in other words, on whether matter in the phase B is or is not in contact with the mass.

In this case the phase (A) is stable in itself, but is liable to have its stability destroyed by contact with the smallest portion of matter in certain other phases.

Finally, if K can be made negative by any infinitesimal variations of the magnitudes of the system (A), the mass will be in unstable equilibrium, and will of itself pass into some other phase.

As no such unstable phase can continue in any finite mass for any finite time, it can never become the subject of experiment; but it is of great importance in the theory of chemistry to know how these unstable phases are related to those which are relatively or absolutely stable.

The absolutely stable phases are divided from the relatively stable phases by a series of pairs of coexistent phases, for which the intensities p, t, μ, &c. are equal and K is zero. Thus water and steam at the same temperature and pressure are coexistent phases.

As one of the two coexistent phases is made to vary in a continuous manner, the other may approach it and ultimately coincide with it. The phase in which this coincidence takes place is called the Critical Phase.

The region of absolutely unstable phases is in contact with that of absolutely stable phases at the critical point. Hence, though it may be possible by preventing the body from coming in contact with certain substances to bring it into a phase far beyond the limits of absolute stability, this process cannot be indefinitely continued, for before the substance can enter a new region of stability it must pass out of the region of relative stability into one of absolute instability, when it will at once break up into a system of stable phases.

Thus in water for any given pressure there is a corresponding temperature at which it is in equilibrium with its vapour, and beyond which it cannot be raised when in contact with any gas. But if, as in the experiment of Dufour, a drop of water is carefully freed from air and entirely surrounded by liquid which has a high boiling-point, it may remain in the liquid state at a temperature far above the boiling-point corresponding to the pressure, though if it comes in contact with the smallest portion of any gas it instantly explodes.

But it is certain that if the temperature were raised high enough the water would enter a phase of absolutely unstable equilibrium, and that it would then explode without requiring the contact of any other substance.

Water may also be cooled below the temperature at which it generally freezes, and if the water is surrounded by another liquid of the same density the pressure may also be reduced below that of the vapour of water at that temperature. If the water when in this phase is brought in contact with ice it will freeze, but if brought in contact with a gas it will evaporate.

Professor Guthrie has recently discovered a very remarkable case of equilibrium of a liquid which may be solidified in three different ways by contact with three different substances. This is a solution of chloride of calcium in water containing 37 per cent. of the salt. This solution is capable of solidification at −37° C., when it forms the solid cryohydrate having the same composition as itself. But it may be cooled somewhat below this temperature, and then if it is touched with a bit of ice it throws up ice, if it is touched with the anhydrous salt it throws down anhydrous salt, and if it is touched with the cryohydrate it solidifies into cryohydrate.

LXX. *On the Atomic Weight of Radium and other Elementary Substances.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the paper which you were good enough to reprint from the Memoirs and Proceedings of the Manchester Literary and Philosophical Society in the Magazine of February last, it was shown from the definite multiple relations of the first and second series of elements, Hn and H2n, that radium was the next higher member to barium of the alkaline earth metals, with an atomic weight of 184 and a proximate specific gravity of 5.

The numerical relations of these series are of so much interest and importance to chemical science, especially in regard to the evolution of elementary substances, that I should like to place on record in the Philosophical Magazine the method by which the atomic weights of the first three series have been determined. Also my complete Table of the elements with their atomic weights, in order to elucidate the subject of this communication and for future reference.

Hn.	**H2n.**
H= 1	He= 2
0 . 0.7 =Li = 7	0 . 0 . 8 =Gl = 8
1×23 . 0 =Na= 23	1×24 . 0 =Mg= 24
2×23−7 =Ka= 39	2×24−8 =Ca = 40
3×23−7 =Cu= 62	3×24−8 =Zn = 64
4×23−7 =Rb= 85	4×24−8 =Sr = 78
5×23−7 =Ag=108	5×24 - 8 =Cd =112
6×23−7 =Cs =131	6×24−8 =Ba =136
7×23−7 =*x* =154	7×24−8 =*x* =160
8×23−7 =*x* =177	8×24−8 =Ra =184
9×23−7 =Hg=200	9×24−8 =Pb =207

It will be seen that if the second member of the series Hn (Na 23) be multiplied by an arithmetical series, then will the products, minus the atomic weight of the first member (Li 7), be the atomic weights of the elements of this series. It will also be obvious that had these relations been known before the discoveries of rubidium and cæsium by Bunsen and Kirchhoff, the numbers in my table would have expressed the atomic weights and other properties of these elements. The like remark also applies to the atomic weight of lithium, which before Bunsen's accurate determination was accepted as 6·5. Again, by multiplying in like manner the atomic weight of the second member of the alkaline earth and zinc series of metals (Mg 24) the products, minus the atomic weight of the first member (Gl 8), are the atomic weights of all the elements of this series.

In a note presented to the French Académie des Sciences* I have shown that helium is the typical element of the series H2n with an atomic weight of 2 (He = 2) ; a value now adopted by French chemists in the table of atomic weights published in the *Annuaire du Bureau des Longitudes.* This value is in accordance with the law that the atomic weights of the other elementary gases (H, O, N, Cl) at ordinary temperatures are expressed by the same numbers as their specific gravities.

I would also direct attention (1) to the common numerical difference of 4 between the halogens and the alkaline metals in homologous positions, and (2) the common difference of 8 between the oxygen series and the alkaline earth metals in similar positions, (3) the natural arrangement and extension of Dumas' triads, in which the sum of the atomic weights of the extremes is equal to double the atomic weights of the means.

The absolute parallelism of the positive and negative series of elements Hn and H2n in their numerical, chemical, and physical relations, together with their close resemblance to homologous series, will be at once apparent to philosophical chemists. The cause of the alternation of light and heavy elements in each of these series, while preserving the same multiple relations, is a problem for future science to solve.

The small differences observable between the experimental and a few of the theoretic atomic weights, when distributed among the twenty-four members of the four positive and negative series, are less than half of one per cent. of the actual determinations.

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* *Comptes Rendus,* tome cxxv. p. 651 (1897).

TABLE I.

Elementary Substances, with their Atomic Weights in Multiple

	+Hn−		**+H2n−**		**H 3n**
1	**H** = **1**		**He** = **2**		
2	**Li** = **7** .. .. 7 * 0·59†		**Gl** = **8** .. .. 9·1 1·64? 1·3‡		**C** = **12** .. .. 12 1·71§
3	**Na** = **23** .. .. 23 0·98	**F** = **19** 19	**Mg** = **24** .. .. 24 1·74	**O** = **16** 16	**Al** = **27** .. .. 27 2·56
4	**K** = **39** .. .. 39 0·86	**Cl** = **35** .. .. 35·2 1·3	**Ca** = **40** .. .. 40 1·58	**S** = **32** .. .. 32 2·05	**Sc** = **42** .. .. 44 3·4
5	**Cu** = **62** .. .. 63·3 8·9		**Zn** = **64** .. .. 65 7·2		**Ce** = **69** 92 : 141 6·5
6	**Rb** = **85** .. .. 85 1·52	**Br** = **81** .. .. 80 3·0	**Sr** = **88** .. .. 87·5 2·54	**Se** = **80** .. .. 79·4 4·8	**Ga** = **96** .. .. 70 5·95
7	**Ag** = **108** .. .. 108 10·6		**Cd** = **112** .. .. 112 8·69		**Y** = **123** 61·7 : 89·5 8·1‡
8	**Cs** = **131** .. .. 132 1·88	**I** = **127** .. .. 127 4·95	**Ba** = **136** .. .. 137 3·75	**Te** = **128** .. .. 128 6·3	**In** = **150** 75·6 : 113·4 7·42
9	*x* = **154** .. .. .. 12·2‡		*x* = **160** .. .. .. 10·13‡		**Er** = **177** .. .. 170·6 9·4‡
10	*x* = **177** 2·2‡		**Ra** = **184** .. .. .. 4·8‡		**Tl** = **204** .. .. 204 11·85
11	**Hg** = **200** .. .. 200 13·6		**Pb** = **208** .. .. 207 11·44		**Th** = **231** .. .. 231·4 11·23

* Accepted Atomic Weights. † Specific Gravities.

⁂ The accepted atomic weights are taken from the standard works and Watts' "Dict. Chem.," Suppl. p. 247—

TABLE I.

Proportions, 1878–1894–1902–1903–1906.

H 4n	**H 5n**	**H 6n**	**H 7n** **Ne** = **7**	
— = **16**	**B** = **10** .. .. 11 2·63	— = **18**	**N** = **14** **Ar** = **21** **Kr** = **42** **Xe** = **63**	
— = **32**	**P** = **30** .. .. 31 1·82	— = **36**	**Si** = **35** 28 : 35 2·49	
Ti = **48** .. .. 48 4·1‡	**V** = **50** .. .. 51·2 5·5	**Cr** = **54** .. .. 52·4 7·3	**Fe** = **56** **Mn** = **56** **Ni** = **56** **Co** = **56**	56—8·14‖ 55—8·00 58—8·66 58—8·96
Ge = **72** .. .. 72·7 5·47	**As** = **75** .. .. 75 5·63			
Zr = **92** .. .. 90 4·15 ? 5·4‡	**Nb** = **95** .. .. 94 6·67	**Mo** = **96** .. .. 96 8·6		
Sn =**116** .. .. 116 7·29	**Sb** =**120** .. .. 120 6·72		**Pd** =**105** **Rh** =**105** **Ru** =**105** **Da** =**105**	105·6—12·0 104·4—11·2 104·4—11·4 ... ...
La =**140** .. .. 139 6·7	x =**140** .. .. .. 8·15‡	x =**144** .. .. .. 10·0‡		
x =**164** .. .. .. 9·11‡	x =**165** .. .. .. 8·30‡			
D =**188** .. .. 95 8·0‡	**Ta** =**185** .. .. 182 10·78 ? 9·8‡	**W** =**186** .. .. 184 18·26		
U =**240** .. .. 240 18·4	**Bi** =**210** .. .. 210 9·83		**Au** =**196** **Pt** =**196** **Ir** =**196** **Os** =**196**	196—19·34 197—21·50 198—22·42 198—22·48

‡ Estimated. § Anthracite. ‖ Electro-deposited.

tables of Wurtz, Roscoe and Schorlemmer, J. P. Cooke, F. W. Clarke, Atomicity, and more recent determinations.

I take this opportunity of remarking, as a principle of scientific reasoning, that when the number of recurring facts are sufficient to establish the relation of cause and effect, or, in other words, the general accuracy of a law, the road to further discovery lies rather in the direction of explaining the anomalous departures from it than in challenging the truth of the law itself. I would also emphasize the fact, the importance of which is hardly yet realized by chemists, that as the received atomic weights are all expressed in units of hydrogen, and are equivalents of this element, the multiple relations subsisting among the higher atomic weights, as shown in my tables, have an immensely greater validity in determining the question of their being whole numbers of hydrogen, than when the atomic weights were compared directly with the hydrogen unit alone by Stas and the older chemists.

It will be observed that there are gaps in the positive series Hn, to be occupied by two elements with atomic weights 154 and 177, and also one in the series H 2n, with an atomic weight 160, which remain to be discovered or identified with known radioactive or other elements.

The multiple relations subsisting among the series H3n are highly interesting on account of the additions that have been made to them by the aid of spectral analysis, and the questions raised respecting the classification and valency of some of its members, which, from their rarity, have not been sufficiently investigated. The atomic weights of this series are calculated on the same principle as those shown in the series Hn and H2n, and are multiples of H3. It will be seen that where the numbers in the table differ from the experimental determinations, the differences are either multiples or submultiples of the received atomic weights. Moreover, as the theoretic atomic weights of thorium, thallium, aluminium, as carbon are identical with the actual determinations, and as triads are formed by Tl, In, Ga, Sc, and Th, Er, Y, Ce, as in the series Hn, H2n, there is a high degree of probability that all the theoretical atomic weights in this series are also correct.

While the atomic weights of the remaining series H4n–H7n are multiples of their typical molecules at the head of each series, their other numerical relations differ from those in the preceding series. The possible causes of the departure from the simple law observable in these series have been briefly stated in my paper "On the Origin of Elementary Substances," published in the Memoirs of the Manchester Literary and Philosophical Society in 1887.

From the definite multiple relations which the atomic weights of mercury, lead, and thorium have to those of the lower members of their respective series, for the same number of elementary condensations, there is abundant reason for concluding that no elements exist of higher atomic weights than those shown in each series of my tables.

The general principles herein set forth enable me now to deal with the anomalously high value assigned to the atomic weight of radium in the most recent experimental determinations, as compared with the theoretical value 184 shown in my tables.

In the determination made by Mme. Curie with the chloride the atomic weight of radium was calculated to be 226[*]. More recently, Dr. Thorpe, F.R.S., has repeated Mme. Curie's experiments with radium chloride and obtained nearly the same result[†].

In both these determinations it will be observed that beyond the statement that radium is a bivalent element, no mention is made of the constitution of the chloride from which the results were obtained, *i. e.* whether a protochloride according to Dumas, Marignac, and Berthelot, or a dichloride in agreement with Cannizzaro. This omission has, however, been supplied in Mme. Curie's 'Thesis on Radioactive Substances,' in which the formula of radium chloride is written $RaCl_2$, and, consequently, a dichloride.

A glance at my complete table of atomic weights will show that the several series of elements, Hn–H7n, are in the order of their quantivalence. It will also be seen that the valencies of the series Hn and H2n are determined solely by the multiple relations herein set forth, as distinguished from the estimated quantities shown in periodic systems of the elements.

That the univalent halogens are negative analogues of the univalent alkaline metals in homologous positions in my table, is evident from their numerical, physical, and chemical relations, just as the bivalent oxygen series have the like relations to the bivalent alkaline-earth metals. The formula for radium dioxide, like that of barium, will therefore be RaO_2. Now it is well known that chlorine combines with the alkaline and alkaline earth metals in one proportion only; and according to Dalton's first canon of chemical synthesis "such combination must be presumed to be a *binary* one"[‡]. Consequently, until radium can be shown to have two

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[*] *Comptes Rendus*, tome cxlv. p. 422 (1907).

[†] Proc. Roy. Soc. vol. lxxx. p. 307 (1908).

[‡] Dalton's 'New System of Chemical Philosophy,' p. 214 (1842).

chlorides, its combination with chlorine is a protochloride and its formula RaCl.

The atomic weight 226 shown for radium will, therefore, require to be reduced by 35 (the equivalent of chlorine), or $226-35=191$. Although this value is still 7 units higher than the value shown in my table, yet, considering the difficulties attending the experiments on account of the minute quantities of the chloride operated upon, the result is as near the theoretical value as might reasonably be expected.

While extreme care has been taken in both these determinations to eliminate barium from the mineral experimented with, which element would reduce the value shown for radium on account of its lower atomic weight (137), no mention is made or indication given by Dr. Thorpe of any residual quantity of uranium that might have remained in the radium chloride from which the atomic weight was determined. His investigation commenced on about half a ton of pitchblende (uranium oxide) residues. It would have been interesting to know the steps by which this large amount of uranium oxide residues was reduced to a single grain of radium chloride.

As the atomic weight of uranium is 240, the elimination of two and a half per cent. of uranium chloride from the grain of radium chloride ultimately obtained would reduce the atomic value 191 to 184, the atomic weight of radium as shown in my tables.

Yours faithfully,
H. Wilde.

Alderley Edge, Sept. 29th, 1908.

LXXI. *Notices respecting New Books.*

The Mathematical Theory of Electricity and Magnetism. By J. H. Jeans, M.A., F.R.S. Pp. viii+536. Cambridge University Press, 1908.

THIS treatise is intended to give the mathematical theory of the fairly well-defined range in Electromagnetic Theory which every student of physics may be expected to have covered, with more or less thoroughness, before proceeding to the study of special branches or developments of the subject. The treatment is considerably more elementary than that in Maxwell's Treatise upon which it is based. It also includes much detail which is not in Maxwell. Although the author makes no claim for much newness or originality of treatment, and even expressly disclaims having taken much interest in the writing of it (!), yet we think that the result is to be highly commended. Undoubtedly it appears to us to be a book which is destined to take a leading place amongst expositions of electromagnetic theory. Mr. Jeans is so thoroughly alive to the logical principles at the foundation of his subject that he is able to lucidly expound them. Take, for example, the question of action at a distance discussed on p. 138. Then again the numerical illustrations are very striking. By no means the slightest feature of the book is the large number of examples at the ends of the chapters. These, as he says, "may provide problems for the mathematical student, but it is hoped that they may also form a sort of compendium of results for the physicist, showing what types of problem admit of exact mathematical solution."

LXXII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 704.]

May 20th, 1908.—Prof. W. J. Sollas, Sc.D., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On some Fossil Fishes discovered by Prof. Ennes de Souza in the Cretaceous Formation at Ilheos, State of Bahia (Brazil).' By Arthur Smith Woodward, LL.D., F.R.S., F.L.S., V.P.G.S.

2. 'The Bala and Llandovery Rocks of Glyn Ceiriog (North Wales).' By Dr. Theodore Groom, M.A., F.G.S., and Philip Lake, M.A., F.G.S.

In the district around Glyn Ceiriog, which the authors have mapped on the 6-inch scale, the following succession is given:—

Denbighshire Slates.		
Ty-Draw Slates, with *Monograptus Marri*		TARANNON and LLANDOVERY.
Fron-Frys Slates, with *Pentamerus undatus*, *Meristina* cf. *crassa*, *Nidulites favus*, etc.		
Glyn-Valley Series	(*b*) Glyn Grit and Limestone	BALA.
	(*a*) Ddolhir Beds, with *Phyllopora Hisingeri*, *Ramipora Hochstetteri*, *Trinucleus seticornis*, species of *Cybele*, *Cheirurus*, *Remopleurides*, and numerous cystids, corals, brachiopoda, etc.	
Graptolite-Slates, with *Dicellograptus elegans*		
Gap.		
Pandy Series.	(*e*) Pen-y-Graig Ash	
	(*d*) Bryn Beds, with *Tetradella complicata*, *Phacops apiculatus*, *Trinucleus concentricus*, *Triplesia spiriferoides*, *Rafinesquina ungula*, etc.	
	(*c*) Craig-y-Pandy Ash	
	(*b*) Teirw Beds, with *Lingula tenuigranulata*, *Bellerophon nodosus*, *Asaphus Powisi*, etc.	
	(*a*) Cwm-Clwyd Ash	

In the Pandy Series the beds *a*, *c*, and *e* consist essentially or wholly of ashes and tuffs (no lava-flows having been detected). Movements have often taken place along the two surfaces of the Craig-y-Pandy Ash, and the rock is commonly foliated, and locally converted into a white or blue china-stone, in which good columnar jointing is sometimes shown. The authors have failed to detect any traces of thermometamorphic action of these bands on the adjoining slates, such as has been recently asserted. It is otherwise with an intrusive sill, which has been commonly mistaken for the uppermost ash.

The Teirw Beds are compared with the Roman Fell Group of the Lake District. The Bryn Beds agree most nearly with the Sleddale Beds of the same district.

The Graptolite-Slates are separated from the underlying Pandy Series by the Ddolhir Fault, which has cut out a considerable part of the succession.

The Ddolhir Beds are extremely rich in fossils, which prove their equivalence with the Ashgillian formation of other districts. They appear to pass up into the Glyn Grit and Limestone, which is essentially a sandy and calcareous facies of the series. The Glyn Grit corresponds in position with the Corwen Grit; but, recognizing that it belongs to the Bala Series, the authors are no longer prepared, without further evidence, to assume the equivalence of the two grits.

The Fron-Frys Slates show the lithological characters of the Grey Slates of Corwen, but belong rather to the shelly than to the graptolitic facies of the Llandovery Series.

The Ty-Draw Slates resemble the pale Tarannon Slates of other districts. They appear to pass up into the Denbighshire Slates.

The authors find no indication of the overlap or overstep of the Wenlock, Tarannon, and Llandovery Beds mapped by the officers of the Geological Survey, or described by previous observers, although there is probably an unconformity at the base of the Fron-Frys Slates.

The beds of the district dip northwards at an almost uniformly low angle, but the structure is considerably complicated by a series of faults, most of which have hitherto escaped notice, some being very elusive. They include :—(1) east-and-west faults, (2) north-north-west and south-south-east, or north-and-south faults, and (3) north-north-west and east-south-east faults.

Of the first series the most important is the Ddolhir Fault, which dips at an angle of 20°, nearly, with the bedding, and may be either a thrust-plane or a lag-fault. Of the second series, the most remarkable is the Caemor Fault, on the east side of which the rocks have been raised nearly a mile, and shifted horizontally to the south for nearly 3 miles. Most of the remaining faults have a simple downthrow on the east.

FIG. 4.—*DARK* IRON.

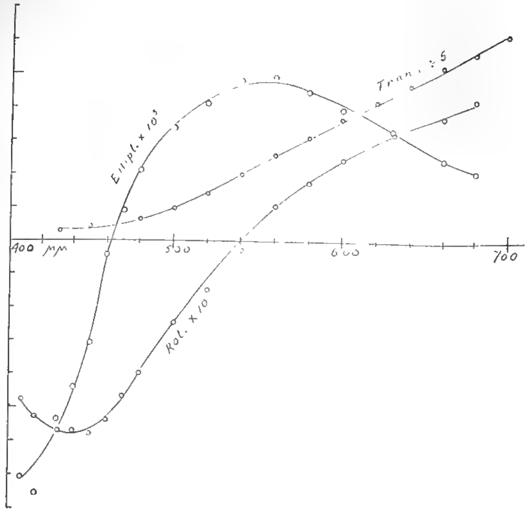


FIG. 5.—*DARK* IRON.

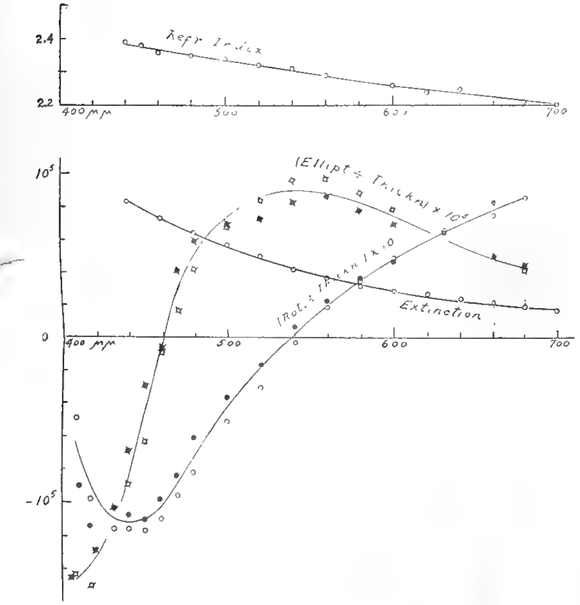


FIG. 6. *ELECTROLYTIC* IRON.

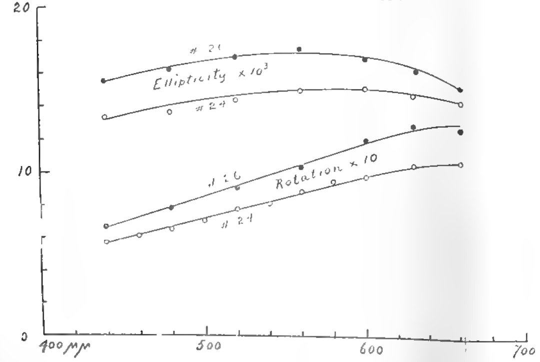


FIG. 7.—*ELECTROLYTIC* IRON.

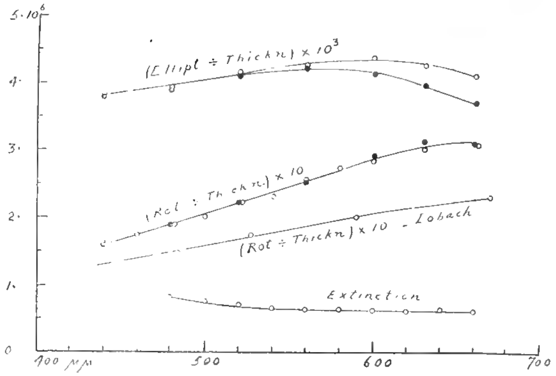


FIG. 8.—*METALLIC* IRON.

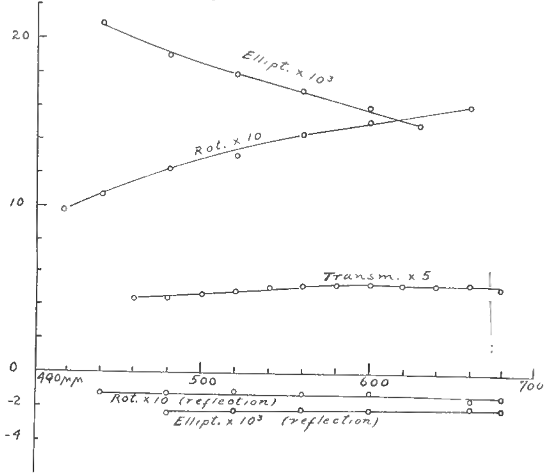


FIG. 9.—*METALLIC* IRON.

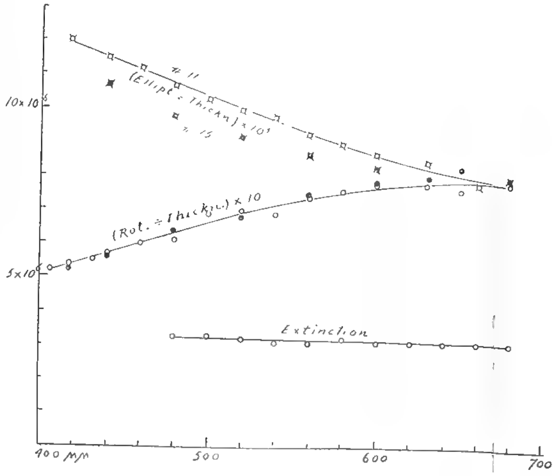


FIG. 10.

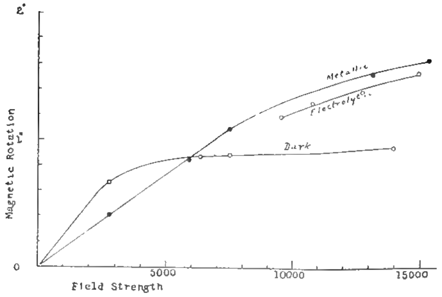


FIG. 11.—*DARK* COBALT.

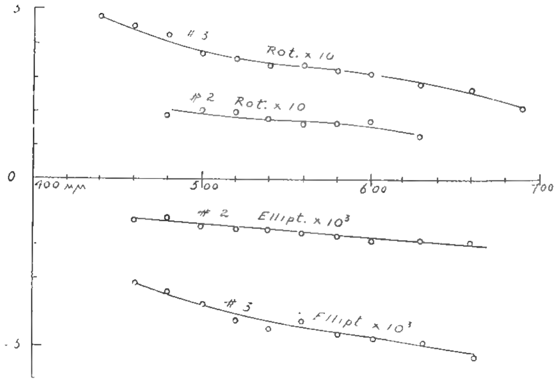


FIG. 12.—*DARK* COBALT.

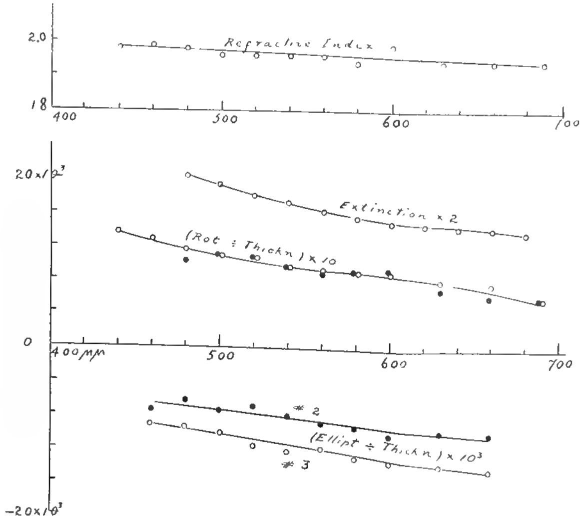


FIG. 13.—*ELECTROLYTIC* COBALT.

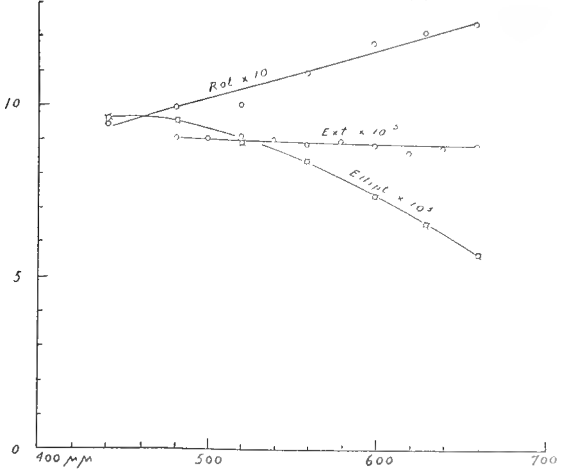


FIG. 14.—*METALLIC* COBALT.

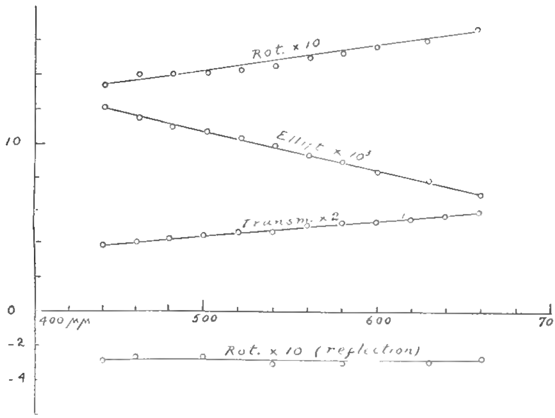
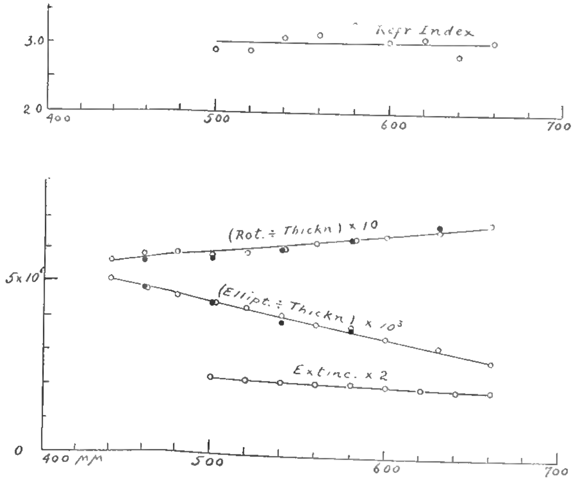


FIG. 15. -*METALLIC* COBALT.



THE
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AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

DECEMBER 1908.

LXXIII. *An Investigation of the Optical Properties of Films of Magnetic Metals. By* CLARENCE A. SKINNER, *Ph.D., Professor of Physics, and* A. Q. TOOL, *M.A., Assistant in Physics in the University of Nebraska* *.

[Plate XXIV.]

THE object of this investigation was to study the magnetic rotation and ellipticity produced in plane-polarized light by films of magnetic metals, along with other properties intimately associated in theory with these—namely, the refractive indices and extinction coefficients.

That a thorough investigation of this kind would prove fruitful seemed evident from the results obtained in this laboratory by W. D. Harris †, who found that iron films, obtained by cathode deposit in a glow current, exhibited magnetic effects differing with the gas in which they were produced. His results also show that the variation in the magnetic rotation of these films with the wave-length of light is strikingly different from that obtained by Lobach ‡ for electrolytic iron.

After improving the optical system used by Harris, we have been able to extend observations on these films into the region of relatively greater absorption, which this type is found to possess. We find there that both magnetic rotation

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* Read at the meeting of the American Physical Society, Chicago, January 1908. Communicated by the Authors.

† W. D. Harris, Phys. Rev. xxiv. p. 337 (1907).

‡ W. Lobach, Wied. *Ann.* xxxix. p. 347.

and ellipticity reverse their direction with respect to the magnetizing current.

By varying the method of producing the films of iron we have obtained three distinct types, one of which, as stated, exhibits a marked absorption region in the visible spectrum, while the other two seem to have the centre of such a region shifted well out in the ultra-violet. Similar characteristic differences are found in films of cobalt. Cathodic films of nickel were found to be almost imperceptibly *active*, though electrolytic nickel gives measurable values.

We have also found that a measurable ellipticity is imparted to the originally plane-polarized light by all films producing a measurable magnetic rotation.

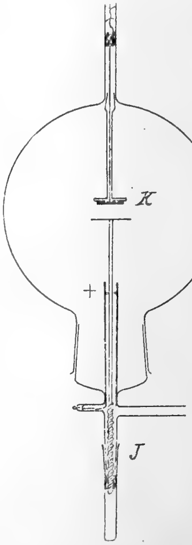
EXPERIMENTAL METHODS.

1. *Production of Films.*

As stated above, three distinct types of both iron and cobalt were obtained—two by the glow current in gases, the other by electrolytic deposition.

Iron.—Using a glow current, the films were deposited from a circular disk cathode of Swedish iron (diam. 10 mm.). The form of discharge chamber is represented in fig. 1. To confine the current to the face of the cathode K, this was backed by a porcelain disk and its stem sheathed in porcelain tubing, the temperature in some cases running too high for glass. The films were deposited on very thin (0·1 to 0·2 mm.) microscope cover-glasses, selected plane, free from double refraction, and of measured magnetic rotation—the latter being generally a small fraction of that imparted by the metal film. To make a film, one of these glasses was mounted parallel to the face of the cathode at an adjustable distance below it. The discharge chamber was then evacuated and usually dried by leaving it in connexion with a chamber containing phosphorus pentoxide. Dry gas (hydrogen, unless otherwise stated) was finally admitted to a pressure of one to three millimetres of mercury. The electric current—furnished by a 1000-volt storage-battery—was then passed from the iron disk as cathode.

Fig. 1.



In those cases where the current was adjusted to a magnitude such that a film of the desired opacity was produced in two to four hours, the appearance of the film, as also its optical characteristics, was very different from those produced in a few seconds on raising the cathode to a white heat by cutting resistance out of the circuit. These latter films appear by reflected light as perfect metallic mirrors, while the former are much like polished dark glass. The latter are very hard, and seem to be fused on to the glass; while the former are soft and brittle, lacking the coherence of fused iron. For the same opacity the *metallic* films are strikingly thinner than the *dark* ones, being too thin to show the least trace of interference-fringes, while with the *dark* these may be very distinct. The *metallic* films impart no tint to transmitted light; the *dark* appear a yellow-brown arising from a marked relative absorption of the shorter waves. When deposited in hydrogen the *metallic* type absorb the gas at a remarkable rate even for some time after the current is broken *; but the *dark,* which exhibit like properties whether deposited in hydrogen or helium, take up no observable quantity of the gas either during or after the process of deposition. For this reason the exceptional properties of the *dark* films must be ascribed to the form in which the metal is deposited, and not to a chemical combination of the metal with the gas.

In a few cases films were obtained which exhibited optical properties intermediate between those of the two types described; but since these appeared to be made up of layers of different hardness, and the conditions of deposit were such as made it likely, we conclude that they were simply a mixture of the two already described †.

Films were also deposited electrolytically from a solution of ferrous ammonium sulphate on glass platinized according to the method of Kundt. The appearance of these is like that of the *metallic* type of cathode film.

Cobalt.—Three types of cobalt films were readily produced in the same way as the corresponding ones of iron. They are similar in appearance to the iron. They differ greatly in their

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* See W. Heald, Phys. Rev. xxiv. p. 269.

† To this mixed type belong, to all appearances, those obtained by Harris (*l. c.*) in hydrogen; while those he deposited in nitrogen belong to that designated here as *dark* (arising probably from less heating of the cathode in nitrogen). Hence the variation which Harris ascribes to a change in the kind of gas was caused in fact by the consequent change in the temperature of the cathode. This, however, does not explain the characteristics exhibited by the films which he deposited in oxygen. These were probably largely oxidized in the process of deposition.

magnetic effects and also in their extinction. Compared with the corresponding ones of iron, cathodic films of cobalt are considerably more transparent; though such is not the case with electrolytic films.

Nickel.—With the glow current, only films giving metallic reflexion could be produced with nickel, though these varied considerably in hardness. The densest revealed only a very faint activity in the magnetic field. As stated above, films of nickel of relatively pronounced activity were, however, obtained by electrolytic deposition, the same as with iron and cobalt.

2. *Thickness of Films.*

This was measured by a slight but very convenient modification of the customary interference method. The film was cleared from the glass to an abrupt edge at the point to be measured. Over this was laid a cover-glass, which produced under perpendicular reflexion of monochromatic light two adjacent sets of interference-bands—one arising from the interference of light reflected from the upper and lower boundaries of the air-space between the two plates of glass; the other from that contained between the upper plate and the film. Obviously the thickness of the film is one-half the relative retardation of the two sets of bands, provided no phase difference arises at the surfaces. That no measurable surface effect of this kind was present was shown by the fact that films known from their magnetic rotation to be too thin to produce, by their thickness alone, a measurable displacement of the bands, gave coincidence of the two sets.

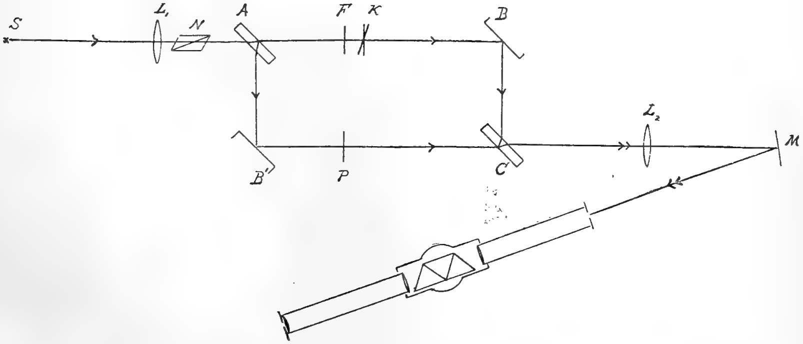
A micrometer microscope was used for measuring the fractional part of a band displacement.

The modification referred to consisted in the use of sunlight passed through a Fuess spectral instrument as a source of monochromatic light, variable in colour and intensity. By varying the width of the collimator-slit of the instrument, that intensity producing the clearest bands—a very important factor—was easily obtained. By changing the colour, the direction of motion of the bands revealed immediately the direction of the relative shift; and by noting the successive wave-lengths that gave coincidence, the whole number of wave-lengths of each colour was obtained readily by inspection, each setting at the same time contributing a measured value to the desired retardation. Finally, in those cases where the film was too thin to give a coincidence of the bands with any colour, the greatest accuracy was attained by using the shortest waves consistent with clear vision. It was found that a wave-length of about 430 $\mu\mu$ fulfilled this condition very satisfactorily, inasmuch as this colour gave generally the most distinct bands of all.

3. *Optical Thickness of Films.*

The refractive index of the films was obtained as the ratio between the *optical thickness* and the *air thickness*—that is, the ratio of the number of wave-lengths in the film to that in the same thickness of air. The *optical thickness* was measured by means of an interferometer of the Zehnder type, following the method used at different times in this laboratory [*]. Fig. 2 presents a diagram of the system. Light from a Nernst glower S (or slit illuminated with sunlight) passes through a lens L_1, a polarizing nicol N, and is divided into two components at the half-silvered surface of the interferometer-plate A. These rays pass respectively over the two paths ABC and AB′C, and recombine beyond the interferometer-plate C under conditions producing interference. The object of the nicol is to eliminate reflexion from the glass-air surface of the interferometer-plates, and the consequent blurring of the bands arising from the superposition of the two sets thus produced. This is possible because the angle of incidence on the plates is very nearly the polarizing angle. The film F whose retardation is to be measured is placed to intercept the lower half of one of the component rays. Just beyond this is placed a compensator K, consisting of two thin mica strips of equal thickness, one placed parallel to the film with its upper edge in line with the upper edge of the film, the other placed to intercept the part of the ray which passes above the film and the companion strip of mica. Both have their optic

Fig. 2.



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[*] Cartmel, Phil. Mag. [6] vi. p. 214; Clark, Phys. Rev. xxiii. p. 422.

axis in the plane of polarization. This upper strip of mica is so mounted that its inclination to the ray can be varied by rotating about a vertical axis, and thus a retardation produced in the upper half of the ray equal to that which the film introduces in the lower half. P is a compensating plate used to right the irregularity of form in the bands arising from the plate on which the film is deposited. Beyond C is placed a lens L_2, which focusses (through the plane mirror M) the film F on the collimator-slit of a spectroscope. Viewed through the spectroscope, the field exhibits two parallel channeled spectra with the interference-bands in the one displaced relative to those in the other. If the movable compensator strip be parallel to its companion strip, the observed displacement arises from the optical path in the film being greater than that in the same thickness of air. The angular displacement of the collimator, which gives coincidence of bands in any part of the spectrum, is used for determining this difference. As a convenient formula for calculating the relative retardation we have used the following, for which we are indebted to Professor Tuckerman of this laboratory :—

$$\delta = k\alpha^2(1 + 5{\cdot}3 \, . \, 10^{-5} \, . \, \alpha^2),$$

where δ is the retardation in wave-lengths, α the displacement of the compensator in degrees, and k a constant depending on the thickness of the mica and its refractive index. The value of k is experimentally determined for the various colours by observing the value of α required to produce one or more wave-lengths' retardation with the film removed. The accuracy (one-half per cent.) of this formula is well within the experimental errors.

The *optical thickness* of the film is obtained for each colour by adding the corresponding δ to the *air thickness* given in terms of the wave-length considered.

4. *Transmission and Reflexion.*

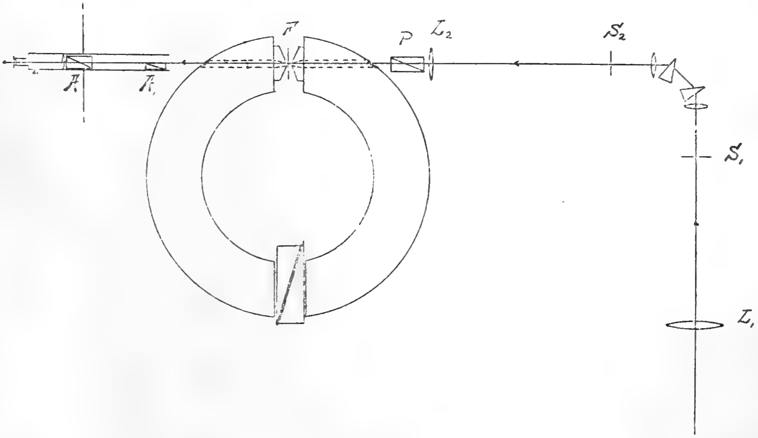
For measuring the ratio of the intensity of the transmitted to the incident light, a Brace spectrophotometer was used in the customary way: a rotating sector and an adjustable slit serving to reduce the intensity of the unabsorbed component to *match* it with that which has passed through (or been reflected from) the film. To eliminate the effect of reflexion in the transmission measurements, the usual method of measuring the transmission of two different thicknesses was followed. For reflexion measurements, an attachment described by Clark (*l. c.*) was used.

5. *Magnetic Rotation and Ellipticity.*

The rotation of plane-polarized light by the films, when subjected to a magnetizing force in the direction of the ray, was measured for both transmission and reflexion. The corresponding ellipticity produced in the originally plane vibration was also measured. Finally, plane-polarized light sent through the films in a direction normal to the field, and with its azimuth of vibration at 45° to it, was tested in the most promising films for ellipticity, but none detected.

Rotation.—Figure 3 presents a diagram of the system used for measuring rotation. A very clear sun as source was necessary for all observations where transmitted light was studied. This was concentrated by a long-focus lens L_1 on the collimator slit S_1 of a Fuess spectral instrument so adjusted as to furnish at the emergent slit S_2 a practically monochromatic bundle of rays of any desired colour. The extremes of the bundle differed in wave-length usually by about 10 $\mu\mu$. These rays passed successively through an achromatic lens L_2, a polarizing prism P, the film F (placed between the magnet-poles), and the Lippich half-shade analysing pair A_1 and A, which were mounted in the axis of a graduated circle. A viewing telescope focussed on the edge of the half nicol A_1 completed the optical system. Settings were made by rotating the analysing pair (fixed relative to each other) until the customary *match* was obtained.

Fig. 3.



For investigating the reflected light the rays from the spectral system were brought in from the side and turned by means of a total-reflecting prism through a polarizer of much smaller aperture than that used in testing the transmitted light. The rays were reflected from F back over the polarizer, entering the analysing system so placed as to receive them. The angle of incidence on the film with this arrangement was not greater than two degrees.

Ellipticity.—For measuring this a Brace half-shade elliptic polarizer and compensator was used. To convert the above rotation system into one for measuring ellipticity, the half nicol A_1 was removed and A fixed at extinction. The mica half-shade elliptic polarizer was placed in the position originally occupied by A_1, covering half the field and fixed at maximum illumination. The compensator, a thicker sheet of mica, was then mounted (covering the whole field) in the graduated circle. Settings were made by rotating this compensator until a *match* was established. To eliminate the effect arising from mere rotation of the plane by the film, the polarizer P was arranged to be conveniently rotated a sufficient amount to compensate for this. This was determined with suitable accuracy by rotating to minimum intensity of field. The half-shade was of the order $\cdot 009\,\lambda_D = 3\cdot 2$ degrees. The compensator, carefully measured according to Stokes' method *, was found to be of the order $6^\circ\cdot 5$ for a wave-length of 560 $\mu\mu$. The order of a similar piece of mica, a quarter-wave plate for the same colour, was carefully measured for the various spectral colours, and these values used in determining the order of the compensator for the various wave-lengths studied. The ellipticity of the light was calculated from the formula

$$E = \tan \nu_1 \left[\sin 2(\phi - \phi_0) + \sin 2\phi_0\right],$$

in which E = ratio of minor to major axis of the elliptic vibration; $2\nu_1$ = order of the compensator; ϕ_0 = angle through which the compensator is rotated to change from a *match* on plane-polarized light to the nearest position of no effect on this light; and ϕ = the angular displacement of the compensator from its position of *match* on plane-polarized light to a *match* on the light having an ellipticity E. If the compensator and half-shade are of the same material, ϕ_0 does not change with the colour. This formula is accurate for thin compensators. All measurements of both rotation and

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* Phil. Mag. [4] ii. p. 420.

ellipticity were obtained by reversing the magnetizing current in the electromagnet, which doubled the magnitude of the quantity sought.

The direction of vibration in the ellipse was determined by comparing the compensator with a quarter-wave plate, the *slow* and *fast* azimuths of which had been determined by means of the interferometer.

EXPERIMENTAL RESULTS.

6. *Dark Iron.*

In Table I. (p. 842) are incorporated the values of the magnetic rotation and ellipticity imparted by three different films of dark iron to light transmitted through them along the lines of force, and with field-strengths giving maximum effects. Two of these films (Nos. 3 and 4) were deposited in an atmosphere of hydrogen, the third (No. 2) in helium. The rotation and compensator values are half the observed, which were, as already stated, obtained by reversing the magnetizing current. The ellipticity (ratio of minor to major axis) was obtained from the compensator values by use of the formula given on page 840. Positive values represent rotation (or vibration) in the direction of the magnetizing current; negative, the opposite direction. By all three films the rotation is reversed in direction at a wave-length of about 540 $\mu\mu$, and the ellipticity at about 460 $\mu\mu$. This similarity in the results from films deposited in hydrogen and in helium indicates that their peculiar properties are to be ascribed to the form in which the iron is deposited rather than to the existence of any chemical combination with the gas. This conclusion is strengthened by the fact that iron deposited by Harris in nitrogen (*l. c.*) gives also zero rotation and ellipticity at the same positions in the spectrum.

Fig. 4 (Pl. XXIV.) represents graphically the results from film 3. The abscissas represent wave-lengths; the ordinates in the rotation curve give the rotation in degrees multiplied by ten, and in the ellipticity curve the ratio of minor to major axis multiplied by one thousand. In the same figure is plotted the transmission curve of the film, the ordinates representing the per cent. transmission divided by five. The values for this latter curve are taken from Table II. The relatively large transmission of the longer waves causes the film to impart a rich golden tint to white light.

In Table II. (p. 843) are given for the same films the values of rotation and ellipticity divided by the thickness of the

TABLE I.—*Dark* Iron.

Thickness : No. 2, 540×10^{-7} cm.; No. 3, 490×10^{-7} cm.; No. 4, 200×10^{-7} cm.

Wave-length. ($\mu\mu$).	No. 2.—Field, 7,600.			No. 3.—Field, 7,500.			No. 4.—Field, 13,200.		
	Rotation. (deg.)	Compens. (deg.)	Ellipticity $\times 10^3$.	Rotation. (deg.)	Compens. (deg.)	Ellipticity $\times 10^3$.	Rotation. (deg.)	Compens. (deg.)	Ellipticity $\times 10^3$.
408	−·48	...	...	−·48	−2·75	−7·08	−·20	−1·18	−3·03
417	−·61	...	...	−·53	−2·98	−7·54	−·25	−1·07	−2·72
431	−·74	−2·10	−5·19	−·57	−2·16	−5·35	−·22	−0·83	−2·05
440	−·76	−1·38	−3·38	−·57	−1·80	−4·41	−·23	−0·54	−1·49
450	−·74	−0·78	−1·88	−·58	−1·29	−3·09	−·24	−0·27	−0·64
460	−·61	+0·63	+1·50	−·54	−0·20	−0·46	−·21	−0·06	−0·14
470	−·52	+1·42	+3·28	−·47	+0·37	+0·84	−·18	+0·38	+0·87
480	−·45	+1·92	+4·35	−·40	+0·91	+2·05	−·13	+0·55	+1·24
500	−·25	+2·58	+5·61	−·25	+1·52	+3·31	−·08	+0·65	+1·40
520	−·10	+2·80	+5·85	−·15	+1·93	+4·04	−·04	+0·72	+1·50
540	+·03	+3·11	+6·40	−·03	+2·31	+4·75	+·02	+0·84	+1·73
560	+·14	+3·13	+6·19	+·10	+2·44	+4·83	+·05	+0·92	+1·81
580	+·25	+2·96	+5·68	+·17	+2·30	+4·42	+·08	+0·87	+1·67
600	+·33	+2·55	+4·75	+·24	+2·10	+3·90	+·10	+0·79	+1·46
630	+·40	+1·94	+3·44	+·32	+1·85	+3·30	+·14	+0·73	+1·30
660	+·47	+1·42	+2·42	+·37	+1·45	+2·46	+·18	+0·61	+1·04
680	+·43	+1·19	+1·98	+·42	+1·23	+2·04		+0·56	+0·92

TABLE II.—*Dark* Iron.

Field : 7,500 C.G.S.

Wave-length.	$\frac{\text{Rotation}}{\text{Thickness}} \times 10^{-3}$.			$\frac{\text{Ellipticity}}{\text{Thickness}}$.			Transmission (per cent.).		Extinction $\times 10^{-4}$.	Refractive Index.
	No. 2.	No. 3.	No. 4.	No. 2.	No. 3.	No. 4.	No. 3.	No. 4.		
408	− 8·8	− 4·9	− 9·1	...	−142	−143				
417	−11·2	− 9·8	−11·4	...	−150	−129				
431	−13·6	−11·6	−10·3	− 92	−109	− 97				
440	−14·0	−11·6	−10·7	− 61	− 89	− 69	1·3	14·4	8·3	2·39
450	−13·7	−11·7	−11·0	− 35	− 63	− 30	...	...	...	2·38
460	−12·0	−11·0	− 9·8	+ 27	− 9	− 7	1·9	15·9	7·3	2·36
470	− 9·5	− 9·6	− 8·4	+ 61	+ 17	+ 41	...	...	...	...
480	− 8·2	− 8·2	− 6·1	+ 80	+ 42	+ 59	3·0	19·2	6·4	2·35
500	− 4·6	− 5·1	− 3·7	+102	+ 67	+ 67	4·7	24·3	5·7	2·34
520	− 1·7	− 3·1	− 1·7	+106	+ 83	+ 72	6·9	29·2	5·0	2·32
540	+ 0·5	− 0·6	+ 0·7	+116	+ 96	+ 82	9·7	33·0	4·2	2·31
560	+ 2·5	+ 1·9	+ 2·3	+113	+ 97	+ 86	12·6	36·3	3·7	2·29
580	+ 4·6	+ 3·5	+ 3·7	+105	+ 88	+ 77	15·3	39·2	3·2	...
600	+ 6·1	+ 4·9	+ 4·7	+ 87	+ 78	+ 69	18·0	41·9	2·9	2·26
620	...	...	...	...	...	...	20·7	44·7	2·7	2·24
630	+ 7·3	+ 6·5	+ 6·4	+ 63	+ 66	+ 61	...	...	...	...
640	...	...	...	...	...	...	23·4	47·0	2·4	2·25
660	+ 8·6	+ 7·4	+ 8·2	+ 45	+ 50	+ 49	26·1	49·2	2·2	...
680	+ 7·8	+ 8·5	...	+ 37	+ 41	+ 44	28·0	50·6	1·9	2·21
700	+ 8·5	...	...	...	...	...	30·9	51·3	1·7	2·20

corresponding film. These show that both rotation and ellipticity are approximately proportional to the thickness of the film, the approximation being on the whole as near as one could expect from the conditions of the experiment. These values for films 3 and 4 are plotted in fig. 5, the results from 3 being indicated by the black dots, from 4 by the circles. The transmission values for the same films, given also in Table II., serve for calculating the extinction coefficients by using the formula

$$\frac{I_3}{I_4} = e^{-K(d_3-d_4)},$$

in which I_3, I_4 refer to the ratio in percent. of transmitted to the incident light of the two films respectively ; d_3 and d_4 the thickness of the films in centimetres ; and K the extinction coefficient sought. These extinction coefficients are also given in Table II. Finally, in the last column of this table are given the refractive indices of film 3 as obtained according to the method described in § 3. They are represented in the upper plot of fig. 5, and the extinction coefficients in the lower.

The rotation, ellipticity, and extinction curves are consistent with each other ; but it appears strange that the refractive-index curve shows no corresponding anomaly in form in this region. Its slope is, however, opposite in direction to that given by other investigators for normal iron. The magnitude (2·2 to 2·4) is about the same here as in normal iron.

In Table III. are recorded the observations of rotation and ellipticity of film 2 with various field-strengths, the magnitude of the latter being determined by the rotation produced in a given length of carbon bisulphide. The bottom line of this table gives the ratio of the mean of the magnitudes contained in each two vertical columns (obtained by ignoring algebraic signs). This shows that, within experimental errors, the ellipticity bears the same ratio to the rotation for all field-strengths. Assuming, as has been shown in some cases by Du Bois *, that the rotation is proportional to the magnetization of the film, we may conclude that the ellipticity produced by the film is also proportional to its magnetization.

Observations on light reflected from these films in a magnetic field gave no conclusive results, arising partly from the fact that so much light is returned from the back surface of the film, especially in the red end of the spectrum.

* Du Bois, Wied. *Ann.* xxxi. p. 941.

TABLE III.—*Dark* Iron.

Field	2,800.		6,300.		7,500. 7,700.		14,100.	
Wave-length.	Rotation.	Ellipticity ×10³.	Rotation.	Ellipticity ×10³.	Rotation.	Ellipticity ×10³.	Rotation.	Ellipticity ×10³.
417	−·49	...	−·61	−6·20	−·61	...	−·67	−4·03
431	−·55	−3·65	−·76	−5·14	−·74	−5·24	−·71	−4·65
440	−·55	−2·52	−·73	−3·51	−·76	−3·40	−·74	−2·58
450	−·57	−1·18	−·70	−1·78	−·75	−1·89	−·71	−1·37
460	−·49	+1·05	−·64	+0·75	−·66	+1·49	−·69	+1·37
470	−·43	+2·02	−·55	+2·98	−·52	+3·32	−·57	+3·15
480	−·32	+2·86	−·41	+4·53	−·45	+4·38	−·45	+4·27
500	−·18	+3·87	−·25	+5·36	−·25	+5·66	−·24	+5·47
520	−·07	+4·29	−·11	+5·73	−·10	+5·93	−·08	+6·02
540	+·01	+4·52	+·03	+6·09	+·03	+6·46	+·01	+6·58
560	+·12	+4·52	+·15	+5·85	+·14	+6·25	+·19	+6·46
580	+·18	+4·03	+·24	+5·38	+·25	+5·73	+·29	+5·97
600	+·23	+3·49	+·31	+4·52	+·33	+4·79	+·39	+4·90
630	+·29	+2·49	+·38	+3·31	+·40	+3·48	+·46	+3·47
660	+·33	+1·79	+·42	+2·43	+·47	+2·44	+·51	+2·13
680	+·33	+1·21	+·44	+2·12	+·43	+2·00	+·54	+1·79
Ratio of Magnitudes	9·4		9·7		9·9		9·2	

This fact was made evident by the coefficient of reflexion being of a wave form in the red end of the spectrum (arising from interference between front and back reflexions) and a flat curve in the blue (where the absorption is large).

About 11 per cent. of the light is reflected at normal incidence from the front surface of these films, this value being practically the same for all colours.

7. *Electrolytic* Iron.

As already stated, the electrolytic films were deposited on microscope cover-glasses which had been platinized after the method of Kundt. As nearly as could be measured, these platinum films were about $6 \,.\, 10^{-7}$ cm. thick in all cases. As a convenient method for measuring the thickness of the various iron films with the greatest accuracy, a comparatively thick film was deposited, its magnetic rotation observed for the more sensitive region of the spectrum (520 $\mu\mu$), and its thickness obtained by subtracting the thickness of the platinum from the combined thickness as measured according to § 2. The following table gives the values obtained, the thinner film merely serving to furnish check-values.

Table IV.

Film.	Thickness × 10^7 (cm.).			Rotation (degrees).	$\frac{\text{Rotation}}{\text{Thickness}}$.
	Pt + Fe.	Pt (approx.).	Fe.		
24	41	6	35	·92	263000
29	67	6	61	1·57	257000

The field-strength used for these measurements was 13,700 (c.g.s.).

From the above value of the rotation divided by the thickness, the thickness of the other films was calculated after measuring their rotation under the same conditions. This assumes that the various films are identical in structure, which assumption later results show to be not rigidly correct. However, the accuracy obtained by this procedure is probably much greater than if the thickness of the thinner films used had been measured directly.

Values of the rotation and ellipticity produced by two different electrolytic films are found in Table V. and the corresponding curves in fig. 6 (Pl. XXIV.). The form of the

Table V.—*Electrolytic* Iron.

Thickness: No. 24, 35×10^{-7}; No. 26, $41{\cdot}5 \times 10^{-7}$ cm.

Wave-length.	No. 24—Field, 14,700.			No. 26—Field, 14,600.		
	Rotat. (deg.).	Compens. (deg.).	Ellipt. $\times 10^3$.	Rotat. (deg.).	Compens. (deg.).	Ellipt. $\times 10^3$.
440 ...	·57	5·6	13·3	·66	6·4	15·5
460 ...	·61	...	...	...	...	...
480 ...	·65	6·2	13·6	·78	7·3	16·2
500 ...	·70	...	...	...	...	..
520 ...	·78	7·1	14·4	·91	8·3	17·0
540 ...	·81	...	...	...	...	...
560 ...	·89	7·8	15·0	1·04	9·2	17·5
600 ...	·98	8·3	15·1	1·20	9·4	16·9
630 ...	1·05	8·5	14·7	1·29	9·4	16·2
660 ...	1·07	8·6	14·3	1·27	9·3	15·2

rotation curve is practically the same in both, but there is an evident difference in the ellipticity, which indicates that the metal giving the upper curve has the centre of its resonance region slightly nearer the visible spectrum than the other. Both indicate the resonance region of electrolytic iron as being much further out in the violet than that of dark iron.

The values of rotation and ellipticity divided by the thickness of the corresponding films are given in Table VI., and

Table VI.—*Electrolytic* Iron.

Field, 14,600 c.g.s.

Wave-length.	$\frac{\text{Rotation}}{\text{Thickness}} \times 10^{-3}$.		$\frac{\text{Ellipticity}}{\text{Thickness}}$.		Extinction, $\times 10^{-5}$.
	No. 24.	No. 26.	No. 24.	No. 26.	
440 ...	163	159	3820	3740	...
460 ...	174	...	...	...	...
480 ...	189	187	3880	3920	8·1
500 ...	199	...	...	...	7·5
520 ...	221	219	4140	4080	7·0
540 ...	230	...	...	...	6·5
560 ...	254	249	4300	4220	6·3
580 ...	270	...	...	...	6·3
600 ...	280	288	4330	4100	6·1
620 ...	...	...	...	...	6·0
630 ...	299	310	4230	3920	...
640 ...	...	...	...	...	6·2
660 ...	306	305	4070	3660	6·0

their curves in fig. 7. The rotation is proportional to the thickness throughout, but with the ellipticity this is true only in the blue end of the spectrum, a considerable divergence being evident in the red. A more remarkable variation in these electrolytic films is found on comparing the rotation curve in this figure with that plotted from Lobach's results (*l. c.*) which is also given. The magnitudes are not only greatly different, but the rotation in our films increases more rapidly toward the red than in his, thus showing that the difference in values cannot be accounted for by assuming an error in thickness measurements.

The extinction coefficients of this type of iron were obtained by measuring the transmission of a very thin film of definite thickness, then repeating the measurements after depositing over this. Two films were thus tested, giving as mean results the values found in Table VI. The corresponding curve is plotted in fig. 7. Compared with dark iron it is noticed that this extinction-curve is much flatter than that of fig. 5, a fact we should expect from the great difference in form of the curves of rotation and ellipticity. Another remarkable difference between these films and those of the dark iron is the relative magnitudes of rotation, ellipticity, and extinction. With the same thickness the magnetic effects of electrolytic iron are about forty times that of the dark, while the extinction ranges from ten to thirty times.

The effect on rotation and ellipticity of varying the strength of the magnetic field is shown in the following table, obtained from film 24 with a wave-length of 520 $\mu\mu$.

Table VII.

Field-strength (C.G.S.).	Rotation (deg.).	Ellipticity $\times 10^3$.	$\frac{\text{Ellipticity}}{\text{Rotation}} \times 10^3$.
9,500	·60	12·7	21·2
10,800	·65	13·8	21·2
12,800	·69	14·8	21·5
15,000	·77	16·2	21·2

As with dark iron, the ellipticity changes with the magnetizing force at the same rate as the rotation, as shown by the last column of this table.

Light reflected from an electrolytic film (No. 22) was tested for both rotation and ellipticity in a field of about 13,000 lines. The results are given in the following table:—

TABLE VIII.

Wave-length	440	480	520	560	600	630	660
Rotation (deg.)	−·16	−·17	−·19	−·19	−·18	−·14	−·18
Ellipticity $\times 10^3$ ...	−·06	−·23	−·42	−·45	−·50	−·90	−·70

These results show that the rotation of reflected light is about the same for all colours, but the ellipticity—on the whole small—increases slightly with the wave-length. We find here that the negative rotation is also accompanied by a negative ellipticity, both being positive in the case of transmitted light.

8. *Metallic* Iron.

The type of films designated as *metallic*, to distinguish them from the other type obtained from cathode deposit *in vacuo*, seem to be produced by sublimation of the cathode. They are probably nearer normal iron in their structure than either of the other types. This is indicated by their appearance, and also suggested by their magnetic characteristics.

The reflexion coefficients as measured are practically constant throughout the spectrum, an average of 37 per cent. of the light being reflected. Their absorption is so great that only very thin specimens could be investigated, the thickest being 19×10^{-7} cm., from which the thickness of the others was obtained by measuring their magnetic rotation. This film (No. 15) was very carefully measured, following the method described in § 2, by two observers independently, whose mean results differed by only three per cent.

In Table IX. are found the magnetic rotation and ellipticity produced by two different films of this type in a field of 13,200 units. The results from film 15 are plotted in fig. 8 (Pl. XXIV.). The form of the rotation curve is very similar to that from electrolytic iron, but the ellipticity curve is distinctly different, the ellipticity, decreasing instead of increasing, with the wave-length. The form of the latter indicates the resonance region as being farther out in the ultraviolet than that of the electrolytic iron type. A more marked difference in the two types becomes evident when the ratio of

TABLE IX.—*Metallic* Iron.

Thickness: No. 11, $15{\cdot}4 \times 10^{-7}$; No. 15, 19×10^{-7} cm.
Field: 13,200 C.G.S.

Wave-length.	No. 11.			No. 15.		
	Rotat. (deg.).	Compens. (deg.).	Ellipt. $\times 10^3$.	Rotat. (deg.).	Compens. (deg.).	Ellipt. $\times 10^3$.
406 ...	·78	...	...	...	...	...
417 ...	·83	7·2	17·7	·98	...	...
431 ...	·85	...	...	...	...	...
440 ...	·87	7·2	17·0	1·07	8·8	20·8
460 ...	·92	7·3	16·7	...	...	...
480 ...	·95	7·3	16·0	1·22	8·7	19·0
500 ...	1·06	7·2	15·2	...	...	...
520 ...	1·08	7·2	14·6	1·30	8·8	17·9
540 ...	1·06	7·3	14·6	...	...	...
560 ...	1·15	7·1	13·7	1·43	8·8	16·9
580 ...	1·17	7·1	13·2	...	...	...
600 ...	1·20	7·0	12·6	1·50	8·8	15·9
630 ...	1·20	7·0	12·1	...	8·6	14·8
660 ...	1·17	7·0	11·5	1·59	...	...
680 ...	1·20	7·3	11·8	..	...	...

rotation and ellipticity to the thickness is considered. Table X. gives these for the two films represented in Table IX. Both possess about the same rotatory power which is three times that of the electrolytic films. The ratio of ellipticity to the thickness is also two to three times as large in the metallic type as in the electrolytic.

The results in Table X. and corresponding curves in fig. 9 show that the ellipticity is not proportional to the thickness, if the two films are of exactly the same type. This inconsistency becomes more marked with thinner films, and leads to the suggestion (discussed below) that an observable part of the ellipticity of the transmitted light arises from reflexion effects, an explanation put forward by Righi * for the existence of ellipticity in the transmitted light.

Table X. also gives the transmission measurements on two films (Nos. 11 and 16) from which the extinction coefficients in the adjacent column are calculated. The transmission curve of film 11 is plotted in fig. 8. It reveals only a slightly greater transparency in the red over that in the blue. The extinction curve, plotted in fig. 9, is practically straight and nearly horizontal. Compared with electrolytic films the extinction here is about five times the magnitude obtained from them.

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* Righi, *Mem. R. Accad. Sc. d. Bologna*, 1886, p. 443.

TABLE X.—*Metallic* Iron.

Thickness: No. 11, $15{\cdot}4\times10^{-7}$; No. 15, 19×10^{-7}; No. 16, 7×10^{-7} cm. Field: 13,200 C.G.S.

Wave-length.	$\frac{\text{Rotation}}{\text{Thickness}}\times10^{-3}$.		$\frac{\text{Ellipticity}}{\text{Thickness}}$.		Transmission (per cent.).		Extinct. $\times10^{-6}$.
	No. 11.	No. 15.	No. 11.	No. 15.	No. 11.	No. 16.	
406 ...	520						
417 ...	535	520	12000				
431 ...	550	...	...				
440 ...	570	560	11500	10700			
460 ...	600	...	11200	...			
480 ...	610	640	10700	9800	·88	8·5	3·3
500 ...	690	...	10300	...	·92	9·0	3·3
520 ...	700	680	10000	9200	·97	8·7	3·2
540 ...	690	...	9800	...	1·01	8·6	3·1
560 ...	740	750	9300	8700	1·03	8·9	3·1
580 ...	760	...	9000	...	1·04	9·3	3·2
600 ...	780	790	8700	8300	1·06	9·2	3·1
620 ...	...	...	...	...	1·06	9·2	3·1
630 ...	780	...	8500	8000	...	...	...
640 ...	...	...	...	...	1·04	9·0	3·1
660 ...	760	830	7800	...	1·06	9·1	3·1
680 ...	780	...	8000	...	1·01	8·5	3·1

The variation of both magnetic rotation and ellipticity with field-strength is given, for film 15, in Table XI. The ratio of the mean ellipticity to the mean rotation for those

TABLE XI.—*Metallic* Iron.

Film No. 15.

Field:	2800	2700	5800	5700	7500	7600	13200	13200	15500	15500
Wave-length.	Rot.	Ellipt. $\times10^3$.	Rot.	Ellipt. $\times10^3$.	Rot.	Ellipt. $\times10^3$.	Rot.	Ellipt. $\times10^3$.	Rot.	Ellipt. $\times10^3$.
440...	·29	5·05	·68	10·2	·74	14·5	1·06	20·4	1·17	
480...	·33	4·7	·66	9·6	·86	13·4	1·21	18·7	1·22	
520...	·34	4·5	·72	9·1	·91	12·5	1·30	17·6	1·34	18·2
560...	·40	4·1	·79	8·4	1·00	11·8	1·43	16·6	1·47	17·1
600...	·35	3·9	·79	8·4	1·08	11·2	1·50	15·6	1·52	16·4
630...	...	3·7	...	7·8	...	...	...	14·6	...	15·1
660...	·40	...	·82	...	1·13	...	1·58	...	1·65	
Ratio of Means	11·8		11·4		11·8		11·8		11·3	

wave-lengths for which values were obtained for all fields, is given at the bottom of the table (corrections having first been made for difference in field-strength). As with both the *dark* and the *electrolytic* types, this shows also the ellipticity proportional to the rotation, hence we assume it to be proportional to the magnetization of the iron.

Fig. 10 shows the variation in magnetic rotation of the three types of films with the strength of field. The curves for *electrolytic* and *metallic* films (plotted from Tables VII. and XI.) are quite parallel; that for the *dark* (Table III.) reaches practically a maximum magnitude at an intensity as low as 5000 lines, though the others still show an observable increase at 15,000.

The effect of reflexion in a magnetic field is given for film 15 in the following table:—

Table XII.

Field: 13,200 c.g.s.

Wave-length	440	480	520	560	600	660	680
Rotation (deg.)	−·12	−·12	−·13	−·12	−·11	−·15	−·13
Ellipticity × 10^3 ...	...	−2·34	−2·20	−2·12	−2·16	−1·92	−2·01

The rotation and ellipticity are both negative, as found in the case of electrolytic films, the rotation in both being of about the same magnitude.

The ellipticity of the *metallic* type (which was found to be the same on both air and glass faces of the film) decreases slightly with increasing wave-length, and averages about four times that obtained from the electrolytic type. The results in Table XII. are plotted in fig. 8.

9. *Elliptic Polarization produced by Transmission should be Proportional to the Thickness.*

It may be easily proved that any ellipticity arising from differential absorption, of the two circular components into which the light is assumed to be resolved, should, for the magnitudes observed here, be simply proportional to the thickness of the film.

Let A_r and A_l be the amplitudes of the "right" and "left" vibrations respectively. These superposed produce an elliptic vibration whose major axis is twice their sum, and minor axis twice their difference. The ratio of minor to major axis is then

$$E=\frac{A_r-A_l}{A_r+A_l}.$$

This we designate the ellipticity of the vibration. If A_r and A_l be equal we have zero ellipticity, a plane vibration. After passing a distance x through a medium possessing the extinction coefficients k_r and k_l (defined in terms of the amplitude) the two vibrations will have the amplitudes respectively

$$A_r e^{-k_r x} \quad \text{and} \quad A_l e^{-k_l x},$$

and will combine to form an elliptic vibration possessing as ratio between the axes the value

$$E=\frac{A_r e^{-k_r x}-A_l e^{-k_l x}}{A_r e^{-k_r x}+A_l e^{-k_l x}}.$$

For A_r and A_l equal, which is the case at the incident face of the film, when there is no ellipticity of the reflected light, this equation readily takes the form

$$E=\frac{e^{+\frac{k_l-k_r}{2}x}-e^{-\frac{k_l-k_r}{2}x}}{e^{+\frac{k_l-k_r}{2}x}+e^{-\frac{k_l-k_r}{2}x}}$$

$$=\tanh\frac{k_l-k_r}{2}x.$$

For values of $E \overline{\gtrless}$ ·15 we may write this (within an error of less than one per cent.)

$$E=\frac{k_l-k_r}{2}x.$$

Within the accuracy of our measurements (which do not exceed an ellipticity of ·02) *the ellipticity arising from differential absorption in the films should therefore be proportional to their thickness.* For those films in which the ellipticity is proportional to the thickness, the tabulated values of the ellipticity divided by the thickness represent therefore $\frac{k_l-k_r}{2}$.

10. *Effect of Elliptic Polarization by Reflexion on that of the Transmitted Component.*

Let R_r^2 and R_l^2 be the ratio of the intensity of the reflected light to the incident for the "right" and "left" components respectively. The corresponding ratio of amplitudes will then be R_r and R_l. The ellipticity of the reflected light when the incident is plane polarized is therefore

$$E_R = \frac{R_r - R_l}{R_r + R_l}.$$

In the measurements given this ellipticity is a very small quantity, that is $R_r - R_l$ is small. Since the reflexion in a magnetic field is not appreciably different from that without it, we may also consider $R_r + R_l = 2R$, in which R^2 is the reflexion coefficient of the metal as commonly determined. The above ellipticity then becomes

$$E_R = \frac{1}{R} \cdot \frac{R_r - R_l}{2}.$$

The ellipticity of the penetrating component is given by

$$E_P = \frac{(1-R_r^2)^{\frac{1}{2}} - (1-R_l^2)^{\frac{1}{2}}}{(1-R_r^2)^{\frac{1}{2}} + (1-R_l^2)^{\frac{1}{2}}},$$

which becomes, by substituting R as above,

$1-R^2$ for $(1-R_r^2)^{\frac{1}{2}}(1-R_l^2)^{\frac{1}{2}}$, and $2R^2$ for $R_r^2+R_l^2$:

$$E_P = -\frac{R_r^2 - R_l^2}{4(1-R^2)}$$

$$= -\frac{R^2}{1-R^2} E_R.$$

For the magnitudes dealt with in this investigation the ellipticity of the transmitted light is obtained by simply adding to the ellipticity produced by differential absorption that produced by differential reflexion. Assuming that the effect of reflexion at both air and glass surfaces of the film is the same, as indicated by the results obtained from film 15 (p. 852), we have for the ellipticity of the transmitted light

$$E_T = E + 2E_P$$

$$= \frac{1}{2}(k_l - k_r)x - 2\frac{R^2}{1-R^2} E_R.$$

By measuring E_T, E_R, R^2, and x the difference of the absorption coefficients $(k_l - k_r)$ may be calculated from this equation. By measuring E_T and x for two films of different thickness the term containing R^2 and E_R may be eliminated.

To test this formula a series of very careful observations were made on three different films, of which the mean results are given in the following table, the "right" vibration being given the positive value:—

TABLE XIII.

Wave-length, 500 $\mu\mu$. Field-strength, 13,600.

Film.	Double Rotation.	Thickness (calc.).	Ellipt. $\times 10^3$.	$\frac{k_l - k_r}{2}$.
16	·99	$7{\cdot}5 \times 10^{-7}$	9·41	$9{\cdot}0 \times 10^3$
11	2·21	16·6 ,,	16·1	8·0 ,,
15	2·61	19·6 ,,	18·8	8·1 ,,

The above values of $\frac{k_l - k_r}{2}$ are calculated by using $E_R = -2{\cdot}07 \times 10^{-3}$ and $R^2 = {\cdot}37$, as found in the case of film 15. By eliminating these last two quantities, however, films 16 and 11 give $7{\cdot}3 \times 10^3$; films 16 and 15, $7{\cdot}8 \times 10^3$; and films 11 and 15, $9{\cdot}1 \times 10^3$ as values for the same expression. The two methods give results which agree as well as the experimental conditions warrant.

11. *Light transmitted at Right Angles to the Magnetic Field.*

To test the possibility of the optical effects in the magnetic field being produced by the presence of free ions (as in the Hall effect), light plane-polarized at an azimuth of forty-five degrees to the field was sent at right angles to the field through the film, and tested for the presence of elliptic polarization. Film 15 was used for this test as it gave the largest effects in the foregoing experiments. *No ellipticity could be detected,* although about one per cent. of that produced on the light transmitted along the lines of force could have been seen.

12. *Dark* Cobalt.

Cobalt films, designated from their appearance by reflected light as *dark,* were obtained in the same manner as the corresponding of iron, that is, deposited from the cathode in hydrogen under a comparatively low current-density. Compared with iron, they are remarkedly transparent but correspondingly less active in the magnetic field. Fig. 11 (Pl. XXIV.) gives curves for the magnetic rotation and ellipticity of two different films, 1870×10^{-7} and 3470×10^{-7} cm. thick respectively. They are strikingly different from all other types of films investigated. The rotation is positive but decreases with increasing wave-length; the ellipticity is negative throughout and increases in magnitude with increasing wave-length. On comparing these curves with those of dark iron (fig. 4) we are inclined to think that the latter would take this form in the region of the spectrum below about 380 $\mu\mu$.

Table XIV. contains the values of magnetic rotation and ellipticity divided by the thickness (plotted in figure 12), and of the transmission of the two films. The rotation is proportional to the thickness, but the ellipticity increases more rapidly than the thickness. Were this caused by elliptic polarization of the reflected light, this latter should be over 4.10^{-3}, but a test revealed that one-fortieth of that magnitude was not present. This indicates that the

TABLE XIV.—*Dark* Cobalt.

Thickness: No. 2, 1870×10^{-7}; No. 3, 3470×10^{-7} cm.
Field: 14,000 C.G.S.

Wave-length.	$\frac{\text{Rotation}}{\text{Thickness}} \times 10^{-3}$.		$\frac{\text{Ellipticity}}{\text{Thickness}}$.		Transmission (per cent.).		Extinct. $\times 10^{-3}$.	Refrac. Index.
	No. 2.	No. 3.	No. 2.	No. 3.	No. 2.	No. 3.		
440	...	1·37	...	...	·5	...	...	1·98
460	...	1·28	− 7·6	− 9·2	·7	·2	...	1·99
480	1·01	1·17	− 6·4	− 9·7	1·0	·2	10·2	1·98
500	1·10	1·07	− 7·6	−10·2	1·5	·3	9·6	1·96
520	1·07	1·05	− 7·0	−11·7	2·1	·5	9·0	1·96
540	·96	·97	− 8·0	−12·2	3·1	·75	8·6	1·96
560	·88	·97	− 8·8	−11·8	4·0	1·1	8·1	1·96
580	·91	·91	− 9·2	−12·8	5·0	1·3	7·6	1·94
600	·94	·89	−10·0	−13·2	6·5	2·0	6·9	1·98
620	...	...	...	...	8·7	2·9	6·7	...
630	·70	·80	− 9·6	−13·5	...	...	...	1·94
640	...	...	...	...	10·6	3·7	6·3	...
660	·61	·76	−10·0	−14·2	11·5	4·0	6·1	1·94
680	...	...	...	...	10·7	5·4	5·6	...
690	·60	·61	...	−14·8	...	...	...	1·94

differential absorption coefficient $(k_r - k_l)$ was not the same in the two films.

The coefficients of extinction and the refractive indices of these films are also given in Table XIV. and plotted in fig. 12. The extinction is much less than that of *dark* iron, and also increases much less rapidly with decreasing wave-lengths. The refractive index rises very slightly in passing from red to blue.

13. *Electrolytic* Cobalt.

Films of electrolytic cobalt were deposited on platinized glass from a solution of cobalt-ammonium-sulphate. They proved remarkably more active in a magnetic field than those of Lobach (*l. c.*). Our experience showed that the concentration of the solution and the rate of deposit affects the hardness of the electrolytic films of both iron and cobalt, and we are inclined to believe that it also affects their magnetic activity as well, though this was not tested. These films hold less closely to a definite type than either the *dark* or the *metallic* films.

Two thick films were produced for the purpose of obtaining their rotatory power for the brightest region of the spectrum. The measurements are given in the following table.

TABLE XV.

Wave-length, 520 $\mu\mu$. Field, 13,600 C.G.S.

Film.	Thickness $\times 10^7$ (cm.).			Rotation.	$\frac{\text{Rotation}}{\text{Thickness}}$.
	Pt + Co.	Pt. (approx.).	Co.		
30	76	6	70	2·31	330,000
32	66	6	60	1·80	300,000

The mean of these values of the rotation divided by the thickness was used for determining the thickness of the other films studied.

Table XVI. contains results from film 31 possessing a thickness of 31×10^{-7} cm. The quantitative results from different films did not agree well enough to warrant a more extended study, especially in reference to their elliptic polarization. Two films as measured gave the same value for ellipticity while their rotation differed by more than thirty per cent. The results from film 31 are, however, typical as regards the variation with wave-length. The curves are given in fig. 13 (Pl. XXIV.). The rotatory power as shown in the table is more than double that obtained by Lobach.

TABLE XVI.—*Electrolytic* Cobalt.

Thickness, 31×10^{-7} cm. Field, 13,500 C.G.S.

Wave-length.	Rotation (deg.).	Ellipticity $\times 13^3$.	$\frac{\text{Rotat.}}{\text{Thick.}} \times 10^{-5}$.	Extinction $\times 10^{-5}$.
440	·94	9·6	3·03	
480	·99	9·5	3·19	9·0
500	......	......	......	9·0
520	1·00	8·9	3·23	9·1
540	......	......	......	9·0
560	1·10	8·4	3·55	8·9
580	......	......	......	9·0
600	1·19	7·4	3·84	8·9
620	......	......	......	8·7
630	1·22	6·6	3·94	...
640	......	......	......	8·8
660	1·25	5·7	4·03	8·9

The extinction (also more than twice that given by Lobach) was obtained in the same manner as that of electrolytic iron, by measuring the transmission of a film of definite thickness, then depositing over this and repeating the measurements. The results as given are the mean of two sets obtained from different films. The extinction curve (fig. 13) is flatter than that of electrolytic iron. The form of the ellipticity curve appears to indicate also that the absorption region is effectively farther out in the ultra-violet than that of the iron. The difference in the results from this form of cobalt and the *dark* is nearly as striking as that between the corresponding types of iron.

14. *Metallic* Cobalt.

Films of cobalt designated as *metallic* were readily obtained by deposit from a very hot cathode with a glow current through hydrogen. Like iron they are brilliant mirrors, though for the same thickness much more transparent. Also like the iron they impart no tint to transmitted light.

In figure 14 are plotted the curves of rotation, ellipticity, transmission, and rotation by reflexion of a representative film. Only a slight trace of ellipticity by reflexion was observed. The forms of the curves are very similar to those of the corresponding type of iron (fig. 8).

Table XVII. and figure 15 embody the results from two films, one of measured thickness (48×10^{-7} cm.), the other calculated from its magnetic rotation (24×10^{-7} cm.). The results show that the ellipticity is proportional to the thickness, as should be expected since there is no appreciable ellipticity in the reflected light. The extinction values are found to be only about one-third those of the corresponding type of iron. The refractive indices as given were obtained from one series of observations. They could be only approximately determined owing to the small magnitudes involved. They are about fifty per cent. higher than those of *dark* cobalt, and like them remain about the same value throughout the spectrum.

Table XVII.—*Metallic* Cobalt.

Thickness: No. 7, 48×10^{-7}; No. 8, 24×10^{-7} cm.
Field: 14,000 C.G.S.

Wave-length.	$\frac{\text{Rotation}}{\text{Thickness}} \times 10^{-5}$		$\frac{\text{Ellipticity}}{\text{Thickness}}$.		Transmission (per cent.).		Extinct. $\times 10^{-6}$.	Refrac. Index.
	No. 7.	No. 8.	No. 7.	No. 8.	No. 7.	No. 8.		
440	......	5·6	......	5050	......	1·9		
460	5·6	5·8	4800	4800	......	2·0		
480	......	5·8	......	4600	......	2·1		
500	5·7	5·8	4400	4450	·17	2·2	1·11	2·8
520	......	5·9	......	4300	·19	2·3	1·08	2·8
540	6·0	6·0	3960	4100	·20	2·3	1·06	3·2
560	......	6·2	......	3850	·22	2·5	1·05	3·3
580	6·3	6·3	3740	3780	·23	2·6	1·05	3·6
600	......	6·4	......	3430	·25	2·6	1·02	3·1
620	......	......	......	......	·27	2·7	1·00	3·2
630	6·8	6·6	......	3200	......	......	......	......
640	......	......	......	......	·29	2·8	0·98	2·7
660	......	6·8	......	2880	·30	2·9	0·98	3·1

15. *Nickel.*

As already stated only electrolytic nickel showed more than a mere trace of optical activity in the magnetic field. This is rather remarkable, for brilliant nickel mirrors are produced by the glow current, and by varying the temperature, films of any hardness, all of which show metallic reflexion, may be obtained.

Table XVIII. (p. 860) contains the results obtained from two different films of electrolytic nickel, one (No. 40) possessing a measured thickness of 71×10^{-7} cm., the other (No. 41) a calculated thickness of $37 \cdot 4 \times 10^{-7}$. The thickness of the second film, as calculated from its rotation, is considered

Table XVIII.—*Electrolytic* Nickel.

Thickness: No. 40, 71×10^{-7} cm. (meas.);
No. 41, $37{\cdot}4\times10^{-7}$ cm. (calc.).
Field: 13,800 c.g.s.

Wave-length.	No. 40.			No. 41.			Extinct. $\times10^{-6}$.
	Rot.	$\frac{\text{Rotat.}}{\text{Thick.}}\times10^{-5}$.	Ellipt. $\times10^3$.	Rot.	$\frac{\text{Rotat.}}{\text{Thick.}}\times10^{-5}$.	Ellipt. $\times10^3$.	
440	·74	1·04	......	·41	1·10		
480	·85	1·20	......	·42	1·12	9·7	1·82
520	·90	1·27	12·7	·47	1·27	9·2	1·82
560	·99	1·39	......	·50	1·34	9·0	1·83
600	1·07	1·51	......	·55	1·48	8·9	1·84
630	......	......	......	·61	1·65	9·0	......
640	......	......	......	......	......	......	1·87

reliable because this ratio is practically the same for all colours. The ellipticity is evidently not proportional to the thickness, shown by comparing the values obtained from the two films at a wave-length of 520 $\mu\mu$. A third film (No. 42) was deposited somewhat differently from the others and tested for magnetic rotation and ellipticity. The results are found in Table XIX. The thickness measured was 35×10^{-7} cm. It may be noted by comparison with film No. 41 of the preceding table that while the rotation of 42 is greater than that of 41, its ellipticity is somewhat smaller. A more striking difference is observed on comparing the rotatory power of the two films. No. 42 exhibits on the average fifty

Table XIX.—*Electrolytic* Nickel.

Thickness, 35×10^{-7} cm. (meas.). Field, 13,800 c.g.s.

Wave-length.	Rotation (deg.).	$\frac{\text{Rotation}}{\text{Thickness}}\times10^{-5}$.	Ellipticity $\times10^3$.
440	·52	1·50	9·1
480	·57	1·64	8·6
520	·55	1·57	8·9
560	·63	1·80	8·8
600	·72	2·06	9·2
630	·79	2·23	

per cent. greater values for the rotation divided by the thickness than No. 41. The magnitudes of both are again, as in iron and cobalt, greatly in excess of those obtained by Lobach for the corresponding type of films.

The extinction coefficients recorded in Table XVIII. were obtained by measuring the transmission and magnetic rotation of a thin deposit, then depositing over this and repeating the measurements. The thickness was calculated from the mean rotatory power of films 41 and 42, hence the values obtained for the extinction are consequently of questionable accuracy.

16. *Summary and Conclusions.*

(*a*) Three types of both iron and cobalt have been investigated with respect to their magneto-optical activity, their optical extinction, and also in part their refractive indices and reflexion. These types are found to differ essentially in the period of their optical resonance; and further also in the magnitude of their optical extinction, which appears to be largely a friction phenomenon. In the *dark* type the resonance region is in or very near the visible spectrum, so that *dark* iron gives a marked anomaly in both magnetic rotation and ellipticity; and *dark* cobalt gives curves for the same of such a form as to suggest, when combined with those of the *dark* iron, the typical form of the rotation and ellipticity on both sides of the resonance region. These hypothetical curves possess positive values for the magnetic rotation outside the resonance region changing through zero to negative within it; and negative ellipticity in the region of periods shorter than that of resonance, changing to positive in the region of longer periods. The rotation increases toward a maximum value on leaving the resonance region in both directions; the ellipticity increases to a maximum magnitude, then appears to decrease asymptotically toward zero on both sides. The hypothetical rotation curve appears to have the general form of that given by Elias * for erbium chloride, but with values opposite in sign.

(*b*) No corresponding anomaly exists in the refractive index curves, leading to the conclusion that the ions producing magnetic anomaly do not appreciably contribute to the refractive index.

(*c*) In the *electrolytic* films the magneto-optical effects indicate that the resonance region lies in the ultra-violet. The magnetic rotatory power, the differential optical

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* *Physik. Zeitschr.* ix. p. 931 (1906).

extinction in the magnetic field, and the optical extinction of these films are all many times larger than those of the dark type. These properties also vary considerably in magnitude with different samples.

(*d*) In the *metallic* films the shift of the resonance region into the ultra-violet, the magnitudes of the magneto-optical properties, and the optical extinction are again all greater than in the *electrolytic*.

(*e*) There appears to be a relation between the granular structure of these films and their period of resonance. Electrolytically deposited metals are known to be granular. The *dark* films are far softer and less tenacious than these. It is therefore natural to suppose them to be made up of larger structural units. The metallic films, on the other hand, produced by cathode sublimation, appear more like the fused metal. Their structure should be of smaller units than either of the other types; they should therefore possess the shortest period of resonance, as the results seem to indicate.

(*f*) All films giving magnetic rotation impart also, under the same conditions, ellipticity to the transmitted light. In some cases an ellipticity was observed in the reflected light. Like the magnetic rotation, the ellipticity produced is proportional to the magnetization of the medium.

Eliminating the ellipticity arising from reflexion, that of the transmitted light was found in several cases to be proportional to the thickness of the film. The exceptions to this rule are considered to arise from a difference in structure of the films.

No ellipticity was observed in cases of light transmitted at right angles to the magnetic field.

(*g*) Films of electrolytic nickel showed marked magneto-optical properties, those obtained from the cathode *in vacuo* scarcely a trace.

(*h*) The extinction coefficients of both *electrolytic* and metallic films are greatly in excess of those obtained by other observers.

(*i*) Existing theories do not appear to lend themselves to explain the results obtained.

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DIFFUSION
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LXXIV. *On the Coefficient of Diffusion.* By Basil W. Clack, *B.Sc., Lecturer in Physics at Birkbeck College*[*].

[Plate XXV.]

1. *Introduction.*

THE following paper contains an account of a series of experiments on the diffusion of various salts through water. The objects with which they were undertaken were:—

1st. To test the practicability of a new method for the determination of the coefficient of diffusion;

2nd. To find how the value of the coefficient varies with the concentration of the solution.

Various methods have been employed from time to time to determine the value of the coefficient of diffusion. In some cases careful chemical analyses are necessary to obtain the amount of the substance diffused; in others it is the density of the solution which must be accurately determined at different points. Graham's, and kindred methods, involve serious disturbance of the solution in commencing an experiment, and also in withdrawing the various specimen layers for analysis.

The present investigation may be called a gravitational method, since the amount of the substance diffused is determined by means of the balance; but the method employed involves little disturbance at the commencement of an experiment, and during its progress the disturbance is quite negligible. Moreover, neither a series of density determinations nor of chemical analyses is required to obtain the amount of diffusion which has taken place.

The method may be looked upon as an extension of that employed by Fick (Pogg. *Ann.* xciv. p. 59, 1855) and by Graham, but the method of obtaining the quantity of salt diffused is essentially different, as they determined this amount by chemical analysis.

Again, it does not appear that Fick took any account of

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[*] Communicated by the Physical Society: read May 22, 1908.

CLACK.

FIG. 4.

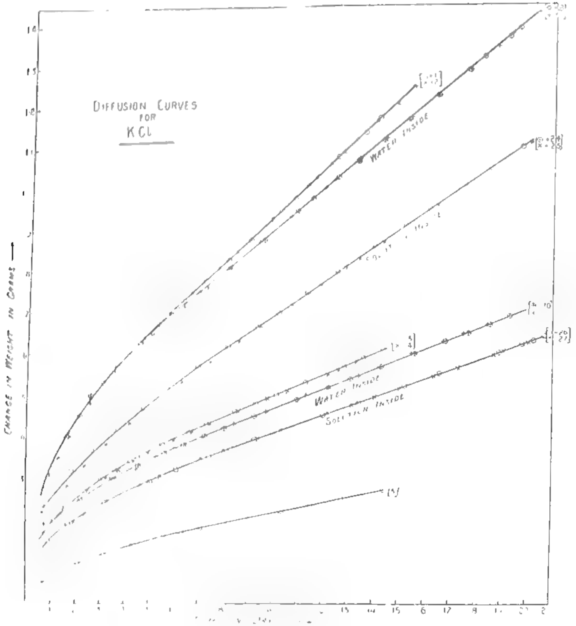


FIG. 5.

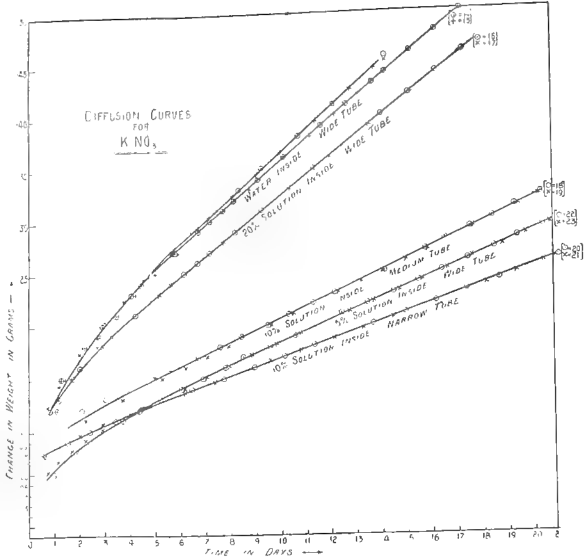
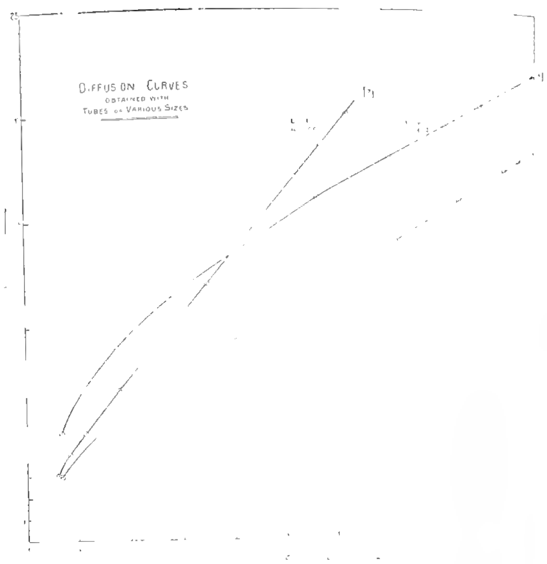


FIG. 6.

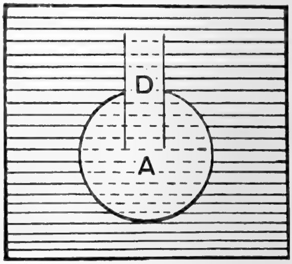


the effect of the movement of the liquid along the tube, mentioned in the next section, on the quantity diffused. Although this omission would produce less effect in his method than in that about to be described, it would nevertheless cause a measurable difference in the calculated value of the coefficient of diffusion.

2. *Theory.*

In the diagram (fig. 1) let A represent a spherical vessel, to the upper side of which is fitted a vertical tube D of unit cross-section.

Fig. 1.



Suppose the bulb A and the tube D to be initially filled with a salt solution of uniform density, and to be suspended in a vessel containing pure water. Further, let it be assumed that the upper end of D is maintained in contact with pure water, and that the concentration of the salt solution at the lower end is also kept constant.

Under these conditions the salt will commence to diffuse up the tube D, and ultimately the diffusion current thus commenced will be found to become uniform.

Now when the steady state has been attained the quantities of water and of salt in tube D remain constant, and in dealing with variations in volume and weight we may confine our attention to the bulb A. When salt leaves A the volume of the liquid originally in it will decrease, since in general the addition of salt to water increases the resultant volume. Hence some of the water outside A will enter the apparatus on account of this decrease in volume, with the result that as the salt diffuses up the tube D it meets a current of liquid which continually passes downwards, and which is due to the decrease in volume mentioned.

The weight of the suspended bulb A will decrease on account of the salt which leaves it, and will increase owing to the water which enters, and the resultant loss in weight is equal to the difference between the two.

Let d=density of solution at a point l cms. from top of tube D.

v=velocity downwards at the same point.

n=concentration in gms. per c.c. at the same point.

v_0=velocity downwards at top of tube where $l=0$.

N=concentration in gms. per c.c. at the end of tube where $l=\mathrm{L}$.

With the degree of accuracy obtained in the present work, it is found sufficiently correct to assume $d=1+an$ where a is some constant.

Since the same mass of water crosses each section of the tube

$$v(d-n)=v_0,$$

i. e. $$v(1-bn)=v_0, \text{ where } b=1-a. \quad . \quad . \quad . \qquad \text{(i.)}$$

Now when the steady state is reached, the weight of salt which flows through each cross-section of the tube per second is constant$=c$, say

i. e. $-vn+k\dfrac{dn}{dl}=c$, a constant, where $k=$coeff. of diffusion;

or $$-\frac{v_0n}{1-bn}+k\frac{dn}{dl}=c.$$

The solution of this equation is

$$-\frac{bN}{v_0-bc}+\frac{v_0}{(v_0-bc)^2}\log_e\frac{(v_0-bc)N+c}{c}=\frac{L}{k}, \quad . \qquad \text{(ii.)}$$

which, as $(v_0-bc)N$ is small compared with c, reduces to

$$\frac{N}{c}\left(1-\frac{v_0N}{2c}+\frac{v_0(v_0-bc)N^2}{3c^2}\ldots\right)=\frac{L}{k}. \quad . \quad . \quad . \qquad \text{(iii.)}$$

As already stated, there will be a contraction in volume produced in the vessel A when salt leaves it, and a corresponding movement downwards will take place in the liquid in the tube D. The amount of water which enters the bulb owing to this movement may be calculated as follows:—

Mass of water in 1 c.c. of solution at bottom of tube D
$=$density of solution at bottom minus concentration of solution at bottom.
$=1+aN-N$,
$=1-(1-a)N$,
$=1-bN$.

Let $\delta=$ the ratio of the increment in volume produced to the increment in the mass of salt dissolved, for a solution of the strength employed in the bulb A; *i. e.* the increase in volume produced when 1 gram of salt is dissolved in a solution of the given concentration, the amount of the solution being so great that the addition of the salt makes no appreciable change in the concentration. The mass of water which enters the bulb due to a small diminution (dm) in the mas (m) of salt in the bulb

$$=\delta\times(1-b\mathrm{N})dm.$$

On integrating, the mass of water which enters the bulb due to a given diminution

$$=\int_{m_1}^{m_2}\delta\times(1-b\mathrm{N})dm.$$

Strictly both δ and N are functions of m, but the change in m is so small that they may both be taken as constants; thus the integral is equal to

$$\delta\times(1-b\mathrm{N})(m_2-m_1).$$

Now in one second $\quad (m_2-m_1)=c.$

Hence the mass of water entering the bulb per second

$$=\delta\times(1-b\mathrm{N})c.$$

Now the decrease, i, in weight per second of the bulb = the weight of salt leaving per second minus the weight of water entering per second; or in symbols

$$i=c-c\delta(1-b\mathrm{N}),$$

$$\text{i. e.}\qquad c=\frac{i}{1-\delta(1-b\mathrm{N})}.$$

Again, the volume of water entering per second, $c\delta$, is equal to the velocity of the liquid at the bottom of the tube

$$=\frac{v_0}{1-b\mathrm{N}}, \quad . \quad . \quad . \quad . \quad \text{(from i.)}$$

$$\therefore\ \frac{v_0\mathrm{N}}{2c}=\frac{\mathrm{N}\delta}{2}(1-b\mathrm{N}).$$

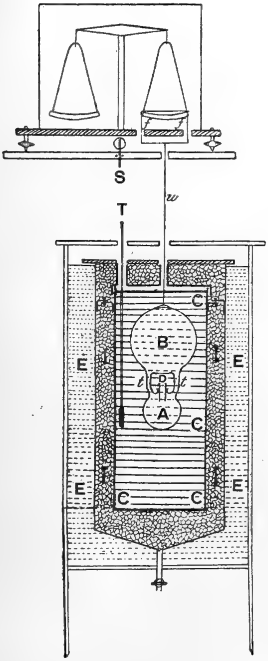
Again, the third term in the bracket in equation iii. is found to be negligibly small; hence this equation is written for practical use

$$k=\frac{\mathrm{L}i}{\mathrm{N}\left\{1-\frac{\mathrm{N}\delta}{2}(1-b\mathrm{N})\right\}\left\{1-\delta(1-b\mathrm{N})\right\}} \quad . \quad . \quad \text{(iv.)}$$

3. *Apparatus.*

A and B are two hollow spherical glass bulbs respectively 5 cms. and 9 cms. in diameter, connected together as shown by two parallel glass quill-tubes *t*, *t* (fig. 2).

Fig. 2.



On the upper side of A the bulb is pierced by an aperture into which the diffusion-tube D is hermetically sealed.

The ends of this tube were ground off perfectly plane and perpendicular to its axis, and its dimensions were, in most of the experiments, 4 cms. long, and 1·694 sq. cms. in cross-section.

The complete apparatus AB was filled with the solution under investigation, and suspended in a cylindrical copper vessel C of about 7 litres capacity, containing distilled water, the temperature of which may be kept constant by means of a surrounding ice-jacket I, protected by a layer of cork-dust E, several inches thick. The mercury thermometer T had a small range on each side of 0° C. and was divided into $\frac{1}{100}$° C.

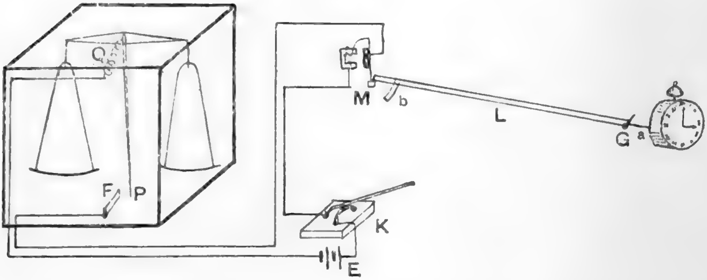
The Sartorius balance used was mounted upon a slate shelf firmly cemented into the stone wall of the laboratory.

Two holes were sand-blasted through the base of the balance-case, and a light frame, *f f*, passed through them as shown, and to this was attached a fine wire *w* which, passing through a third hole, in the slate shelf, sustained the apparatus already described. The movement of the balance beam was limited by means of stops shown at *s*, so that the pointer could only move over 1 scale-division, and the vertical movement which this permitted to the suspended system was only ·12 mm., so that any disturbance which might arise from this small and very slow movement will be quite negligible.

4. *Method of Experiment.*

As the salt diffuses up the tube, the stronger solution in the upper larger bulb, B, sinks by gravity, by means of the side tubes *t t*, and maintains the initial concentration of the solution at the lower end of the tube D; while the upper end is in contact with such a large volume of water that it may be considered to remain practically pure. The conditions studied in § 2 thus apply, and as diffusion proceeds the weight of the suspended system will decrease. If, then, a slightly deficient weight be placed in the opposite scale-pan, the beam will turn until it reaches the supports. As time proceeds, however, the weight of the apparatus will ultimately become equal to that on the balance-pan, and the pointer will move to the zero of its scale. An automatic device was designed which would register the exact time at which this occurred. A very fine platinum wire P (fig. 3) was soldered on to the lower end of the balance-pointer, and when the beam is in equilibrium, P makes contact with a fine strip of platinum-foil F, suitably mounted opposite the zero of the balance-scale. A delicate phosphor-bronze strip Q, such as is employed for galvanometer suspensions, served to connect the upper end of the pointer to a battery E, which was connected in series with a mercury lever-switch K, and an electromagnetic trigger M.

Fig. 3.



On contact being made between P and F the armature of the trigger is attracted, thus allowing a light wooden lath L, which is resting upon the trigger, to fall. This lath is pivoted at G, and is provided at this end with a flexible copper strip *a*, which, as the lath falls, is brought into contact with the balance-wheel of a common alarm-clock, from which the back has been removed, and which is suitably placed on the table.

The clock is thus stopped at the exact time at which the pointer reached the zero of the balance-scale.

In its fall another copper strip *b*, attached to the lath, knocks over the mercury switch K, and thus breaks the electric circuit.

The time recorded by the clock and the corresponding mass on the pan of the balance are recorded in tables, and from these the graphs following have been drawn.

A slightly smaller mass is then placed on the pan. The lath is replaced on the trigger, the clock reset and restarted, and the key K switched on, and the whole process repeated. This method, involving the determination of the time required for a given decrease in weight to take place, has an advantage over the converse process, in that it causes far less disturbance in the solution, and hence it has been adopted in the present investigation.

Another precaution which should be mentioned is that, the arrangement employed being extremely sensitive to changes in density, great care must be taken to prevent any but minute changes in temperature occurring in the solution.

The large amount of damping introduced, and the effect of the surface-tension of the liquid, prevented any accurate work being done until the effect of a film of oil on the surface of the solution was tested. This greatly reduces the surface-tension, and increases the accuracy of weighing to a remarkable extent. Of a large number of oils tested, Fleuss pump-oil was found to be superior to any of the others, in that it always remained quite fluid.

As showing the effect of this oil-film a few figures might be quoted.

The apparatus was filled with water and suspended in water at a constant temperature. If set in oscillation, in no case would the balance-beam make more than two swings, and the resting place varied in different attempts between 10 and 15 on the scale for the same mass in the pan. Two drops of Fleuss pump-oil allowed to fall on the liquid near the suspending wire made a remarkable difference. Five turning-points could now be easily obtained, and assuming the ratio between any two consecutive deflexions to be constant, great consistency was found between the calculated positions of the resting place of the balance. For example,

Turning Points.		Resting Points.
20·8		10·0
	3·2	
14·4		10·2
	7·8	
11·5		10·1
		10·2
19·1		10·3
	4·7	
13·8		10·0
	8·1	
11·0		

Now in the diffusion experiments the beam does not oscillate, but slowly takes up its new position. The consistency obtained under these static conditions was tested, and the following is a sample of the figures obtained:—

Mass on pan in gms..........	37·105	37·104	37·103	37·105
Resting Point observed ...	10·2	11·9	13·5	10·0
Repeated.				
Resting Point observed ...	10·0	12·0	13·9	10·2

Moreover, it was found that the position of the pointer remained constant to within 1 scale-division for a week, the temperature being meanwhile kept at 0° C. by the surrounding ice-jacket.

The sensitiveness of the balance under the actual conditions holding in a diffusion experiment was found from a large number of readings to be ·00052 gm. per scale-division, *i. e.* a movement of 1 scale-division in the resting point was produced by ·00052 gm.

5. *Determination of the Concentration.*

Sodium chloride and potassium chloride prepared by Kahlbaum, of Berlin, were the first salts experimented upon. Solutions were prepared of approximately 0·2 gm., 0·1 gm., and 0·05 gm. of salt per c.c. of the solution, and in each case a check experiment was carried out to ensure experimental consistency. The concentration of these solutions was determined in most cases by three different methods: (1) From the density, making use of the results given in the *Physikalisch-Chemische Tabellen*, published by Landolt and Börnstein; (2) Precipitation by $AgNO_3$; (3) Evaporation to dryness in a platinum crucible.

The results obtained by all three methods usually agreed to within less than 1 per cent., as the following figures will show:—

Values of N in gms. of KCl per c.c. of Solution at 0° C.

Solution	2.	3.	4.	5.	6.	7.
By Density	·1990	·1009	·1004	·05122	·05147	·05106
By Precipitation ...	·1989	...	·1004	·05128	·05106	·05092
By Evaporation ...	·1988	·1008	·1004	·05100	·05097	·05113
Mean	·1989	·1008	·1004	·05117	·05117	·05104

The densities were obtained in the first place at the temperature of the laboratory; but the concentrations have been calculated at 0° C., the temperature of the experiments, by means of a determination of the absolute coefficient of expansion of the several solutions over this range of temperature, using for this purpose apparatus identical in principle with that employed by Dulong and Petit for a similar purpose.

6. *Determination of* δ.

It has been long known that when salts enter into solution, a change usually takes place in the volume occupied by the solvent.

F. Kohlrausch and Hallwachs (Wied. *Ann.* liii. 1894, p. 1) and Thomsen have studied these phenomena and have estimated the change in volume produced in several cases by the determination of the density of the solution formed, when a known mass of salt is dissolved in a known mass of water. W. F. Magie (Phys. Rev. xviii. 1904, pp. 449–452) and Macgregor have endeavoured to express in a formula the results obtained by previous experimenters.

We have seen that in the present investigation the phenomena referred to play an important part, and have deduced an expression for k involving the knowledge of the change in volume which accompanies a slight change in concentration.

Now δ is not a constant, but varies with the strength of the solution, and according to Magie depends on the relationship existing between the volumes occupied by the dissociated and the non-dissociated molecules of salt.

Its value can be easily deduced from the published tables giving the density of salt solutions of known concentration.

7. *Results for* KCl *and* KNO_3.

The accompanying graphs (Pl. XXV.), which are numbered in accordance with the order of the experiments, show some of the curves obtained by plotting the weight of the suspended apparatus against the time as abscissæ.

The curves suggest that the method is at any rate capable of giving fairly consistent results, and they indicate a diminution in the coefficient of diffusion with a decrease in the concentration in the cases of both NaCl and KCl, a result which has been found by several other observers.

The actual figures obtained in this work are omitted for the reason mentioned below.

Before proceeding further, it was decided to test whether the outer vessel containing the salt solution was large enough.

As the salt diffuses up the tube D the water outside becomes slightly denser, but the change in concentration is so small that it does not appreciably affect the quantity of salt diffused up the tube; but the suspended apparatus has such a large volume, that a very slight variation in the density of the water outside has a considerable effect on the hydrostatic force upwards. When the earlier experiments were performed, the importance of this action was not fully appreciated.

It is impossible to calculate the change in the buoyancy of the water, but there is no doubt that the heavier liquid will tend to sink to the bottom, and that then diffusion will tend to make the density uniform. Any variation in the density of the liquid below the suspended apparatus will produce no effect on its weight, and so it is an advantage to have as deep a vessel as possible; to have the suspended apparatus as high as possible in the water; and to have the volume of the water as great as possible.

Experiments similar to the preceding were carried out with a deeper vessel, C C, shown in fig. 2, having also a volume about twice that of the original one, and they proved that the first vessel was undoubtedly too small. For this reason a number of results obtained with the earlier vessel must be discarded. The results given below have all been obtained with the larger vessel.

In the theory it has been assumed that the density of the solution at the bottom of the tube is constant over a horizontal plane, and that this density is the same as that of the mass of the solution in the neighbourhood. It has likewise been assumed that the density at the top of the tube in a horizontal plane is constant, and practically the same as that of pure water. These assumptions would only be strictly true if gravity were infinitely powerful, and in practice one would expect the density at the bottom of the tube to be rather less than that assumed, and at the top rather greater. These deviations from the assumptions will give a calculated value of k smaller than the true one, but even in the worse possible case studied, it can be shown by an approximate calculation that the error introduced is certainly much less than 1 per cent.

The narrower the tube the nearer will the assumptions be to the truth, but a narrow tube permits only a small amount of diffusion to take place.

In order to test whether it was necessary to have a tube of extremely narrow bore three diffusion-tubes were prepared, each 4 cms. long, but of different cross-section, as shown in the table below.

Using 10 per cent. KNO_3 solution, the following results were obtained using these tubes:—

Experiment.	$iA \times 10^6$ Mean Slope.	$k \times 10^5$.	Mean value $k \times 10^5$.	L.	A.
16	·2154	·843	·844	4·00	1·694
17	·2159	·845			
18	·1294	·836	·843	3·990	1·024
19	·1316	·850			
20	·0956	·852	·853	3·993	0·743
21	·0959	·855			

The results obtained, using different tubes, do not vary more than the individual experiments on the same tube, so that for the present at any rate we may neglect any end correction to our tubes of 4 cms. length. The results also suggest that the vessel containing the water is large enough; for, although the quantity of salt diffused into the water varies considerably, the quantity in the last case being less than half that in the first, yet we get approximately the same calculated value for the coefficient of diffusion.

The next table gives the results for 5 per cent. solution of KNO_3.

$L=4·00$ cms.; $A=1·694$ sq. cms. N=gms. KNO_3 per c.c. solution at 0°

Experiment.	N.	$iA \times 10^6$.	$k \times 10^5$.	Mean $k \times 10^5$.
22	·0521	·1174	·870	·871
23	·0521	·1177	·872	

Comparing this result with the value obtained in Experiments 16 and 17 shown in the previous table, we see that the coefficient of diffusion of KNO_3 increases as the concentration decreases, as was noticed by Scheffer in 1888, a phenomenon contrary to that which holds for KCl and NaCl.

The results obtained with solutions of KCl are tabulated below.

L=4·00 cms. A=1·694 sq. cms. N=gms. KCl per c.c. solution at 0° C.

Experiment.	N.	$iA\times10^6$.	$k\times10^5$.	Mean $k\times10^5$.	Approx. concentration.
24	·1975	·4748	·966	·972	20 p. cent.
25	·1975	·4810	·978		
26	·1034	·2518	·953	·954	10 p. cent.
27	·1021	·2491	·956		

8. *Earlier Method of Experiment.*

It might be mentioned that a number of experiments were carried out by a somewhat different method, denoted in the following section as Method A.

The diffusion apparatus, filled with distilled water, was inverted, so that the smaller bulb A (fig. 2) was uppermost, in a solution of the salt under investigation, thus allowing the salt to diffuse into instead of out of the apparatus, and the resultant rate of increase in weight was determined.

Some of the results obtained with solutions of KCl by this method are given in the next table in order to indicate the agreement.

L=4·00 cms. A=1·694 sq. cms. N=gms. KCl per c.c. solution at 0° C.

Experiment.	N.	$iA\times10^6$.	$k\times10^5$.	Mean $k\times10^5$.	Approx. concentration.
8	·1997	·5729	1·011	1·009	20 p. cent.
9	·1997	·5703	1·007		
10	·1014	·2786	·952	·953	10 p. cent.
11	·1016	·2799	·955		

If the results of Experiments 26 and 27 be compared with those of 10 and 11, it will be seen that the agreement in the case of the 10 per cent. solution is almost perfect, but it is not quite so satisfactory in the case of the 20 per cent. solution, for there is a difference of 3 per cent. The actual measurements are believed to be more accurate than this.

Some of the difference may be due to uncertainty in the value of δ, but this would not produce so great an error as 3 per cent. It may be that part of the difference is due to condensation of water from the air on the salt solution in Method A, so that part of the increase in weight of the suspended apparatus may be due to the diminution of buoyancy of the solution, on account of its dilution with this condensed water.

The error produced by this cause would probably not be great, but no quantitative experiments were actually carried out on the subject, as the experience gained in the research convinces us that the first method described in this paper is distinctly superior to Method A.

For this reason no further experiments are being carried out by the earlier Method A.

Some of the points in which the method mentioned in § 4 shows superiority over Method A may be summarized. First, in this better method, the condensation of water mentioned above, instead of being harmful, is even somewhat of an advantage.

Again, this method necessitates the preparation of much smaller amounts of solution; then it requires much less manipulation in commencing an experiment, as the apparatus, filled with the solution and having the open tube temporarily closed by a thin glass plate, may be simply lowered into the cooled distilled water.

Instead of this simple process, in the Method A in commencing an experiment, the solution under investigation was slowly run in through a glass tube passing to the bottom of the vessel C (fig. 2), while the distilled water, which is thus displaced, was removed from the top by means of a syphon. Great care was taken to ensure the complete removal of the water, so that the vessel C was filled with a solution of uniform density.

Thus the whole of the suspended system remains filled with distilled water, but is immersed in a salt solution of uniform density, so that the diffusion-tube, initially filled with pure water, is brought into contact at its lower end with a salt solution whose concentration, on account of the large volume present, may be considered to remain constant.

Again, the better method enables an experiment to be repeated with precisely the same solution, so that the working details are much more under control. Moreover, it has another advantage in that greater accuracy is introduced in the determination of the quantity δ.

It is only in very dilute solutions that the value of δ is doubtful, and as only a very slight decrease occurs in the concentration of the solution inside the diffusion apparatus as the salt diffuses out, these very dilute solutions are not produced in this method.

Since no experiments were made by Kohlrausch with solutions as dilute as those produced by the diffusion of the salt into the suspended apparatus in Method A, it was necessary to make a special series of experiments to determine the value of δ. Moreover, as the solutions were so dilute, it was thought advisable to use a larger flask than than that employed by Kohlrausch. In place then of his flask of about 130 c.c. capacity, one was taken having a volume of about 300 c.c. and it was loaded with shot, so as to weigh about 4 gms. when immersed in water. The neck was drawn off and sealed up in the blowpipe, and the flask was then suspended by means of a pair of fibres of unspun silk attached to the pan of the balance, in distilled water cooled to 0° C.

It is very necessary that the fibres should be thoroughly wetted before use. They must also be smooth, and dust should be removed as far as possible from the water, otherwise the balance-beam refuses to swing, or only swings in a very erratic manner.

When the flask has been weighed in distilled water at 0° C. it is clamped by means of a suitable device, and a standardized solution of the salt is added to the distilled water (over 6 litres) 10 c.c. at a time. A series of very dilute solutions of known strength are thus obtained, and the corresponding density may be found, from which the value of δ easily follows.

NaCl.		KCl.		KNO_3.	
Concentration.	δ.	Concent.	δ.	Concent.	δ.
·0008453	·2152	·0004153	·3054	·0004146	·3097
·001265	·2208	·0008290	·3072	·0006211	·3072
1684	·2252	·001241	·3079	·0008267	·3061
2102	·2281	1652	·3074	·001032	·3042
2516	·2308	2061	·3089	1440	·3038
2931	·2329	2469	·3091	2047	·3037
3343	·2354	2875	·3094	2449	·3052
3754	·2363	3280	·3095	3046	·3061

It might be mentioned that a comparison of the weighings from which the above figures were obtained with the earlier ones mentioned in § 4, using a wire suspension, show that they are apparently equally consistent and trustworthy. It seems probable that the disadvantage of using such a delicate suspension as a fibre of unspun silk may be overcome by using a fine wire in its place, provided that the surface of the liquid be covered with a film of oil. When it is remembered that the fibre supports the flask inside a metal vessel surrounded by ice, and that clamping and stirring must be carried on without the experimenter being able to see what is happening inside the vessel, the advantage of using a somewhat stronger suspension will be apparent.

In the present experiments, however, the cocoon suspension was adhered to, and with this no oil-film should be used.

In order to find what value must be taken for δ in the various diffusion experiments, the method of successive approximations was used. The final rate of increase in weight is first assumed to be due entirely to the salt which enters the apparatus. In this way a rough value of the concentration inside the apparatus at the end of, say, a fortnight, is deduced. This gives us a rough value for δ, by means of which our first assumption may be corrected, and so yield a more exact value of δ.

9. *The Length of the Tube.*

Some experiments were also carried out with tubes of various lengths. It has already been shown that it is likely that to our present degree of accuracy no end correction is requisite to the tube of 4 cms. length. It may be pointed out that the end correction must depend on both the length and the diameter of the tube. The longer the tube the less is the rate of diffusion through it, and therefore the more perfectly can gravity regulate uniformity of density in a given horizontal plane.

Three tubes were employed, the lengths being 4 cms., 2 cms., and 1 cm.; the areas of cross-section being respectively 1·697, 1·025, and 1·059 sq. cms., and the diameters being 1·465, 1·14, and 1·16 cms. respectively; and the solution employed was a 5 per cent. solution of KCl. The results are plotted on the accompanying graph (Pl. XXV. fig. 6).

Assuming no appreciable end correction to the tube of 4 cms. length, it is found that to give the same value for the Coefficient of Diffusion in each case, 0·036 cm. should be added to each end of the 2 cm. tube (*i. e.* ·032 of the diameter), and 0·045 cm. to each end of the 1 cm. tube (*i. e.* ·039 of the diameter). The results prove conclusively that it will not be possible to accelerate the work by using tubes much shorter than 4 cms., unless perhaps a battery of short and narrow tubes can be employed.

10. *Conclusion.*

My chief object in bringing this paper before the Physical Society of London in its present state has been the hope of obtaining from the Fellows some useful suggestions for future work, or improvements in the method.

In all 43 experiments have been performed; many of them, described in this paper, have had the sole object of endeavouring to obtain information of the best experimental conditions.

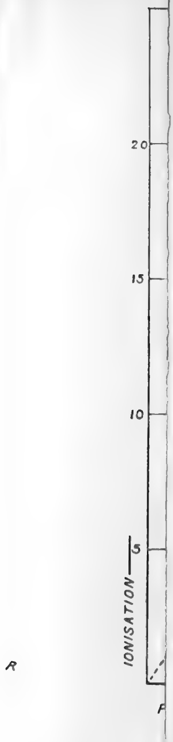
The numerical results of some of the others have not been stated, as improvements in the method, which they have suggested, have rendered the numerical result unsatisfactory.

The values of the coefficient of diffusion at 0° C., which the investigation indicates to be most trustworthy, are those obtained with the suspended apparatus filled with the salt solution, in the larger copper vessel containing distilled water. These results are

Experiment.	Salt KNO_3.		Experiment.	Salt KCl.	
	Concen.	$K \times 10^5$.		Concen.	$K \times 10^5$.
16	10 p. cent.	·843	24	20 p. cent.	·966
17	10 „	·845	25	20 „	·978
22	5 p. cent.	·870	26	10 p. cent.	·953
23	5 „	·871	27	10 „	·956

The results show that the method is capable of yielding consistent values, and if compared with those obtained by other observers in the same subject, although the concentration of the solutions and the temperatures at which they were employed vary considerably, thus making comparison difficult, yet the agreement, as far as can be judged, appears to be satisfactory.

For instance, results expressed in C.G.S. units, obtained by Schuhmeister and by Scheffer for KCl and for KNO_3 respectively are shown below


20
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Salt.	Temp.	N.	$k\times10^5$.	Observer.
KCl.........	17°·5	·022	1·47	Schuhmeister.
	10°	·007	1·27	
KNO_3......	7°	·031	·98	Scheffer.
	7°	·0093	·06	
	10°	·015	·92	Schuhmeister.

The absence of any trustworthy values for the temperature coefficients, and more especially the fact that the concentrations shown above are so much lower than those employed in the present paper, render further comparison difficult.

In conclusion, I should like to offer my thanks to the Principal and Council of Birkbeck College for assistance in carrying the experiments into effect, and especially to Dr. A. Griffiths, who not only suggested the research, but has been always ready to assist me when in trouble or difficulty.

LXXV. *Gaseous Ionization and Pressure.* *By* T. H. Laby, *B.A., Emmanuel College, Exhibition of* 1851 *Scholar, Joule Student of the Royal Society, and* G. W. C. Kaye, *B.A. (Cantab.), B.Sc. (Lond.), A.R.C.Sc., Trinity College, Cambridge* *.

[Approved as an additional Thesis, in the case of the latter author for the Degree of Doctor of Science in the University of London.]

[Plate XXVI.]

WHEN γ rays act on a constant volume of a gas, it is to be expected that they will produce an amount of secondary radiation proportional to the pressure of the gas; further, the ionization arising from this secondary radiation is also proportional to the gas pressure: thus the ionization would be proportional to the square of the pressure. This view of the dependence of gaseous ionization on pressure is given in more detail later.

Though several experiments have been recorded of the variation of gaseous ionization with pressure, they do not support the above relation; none of them, however, was for

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* Communicated by Professor J. J. Thomson.

Fig. 1.

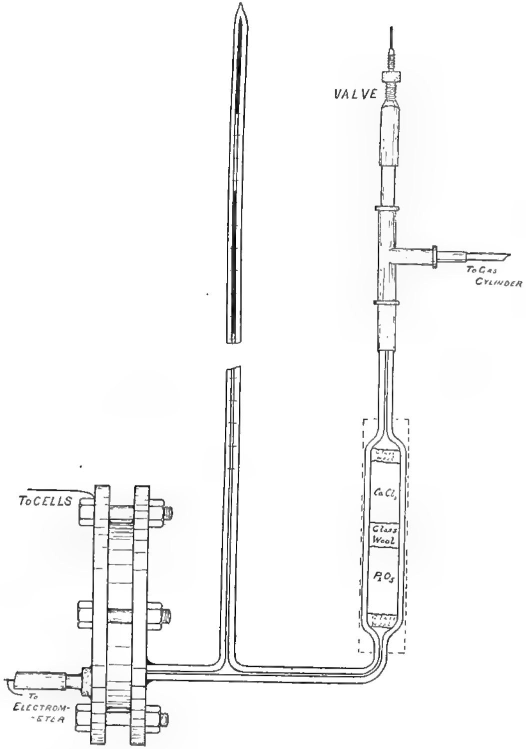


Fig. 3.

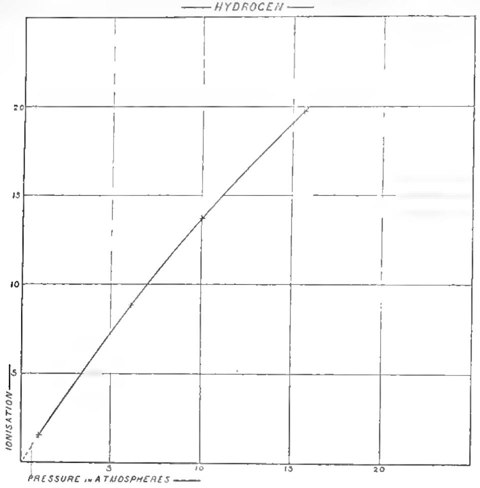


Fig. 5.

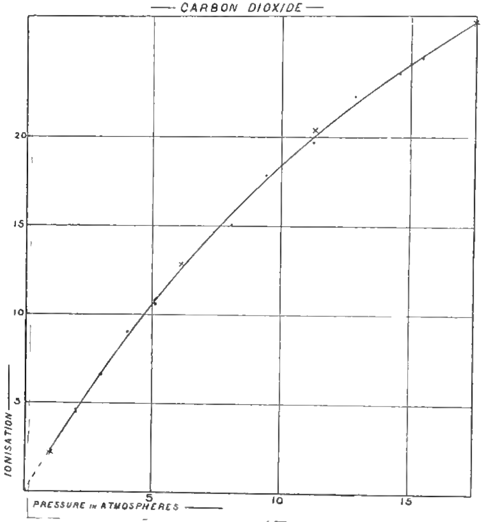


Fig. 4.

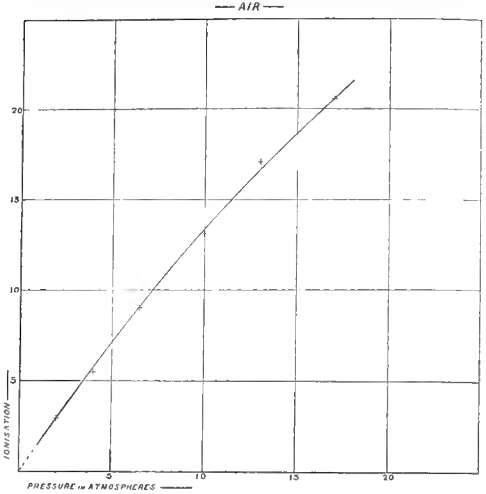
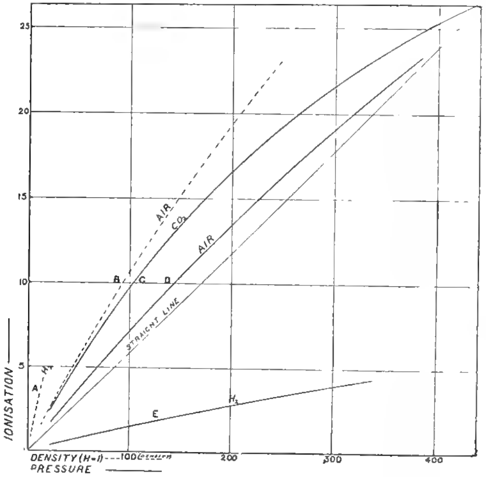


Fig. 6.



pressures over one atmosphere. Perrin [*] found for Röntgen-ray ionization that "the quantity of electricity dissociated by unit mass (of gas) is independent of the pressure and proportional to the absolute temperature" [†]; or, in other words, the ionization in a constant volume of gas is proportional to the pressure.

Experimental.

Some preliminary experiments on the effect of pressure on the ionization in air were made using an aluminium ionization chamber of cylindrical form with a central wire electrode. The results were sufficient to show that the field necessary to produce a saturation current was a strong one—over 1000 volts per cm. for the higher pressures and the intensity of ionization of the experiment. The cylindrical form of apparatus was abandoned, for the lack of uniformity in the field made it impossible with the voltage available to ensure a saturation field over the whole volume of the gas. For two concentric cylinders, with a potential-difference of V volts between them, the electric field falls from $\frac{V}{\left(r \log_e \frac{R}{r}\right)}$ at the inner cylinder to $\frac{V}{\left(R \log_e \frac{R}{r}\right)}$ at the outer cylinder, where r is the radius of the inner cylinder, R that of the outer. Thus for complete saturation of all the gas V must not be less than $XR \,.\, \log_e \frac{R}{r}$, where X is the least saturation field for the conditions of the experiment. Thus, for example, if $R = 10r$, the field will fall from $V/2{\cdot}3r$ at the inner cylinder to $V/23r$ at the outer cylinder. If the saturation field be equal to the mean field $= V/(R-r) = V/9r$, then 86 per cent. of the gas is subjected to a field less than this, and is therefore unsaturated. A uniform ionization is of course assumed. We mention this as showing that this form of vessel is unsuitable for experiments in which one of the difficulties is to saturate a dense gas at high pressures.

Apparatus.

The apparatus, which was made by the writers, is shown in plan in fig. 1 (Pl. XXVI.). It consisted of an ionization vessel connected by thick-walled capillary tubing of glass to a drying-tube, and to an air-pressure manometer placed horizontally. A scale of centimetres was etched on the

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[*] *C. R.* cxxiii. p. 878 (1896).

[†] This temperature effect has not been confirmed by later observers.

manometer-tube, and its bore (1·8 mms.) was carefully calibrated by the mercury-thread method. The thoroughly cleaned tube was filled with air which had been dried over P_2O_5; it was then sealed at one end. A thread of mercury several centimetres long enclosed a 75 cm. length of this air at atmospheric pressure. There was very little sticktion, and the mercury thread was found always to return to its zero, showing that there was no leakage past the mercury. A short length of mercury also occupied the closed end of the manometer; by this means the determination of the volume end correction was avoided. The readings of the manometer were made to 0·1 mm. by means of a travelling microscope.

Assuming a spherical bounding surface for the mercury and an angle of contact with glass of 53°, the height of the meniscus works out to be almost exactly $1/3r$, where r is the radius of the tube. A reading taken at the tip of the meniscus should be corrected by an amount $1/6r$ to give the length of the air-thread.

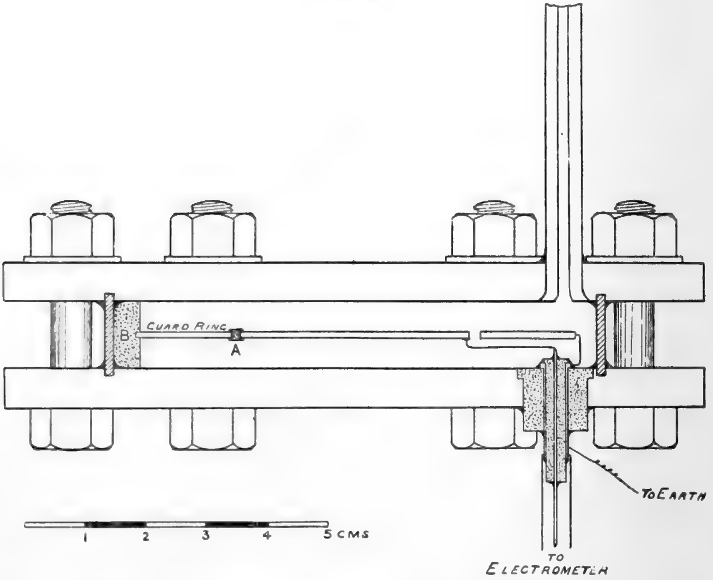
In calculating the pressure (up to 17 atmospheres) from the manometer readings, it was assumed that Boyle's law held exactly, for Amagat has shown that for pressures up to 20 atmospheres the above law is true to half a per cent. for dry air. The reagents in the drying-tube, through which the whole of the gas entering the apparatus had to pass, were $CaCl_2$ and P_2O_5 separated by glass-wool. As a safeguard against explosion the glass drying-tube was provided with a brass sheath. A metal T-piece was joined by sealing-wax to the remote end of the drying-tube. One limb of the T was soldered to a length of flexible metal tubing connected to a cylinder of compressed gas; the other limb was joined to a motor-tyre valve, which could be used to release the pressure in the apparatus. Hydrogen and carbon dioxide were used direct from the gas cylinder, which gave of course the desired pressure without difficulty. The carbon dioxide obtained in this way from the liquid is known to be very pure; the hydrogen contained from 2 to 3 per cent. of light gaseous impurity. With air the pressure was obtained by a motor-tyre pump joined to the valve for the time being.

When a new gas was being admitted into the apparatus, the pressure was several times slowly raised to about 15 atmospheres, and then lowered to atmospheric pressure by opening the valve.

The final form of ionization-chamber adopted is shown in section in figure 2, which is drawn to scale. It allowed a uniform field and a pressure of 20 atmospheres to be obtained.

Two stout circular aluminium plates 1·1 cm. apart, separated by a ring of brass, were fastened together by six bolts. The brass ring was let into a circular groove cut in each of the plates. A central disk of aluminium 1 mm. thick was mounted midway between the plates and surrounded by an earthed aluminium guard-ring held in place by three small ebonite blocks (B). Three small dumb-bell shaped pieces of ebonite (A) insulated the central disk from the guard-ring: these pieces could be slipped into place when the disk was eccentric and afterwards moved around in the slot into position. The central disk was joined to the electrometer quadrants by a wire and an insulated rod which passed through the wall of the vessel; the insulation was of ebonite and was provided with the usual earthed guard-tube to which the guard-ring was connected by a wire. The different parts of the ebonite plug were each fitted with a shoulder on the inside surface, to withstand the high pressures, and for the same reason the end of the glass capillary connecting tube, which was let into the opposite face, was expanded.

Fig. 2.



All the joints were made gas-tight with a mixture of beeswax and resin in proportions that yielded a flexible cement which held up to 20 atmospheres pressure. The bolts were tightened up with the apparatus hot enough to keep the cement fluid. Sealing-wax was tried and abandoned as it cracked with the flexure of the apparatus.

A Dolezalek electrometer was used, which gave at 2 metres about 5000 mms. deflexion for a volt. The earth connexion to the central plate of the ionization-chamber was made or broken through a calcium-chloride solution key. The radium was placed opposite one of the faces of the chamber at a distance which gave a convenient leak. In addition to the 7 mm. aluminium wall the γ rays passed through about 1 cm. of brass before they entered the chamber. The electrometer was shielded from the radium by a heavy composite lead-iron screen.

Measurements.

To obtain some information as to stray ionization, observations were made, in the case of air, at pressures less than atmospheric down to the vacuum produced by a charcoal tube in liquid air. We found there was, in spite of all shielding precautions, a small quantity of residual ionization in a zinc box which surrounded the key. The amount of this was applied as a correction to all the readings.

Saturation Current.—We first determined the saturation field for the highest pressures used. The values below, taken from our curves, give the order of magnitude of the field required for air. The values of the current for the two sets of pressures are not comparable.

Pressure 8 *atmospheres.*

Field in volts/cm.	Current.
100	18·5
500	20·2
1000	21·7
1500	22·0
2000	22·0

Pressure 15 *atmospheres.*

500	42·0
1000	44·3
1500	46·0
2000	47·3
2500	47·9
3000	48·0
3500	48·1

Ionization and Pressure.—Figs 3, 4, and 5 (Pl. XXVI.) show the relation between ionization and pressure for the gases hydrogen, air, and carbon dioxide over the range 1 to 17 atmospheres, the unit of ionization being an arbitrary one for each curve.

It will be noticed that, for hydrogen at the lower pressures the graph is almost a straight line, and becomes only slightly bent at the highest pressures. The corresponding curve for air (fig. 4) shows a resemblance to that of hydrogen, though the curvature of the former is a little more pronounced. In fig. 5 we have a similar curve for carbon dioxide but with a curvature much more marked.

The readings connecting ionization with pressure are indicated in fig. 5 for two positions of the radium.

(1) The dots (from which the graph is drawn) denote readings obtained when the γ rays entered the vessel through its aluminium ends.

(2) The crosses are the readings when the γ rays entered the vessel through its brass sides. A line through the crosses would be slightly more curved than the one drawn. According to the interpretation given later, this would show that the secondary radiation from brass is much the same as from aluminium.

The graphs of figs. 3, 4, & 5 are reduced in fig. 6 to the same coordinates for each gas; to do this we determined the relative ionization in our apparatus of the three gases when at atmospheric pressure. In curves A, B, C of that figure ionization is plotted against density, the density of hydrogen at 17° and 760 mm. being taken as unity.

In the case of air and hydrogen the curves (D and E) are ionization-pressure curves; to the corresponding graph C for CO_2 a correction has been applied to allow for the deviation of this gas from Boyle's law: Regnault's results have been used to make the correction. It should be noticed that the lengths which the curves C, D, and E (fig. 6) cut off from any ordinate give the relative ionization in the three gases when their relative densities are as their molecular weights, namely, 44, 28·4, and 2. For convenience we shall refer to C, D, and E as pressure-ionization curves.

No correction was made for the deviation of air from the gas laws, for the readings of an air-manometer give exactly the corresponding densities of air in the apparatus; no correction was applied in the case of hydrogen.

The curve C represents carbon dioxide on both the systems of coordinates of fig. 6.

Discussion of Results.

It will be seen from the density-ionization curves (B and C, fig. 6) that the amount of ionization in carbon dioxide relative to air decreases regularly with increasing density.

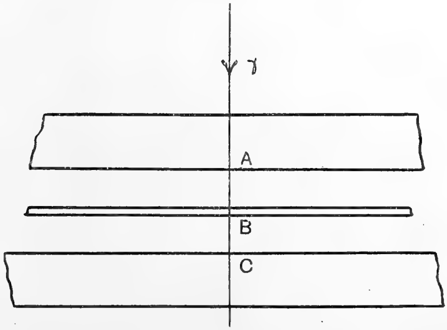
All the curves in fig. 6 are convex to the ionization axis with curvatures which increase in the order, hydrogen, air, carbon dioxide.

At any given pressure employed in these experiments, the ionization in carbon dioxide is greater than that in air, but as the pressure increases, this difference diminishes, and in the apparatus used, the curves indicate that at about 33 atmospheres the ionization would be the same for both gases.

Gas Pressure and Ionization.

To understand these curves, let us consider the nature of the radiation to which the gases were subjected.

Fig. 7.



There are two classes of radiation present :—

(1) The *incident γ radiation* of a very penetrating nature* together with any secondary γ rays from the gas and the walls of the vessel.

(2) The *secondary β radiation* produced from the gas and the walls of the vessel by the original γ rays.

(1) The ionization arising from the very penetrating γ rays forms a small proportion of the whole ionization, and is

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* λ for Al about ·08. McClelland, Trans. Roy. Dubl. Soc. viii. p. 107, July 1904.

probably proportional to the number of molecules present, that is to the pressure.

(2) The ionization due to the secondary β radiation from the gas is small * compared to the ionization arising from secondary β radiation from the walls, the latter need only be taken into consideration when the gas between the electrodes is dense.

The ionization excited in the gas by (say) unit intensity of the secondary β radiation will vary as the gas pressure, but the intensity of this radiation itself varies as the pressure: thus this ionization is proportional to the product of the intensity of the secondary β radiation into the pressure, that is, to the square of the pressure.

The intensity of the secondary β radiation excited in the walls is constant in amount, so that the ionization produced by it varies as the pressure.

We have seen that the ionization arising from the gas radiation will be less than that arising from the wall radiation. Consequently the ionization which varies as the square of the pressure is less in amount than that varying directly as the pressure.

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* Bragg and Madsen (Trans. Roy. Soc. S. Australia, xxxii. 1908) have shown that the secondary β radiation excited by hard γ rays in a plate of aluminium have a λ, when absorbed by aluminium, of 11 cm.$^{-1}$; further, that the secondary β radiation proceeds originally (before any scattering occurs) in the same direction as the primary β, and that the intensity of the emergence radiation considerably exceeds that of the incidence. These results enable us to calculate the amount of secondary β radiation from the aluminium walls in our vessel, and show that the emergence radiation from the two surfaces A and B (fig. 7, p. 885) remote from the radium need only be considered. The amount of radiation in question from either A or B which escapes from the aluminium is

$$I = I_0 \cdot \frac{1}{1-e^{-\lambda\delta x}},$$

where I_0 is the total emergence radiation from an elementary layer of thickness δx: putting $\lambda = 11$ cm.$^{-1}$, then $I = \cdot 1$ or the secondary β radiation from the two surfaces A and B is equivalent to the total emergence radiation from a layer of aluminium $2 \times \cdot 1$ cm. thick, and having a mass of ·54 grams per sq. cm. The radiation from such a layer should considerably exceed the radiation from the layer of gas in any of our experiments. Of the gases used, carbon dioxide, when most dense (at 17 atmospheres) would give the largest amount of secondary radiation; the layer of it 1 cm. thick, between A and C (fig. 7), has a mass of ·03 gram per sq. cm., which is only 1/17 of the mass of the aluminium walls which emits secondary radiation. In the case of air this radiation from the walls would exceed that from the gas to an even greater extent: for hydrogen the secondary β radiation from the gas may certainly be neglected.

To sum up, it is to be expected that:

(*a*) the ionization produced by the γ rays and the secondary β radiation from the walls will vary as the pressure;

(*b*) the ionization due to the secondary β radiation from the gas will be small in amount and vary as the square of the pressure.

It will be shown below how the above factors partly account for the pressure-ionization curves we have obtained for hydrogen, air, and carbon dioxide. To completely account for the curves it is necessary to assume the presence of soft tertiary β radiation in the ionizing vessel.

Soft Tertiary β Radiation.

The convexity of the ionization axis of the curves of ionization and pressure (which is slight, however, in the case of hydrogen) indicates the presence of soft tertiary β radiation of considerable ionizing power. For if such radiation is excited in the ionization chamber, and the gas present is sufficiently transparent to it, then the ionization produced by it will vary at first as the pressure of the gas. But as the pressure increases the absorption of this radiation in the gas will increase until some of the tertiary β rays are completely absorbed. The tertiary β rays remaining will contribute less and less ionization for each equal increment of the pressure, and so the ionization-pressure curves will bend towards the pressure axis.

The excitation in the walls and gas of this radiation by the secondary β radiation is certainly to be expected from what is known of cathode radiation. Gehrcke [*], for example, has shown that cathode rays, when incident on a magnesium plate, produce reflected or secondary rays with a wide range of velocities up to that of the primary rays.

The increase in the convexity of the ionization-pressure curves with the opacity of the gases H_2, air, CO_2, is the most striking evidence in favour of the existence of this soft radiation. Lenard [†] found that cathode rays were less absorbed by H_2 than by air or CO_2: with rays having 1/10 of the velocity of light, λ for H_2 is ·19, for air ·85, for CO_2 2, each gas being at 1 mm. pressure. These numbers are just in the order required by the curves C, D, E of fig. 6 (Pl. XXVI.), where the CO_2 curve is more bent than the air one, and both are much more bent than the one for H_2; in other words, the

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[*] *Ann. der Physik,* viii. p. 81 (1902).

[†] *Ann. der Physik,* xii. p. 732 (1903).

complete absorption of a part of the tertiary β radiation occurs more in CO_2 and in air than in H_2.

It is more probable that the soft radiation, whose existence we have inferred above, is excited by the absorption of β radiation, having a velocity about half that of light, than that it is produced directly by the γ rays. While it is tertiary radiation for our purposes, it should be excited just the same when β rays from radium having a velocity of $\frac{1}{2}$V are absorbed in matter: it would then be called secondary β radiation.

The above sources of ionization are sufficient to account for the experimental results we have obtained, as is shown below.

Hydrogen.—The ionization due to

(*a*) the primary γ rays,
(*b*) the secondary β radiation from the walls,
(*c*) the soft tertiary β radiation,

will all vary as the pressure in this transparent gas. The ionization arising from the secondary β radiation from the hydrogen itself, which varies as the square of the pressure, may be neglected. Finally, there is little complete absorption of the tertiary β rays, and thus the ionization in this gas varies very nearly as its pressure.

Air.—The ionization arising from (*a*) and (*b*) above is just as for hydrogen proportional to the pressure: that due to the secondary rays from the gas may be neglected. Some of the soft tertiary β rays are completely absorbed, so that the remaining rays contribute for each increment of the pressure a decreasing amount of ionization. The sum of these ionizations would increase less rapidly than directly as the pressure, which is in agreement with our observations.

Carbon dioxide.—The ionization is made up in much the same way as that of air. The effect of the secondary β radiation excited in the CO_2 itself may need to be taken into account: it contributes ionization varying as the square of the pressure. The shape of the CO_2 curve is consistent with the existence of a small proportion of such ionization, for the curve exhibits the necessary initial curvature. The absorption of the soft tertiary β rays would be more marked in CO_2 than in air; the effect of this is seen in the greater curvature of curve C (fig. 6).

Since the present experiments were completed Erikson* has published in abstract some results on the "Ionization of Gases at High Pressures." He found with a constant potential-difference between two cylindrical electrodes, that the

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* Erikson, Phys. Rev. xxvi. p. 199 (1908).

ionization current reaches a maximum at a certain pressure, and afterwards diminishes with a further increase in the pressure. For example he quotes a result which indicated, in the case of air, a maximum current at 70 atmospheres, when the potential-difference between two concentric cylindrical electrodes separated by 6 mms. was 18 volts; with a potential-difference of 1000 volts, the maximum current occurred at 150 atmospheres. Now we find (p. 883) that for the intensity of ionization we used—and it was small—air at 15 atmospheres requires a field of 2500 volts per cm. to produce a saturation current. Thus the air in Erikson's experiments, unless his degree of ionization was exceptionally small, was unsaturated for pressures over about 15 atmospheres. His published abstract is silent on the point, but his results are such as would be expected if the velocity of the ions diminished as the pressure increased, and in consequence a larger and larger proportion of the ions present recombined and never reached the electrodes.

Summary.

1. The ionization-pressure curves have been determined over a range of pressures from 1 to 17 atmospheres for hydrogen, air, and carbon dioxide, when contained in an aluminium vessel and exposed to hard γ rays from radium.

2. The amount of ionization in hydrogen is approximately proportional to the pressure; in air it increases less rapidly than the pressure; in carbon dioxide still less rapidly than the pressure, especially at the higher pressures.

3. We conclude from a discussion of these results that the ionization arising from

   (*a*) the γ rays, which is small in amount, varies as the pressure;

   (*b*) the secondary β rays (excited by the γ rays) from the aluminium electrodes, varies as the pressure; while that excited in the gas itself produces ionization small in amount and proportional to the square of the pressure;

   (*c*) a soft tertiary radiation, increases less rapidly than the pressure.

4. It is inferred from these results that when β rays (velocity about half velocity of light) are absorbed they excite soft secondary β radiation.

We wish to thank Professor Thomson for the interest he took in these experiments.

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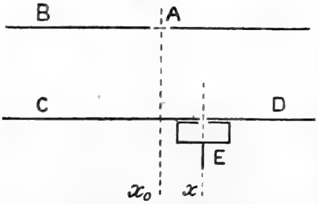
Cambridge.

LXXVI. *The Kinetic Energy of the Ions emitted by Hot Bodies.* *By* O. W. RICHARDSON [*].

§ 1. IN a recent paper the Author and Dr. F. C. Brown [†] have shown how the magnitude and mode of distribution of that portion of the translational kinetic energy of the ions emitted by hot bodies, which depends on their velocity component perpendicular to the surface at which they originate, may be measured. This was done by observing the way in which an insulated plate charged up, when it was placed at a short distance from a similar and parallel plate, a portion of the surface of which consisted of the hot metal. The two plates were initially at the same potential. The results of the experiments showed that the mean value of this portion of the kinetic energy was the same as the corresponding quantity for a molecule of gas at the temperature of the hot metal, and that the velocity component perpendicular to the metal surface was distributed among the negative ions in accordance with Maxwell's law of the distribution of velocity among the molecules of a gas. By using the same method, Dr. Brown, in an investigation which is not yet published, has succeeded in showing that the magnitude and mode of distribution of this portion of the kinetic energy follows the same laws in the case of the positive ions also.

§ 2. The method employed in those researches yields no information about the part of the kinetic energy which depends on the component of velocity of the ions parallel to the emitting surface. Both the magnitude and distribution of this among the ions may, however, be investigated by experiments of a somewhat different character. Consider the arrangement, of which fig. 1 is a section, to extend indefinitely perpendicularly to the plane of the paper. A is a section of an infinitely long narrow strip of hot metal which almost fills a

Fig. 1.



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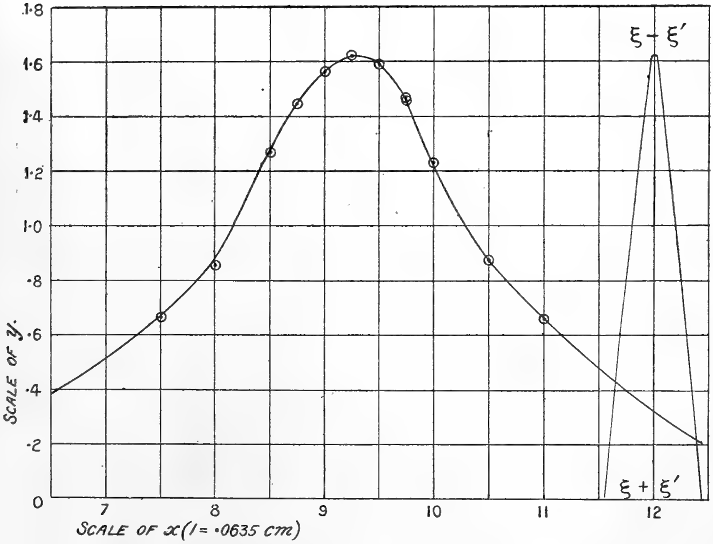
[*] Communicated by the Author.

[†] Phil. Mag. [6] vol. xvi. p. 353 (1908).

narrow gap in the infinite conducting plane B. At a short distance from B, and parallel to it, is another infinite conducting plane CD divided into two portions by a narrow slit parallel to the edges of A. A and B are charged to the same potential and the resulting current to the plane CD is measured. Simultaneously the ions which pass through the slit are measured by means of the box-shaped electrode E. The whole system CED can be pushed along bodily by a fine screw and the current through the slit is compared with the sum of the currents to the plates CD and the slit, for a series of positions of the latter. In this way a curve is obtained which gives the fraction of the total current passing through the slit in any position. The curve on the left in fig. 2 has been obtained in this way. If the emitted ions possessed no sideways velocity this curve would consist of one horizontal and two inclined straight lines, as shown on the right. Since it does not do so it follows that the ions are emitted with a finite sideways velocity.

Fig. 2.



Let us see how the form of these curves depends on the distribution of velocity among the ions. Let the figure (fig. 1) lie in the plane of xz, the axis of z being perpendicular to B and CD. Consider an ion whose coordinates at any instant are x, y, z. Let the plane of A be the plane $z=0$. The electric field between A and CD is uniform and equal to Z.

If V is the difference of potential, and z' the distance, between the planes $V=Zz'$. The equations of motion of the ions are

$$m\frac{d^2x}{dt^2}=0, \quad m\frac{d^2y}{dt^2}=0, \quad m\frac{d^2z}{dt^2}=Ze.$$

Integrating, subject to the conditions that, when

$$t=0, \quad \frac{dx}{dt}=u_0, \quad \frac{dy}{dt}=v_0, \quad \frac{dz}{dt}=w_0,$$

we get

$$\frac{dx}{dt}=u_0, \quad \frac{dy}{dt}=v_0, \quad m\frac{dz}{dt}=Zet+mw_0\,;$$

so that if, when

$$t=0, \quad x=x_0, \quad y=y_0 \text{ and } z=0,$$

$$x-x_0=u_0t, \quad y-y_0=v_0t, \quad z=w_0t+\tfrac{1}{2}Z\frac{e}{m}t^2.$$

Since in the present problem everything is independent of y we only need to consider the relation between the z and x coordinates of the particle. Eliminating the time, we have

$$z=\tfrac{1}{2}Z\frac{e}{m}\left(\frac{x-x_0}{u_0}\right)^2+\frac{w_0}{u_0}(x-x_0) \quad . \quad . \quad . \quad (1)$$

We may regard this equation in two different ways. If we start with assigned values u_0 w_0 of the velocity components then the equation gives us the relation between the coordinates x and z of any point in the subsequent path of the particle. On the other hand, if we consider two fixed points, x_0, 0 in A and x, z' in C, the equation (1) will give us the relation which has to hold between u_0 and w_0, for an ion emitted from x_0, 0 to reach x, z'. This relation may be expressed more conveniently by solving the equation as a quadratic for u_0, which gives

$$u_0=\tfrac{1}{2}w_0\frac{x-x_0}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right). \quad . \quad . \quad (2)$$

If u_0 has this value the particle will strike the plate D at the point $x=x$, if u_0 is greater than this the particle will go to the right, if u_0 is less it will go the left, of $x=x$. The number of particles which go to the right of $x=x$ will therefore be the number of those which have values of u_0 greater than

$$\tfrac{1}{2}w_0\frac{x-x_0}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right).$$

It is to be borne in mind that only positive values of w_0 are admissible in this expression. Those which start from the back of the strip are supposed to be caught by the upper plate and have no opportunity to reach the plane below. The conditions which have to be satisfied are therefore

$$\left.\begin{aligned} &u_0 \geqq \tfrac{1}{2} w_0 \frac{x-x_0}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right) \\ &w_0 \geqq 0. \end{aligned}\right\} \quad . \quad . \quad (3)$$

Suppose that out of any large number n_1 of ions emitted by the strip, the number which have velocity components lying, at the same time, between u_0 and u_0+du_0 and w_0 and w_0+dw_0 is denoted by $n_1 F(u_0, w_0)\, du_0\, dw_0$. Then the number which reach the lower plane at points to the right of the line $x=x$ will be

$$= n_1 \int_0^\infty dw_0 \int_{\frac{1}{2}w_0 \frac{x-x_0}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}^{\infty} du_0 F(u_0, w_0).$$

If, as in the kinetic theory of gases, the probabilities of given values of the components of velocity along two mutually perpendicular directions are independent of each other, the last expression may be written

$$I = n_1 \int_0^\infty f'(w_0)\, dw_0 \int_{\frac{1}{2}w_0 \frac{x-x_0}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}^{\infty} du_0 f(u_0),$$

where $n_1 f(u_0) du_0$ and $n_1 f'(w_0) dw_0$ are respectively the number of emitted ions having velocity components between u_0 and u_0+du_0 and w_0 and w_0+dw_0.

If we consider a narrow slit of width ξ in the lower plane, bounded by the lines $x=x-x_0+\xi/2$ and $x=x-x_0-\xi/2$ it follows from the preceding expressions that the number of ions which pass through the slit will be equal to

$$n_1 \int_0^\infty dw_0 \int_{\frac{1}{2}w_0 \frac{x-x_0-\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}^{\frac{1}{2}w_0 \frac{x-x_0+\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)} du_0 F(u_0, w_0).$$

If in addition the strip is of finite width ξ' and extends from $x_0 = -\xi'/2$ to $x_0 = +\xi'/2$, the total number which pass through the slit will be

$$\frac{n_1}{\xi'} \int_{-\xi'/2}^{+\xi'/2} dx_0 \int_0^\infty dw_0 \int_{\frac{1}{2}w_0 \frac{x-x_0-\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}^{\frac{1}{2}w_0 \frac{x-x_0+\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)} du_0 F(u_0, w_0).$$

The experiments of Richardson and Brown (*loc. cit.*) have shown that in the case of hot platinum under certain conditions the normal velocity component w_0 is distributed among the emitted ions according to Maxwell's law, and the value of the constant which determines the mean kinetic energy is the same as that for a molecule of a gas at the temperature of the metal. Under these conditions it seems likely that the same law will hold for the component of velocity parallel to the surface, and it is interesting to examine the consequences of this hypothesis. If Maxwell's law holds we have

$$F(u_0, w_0)=f(u_0)f'(w_0),$$

where

$$f(u_0)=\left(\frac{km}{\pi}\right)^{\frac{1}{2}}e^{-kmu_0^2}$$

and

$$f'(w_0)=2kmw_0e^{-kmw_0^2},$$

where m is the mass of the ions and $\frac{3}{4}k$ their mean translational kinetic energy. On this view the number which pass through the slit of width ξ' is therefore

$$2\frac{n_1}{\xi'}\frac{(km)^{\frac{3}{2}}}{\pi^{\frac{1}{2}}}\int_{-\xi'/2}^{+\xi'/2}dx_0\int_0^{\infty}dw_0w_0e^{-kmw_0^2}\int_{\frac{1}{2}w_0\frac{x-x_0-\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}^{\frac{1}{2}w_0\frac{x-x_0+\xi/2}{z'}\left(1+\sqrt{\left(1+\frac{Ve}{\frac{1}{2}mw_0^2}\right)}\right)}du_0e^{-kmu_0^2}\quad . \quad . \qquad (4)$$

We can test the correctness of the substitutions which have been made by calculating the total number of ions which reach the lower plate. This will evidently be

$$2\frac{n_1}{\xi'}\frac{(km)^{\frac{3}{2}}}{\pi^{\frac{1}{2}}}\int_{-\xi'/2}^{+\xi'/2}dx_0\int_0^{\infty}dw_0w_0e^{-kmw_0^2}\int_{-\infty}^{\infty}du_0e^{-kmu_0^2},$$

This, as it should be, is equal to n_1 the number of ions emitted by the strip.

The integral (4) cannot be evaluated in finite terms, and there is no single method of approximation which can be made to cover the whole range of experimental conditions. There are, however, two special cases in which the expression assumes a very simple form. In both of these ξ and ξ' are regarded as very small quantities. In addition, Ve is large compared with $\frac{1}{2}mw_0^2$ in the first case and is equal to zero in the second. We shall consider first the case in which Ve is great compared with $\frac{1}{2}mw_0^2$.

It will be observed that Ve can never be great compared with *all* the values of $\frac{1}{2}mw_0^2$, since infinite values of this quantity are theoretically possible ; but the number of such cases is so small that it makes no difference whether they are included or not. We shall suppose that the condition is satisfied if Ve is great compared with the average value of $\frac{1}{2}mw_0^2$. It will be noticed that $\mathrm{V}e/\frac{1}{2}mw_0^2$ is the ratio of the kinetic energy communicated by the electric field, during the passage from the strip to the plate, to the "normal component" of the kinetic energy of the ion when it was emitted from the strip.

If ξ and ξ' are both infinitesimal and $x_0=0$ (4) becomes

$$2n_1\frac{(km)^{\frac{3}{2}}}{\pi^{\frac{1}{2}}}\int_0^\infty dw_0\,\frac{w_0^2\xi}{2z'}\left(1+\sqrt{1+\frac{\mathrm{V}e}{\frac{1}{2}mw_0^2}}\right)e^{-kmw_0^2\left(1+\frac{x^2}{4z'^2}\left(1+\sqrt{\left(1+\frac{\mathrm{V}e}{\frac{1}{2}mw_0^2}\right)}\right)^2\right)}$$

If in addition $\mathrm{V}e/\frac{1}{2}mw_0^2$ is large compared with unity, this reduces to

$$\frac{n_1\xi}{\pi^{\frac{1}{2}}}\sqrt{\frac{2k\mathrm{V}e}{4z'^2}}\,e^{-\frac{2k\mathrm{V}e}{4z'^2}x^2}.$$

The number of ions which are received by a width dx of the lower plane at x is therefore

$$\frac{n_1}{\pi^{\frac{1}{2}}}\sqrt{\frac{2k\mathrm{V}e}{4z'^2}}\,e^{-\frac{2k\mathrm{V}e}{4z'^2}x^2}\,dx$$

and the total number of ions received by the whole of the lower plane is

$$\frac{n_1}{\pi^{\frac{1}{2}}}\int_{-\infty}^{\infty}\sqrt{\frac{2k\mathrm{V}e}{4z'^2}}\,e^{-\frac{2k\mathrm{V}e}{4z'^2}x^2}\,dx=\frac{n_1}{\pi^{\frac{1}{2}}}\int_{-\infty}^{\infty}e^{-x^2}\,dx=n_1.$$

Since this is otherwise obvious the result may be considered as a check on our previous calculations.

The fraction of the total number of ions received by the lower plane which pass through a narrow slit of width ξ, distant x from the line of symmetry, is thus

$$i=\frac{\xi}{\sqrt{\pi}}\sqrt{\frac{2k\mathrm{V}e}{4z'^2}}\,e^{-\frac{2k\mathrm{V}e}{4z'^2}x^2}.$$

Since $k=\frac{1}{2\mathrm{R}_1\theta}$ where R_1 is the gas constant reckoned for a single molecule, and θ is the absolute temperature, the above may be written, changing z' to z,

$$i=\frac{\xi}{\pi^{\frac{1}{2}}}\sqrt{\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2}}\,e^{-\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2}x^2}\quad.\ .\ .\ .\ .\ .\ .\quad(5)$$

where n is the number of molecules in 1 c.c. of a gas at 0° C. and 760 mms. pressure and $R=nR_1$ is the constant in the equation $pv=R\theta$, referred, as is usually the case, to a cubic centimetre of gas under standard conditions. If the charge on an ion is equal to that carried by a monovalent atom in electrolysis, ne will be equal to the quantity of electricity required to liberate half a cubic centimetre of hydrogen in a water voltameter at 0° C. and 760 mms. This quantity is ·407 E.M. units.

When the centre of the slit is in the plane of symmetry $x=0$ and the value of i is

$$i_0=\frac{\xi_1}{\pi^{\frac{1}{2}}}\sqrt{\frac{Vne}{4R\theta z^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

The fraction passing through the slit in different positions, which is the quantity measured experimentally, may therefore be expressed by the equations,

$$i/i_0=e^{-\frac{ne}{4R\theta z^2}x^2} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

or

$$\log i/i_0=-\frac{Vne}{4R\theta z^2}x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

§ 3. The equations (5) to (8) point out a number of different ways in which the theory may be subjected to the test of experiment. It will be observed that the apparatus required for this purpose is the same in general design as that already described, and used by the author * to measure the value of e/m for the ions emitted by hot bodies. While that investigation was in progress experiments were made which afford a preliminary examination of the ground covered by the theory under consideration. The results of these experiments are incorporated in the present paper. They are necessarily somewhat rough, for a variety of reasons. In the first place, the apparatus used for measuring e/m had to be made very small as it was necessary to place it in a strong uniform magnetic field. The smaller the apparatus is, the more it deviates from the condition of infinite parallel planes, so that we should expect an error due to the electric field not being uniform and equal to the value calculated from the difference of potential between the plates. Undoubtedly one of the worst sources of error in these experiments arose from the strips used not being quite plane and not lying accurately in the plane of the "upper" plate.

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* Phil. Mag. vol. xvi. [6] p. 740 (Nov. 1908).

This was shown by the fact that the ratio of the current through the slit to the total current was never quite symmetrical about the centre of the pattern. This lack of symmetry was of little importance in the experiments on e/m where the deflexion of the whole pattern in a magnetic field was measured, but it is of vital importance in the present experiments. If the strip is bent the applied electric field alone will cause a spreading of the ions which may easily be greater than that due to their original kinetic energy. The author now believes that he has obtained a better method of cutting the strips which will avoid these difficulties in future experiments.

There were other errors arising from the finite widths of the strip and the slit, from the finite length of the strip, and from the scattering of the ions by the small quantity of gas present in the apparatus. It is difficult to see how this could be reduced much below the value (about 3×10^{-4} mm.) it had in most of the experiments, with apparatus of this degree of complexity. This difficulty could be allowed for to some extent by making observations at different pressures. A rough attempt to correct some of the observations for the effect of the gas was made in this way.

Originally it was intended to determine the temperature of the strip from its resistance by the usual methods, but this part of the plan was not successful as the strip broke before the necessary observations could be completed. The temperature was therefore estimated from the magnitude of the ionization currents and the dimensions of the strip. It is subject to a possible error of about 10 per cent. (100° abs.), but the uncertainties arising out of the structure of the apparatus do not warrant our proceeding to a higher order of accuracy than this in the determination of the temperature.

The experimental points from which curves like that shown in fig. 2 were constructed represent the values of the electrometer reading for the current through the slit, divided by that for the slit and the plates together. These measurements were taken precisely as described in the author's previous paper [*]. To obtain the value of the quantity denoted by i in the preceding equations it is necessary to divide each ordinate by the ratio of the sum of the capacities of the electrometer and the condenser to the capacity of the electrometer alone. This ratio was not determined accurately but it was known to be not far from 12. The relative values of the different ordinates do not, of course, depend on the

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[*] Phil. Mag. [6] vol. xvi. p. 740 (Nov. 1908).

magnitude of this ratio; and the only method of measurement which makes use of it in the sequel is vitiated by a far greater source of uncertainty arising from the geometrical construction of the apparatus employed. So far as the present observations go, therefore, the absence of this particular piece of information is not a matter of great moment.

With the positive ionization consistent results were obtained throughout the range of potential-difference from 40 to 360 volts, but this was not the case with the negative ionization. Whatever the distribution of sideways velocity may be, it is clear that the height i_0 of the central ordinate in curves like that in fig. 2 will be greater the greater the applied potential-difference; since with greater potential-differences the ions have less opportunity to spread out sideways. In the case of the positive ionization this conclusion was borne out by the experiments. It was found that with ions of the same valency (*ne* constant) and for constant values of ξ, the width of the slit, θ, the absolute temperature, and z, the distance between the plates, the relation $i_0/\sqrt{V} =$ constant, required by equation (6), was always fulfilled. Experiments made to test this point gave the following numbers. With $V=78$ volts two curves under identical conditions gave for i_0 the height of the central ordinate the same value 2·85 in arbitrary units. The mean is therefore 2·85 and the value of $i_0/\sqrt{V} = {\cdot}322$. The potential was then changed to 324 volts, the other conditions remaining the same; two determinations of i_0 gave 5·35 and 5·90 in the same units. The mean is thus 5·63 and the value of $i_0/\sqrt{V} = {\cdot}312$. The two values of this ratio are constant within the limits of experimental error, in agreement with the theory.

With the negative ionization the value of i_0 increased with the applied potential-difference to a little beyond 40 volts when it reached a maximum; it then diminished in a very marked way as the potential was increased up to 320 volts, at which point the experiments were discontinued. Not only was this the case, but with voltages greater than 80 the central maximum in the *ix* curve was replaced by a central minimum with a maximum on each side of it. The cause of this exceptional behaviour of the negative ions is not quite certain. It may be that a large number of secondary negative ions are emitted by the electrode when it is struck by the primary ions, and that some of these escape out of the box. Reflexion of the primary ions at the electrode would act in the same way. The fact that the abnormal behaviour is more marked the higher the potential-difference is in favour of some such view. In order to avoid effects of this kind a very low potential-difference, 10·6 volts, was used in the experiments on the negative ions. This is a long way below the potential at which i_0 reaches its maximum value. It was not considered advisable to use lower potentials than this on account of the assumption, made in working out the theory, that $\mathrm{V}e$ is large compared with $\frac{1}{2}m\overline{w_0^2}$. The ratio $\mathrm{V}e/\frac{1}{2}m\overline{w_0^2}$ with $\mathrm{V}=10{\cdot}6$ volts is about 120.

Three different methods of applying the experimental results so as to test equations (5) to (8) have been made use of. These will be considered separately, and under each method we shall consider, first the experiments with the negative ions, and afterwards those with the positive ions.

§ 4. METHOD I.

(*a*) *Negative ions.*—This method is based on equation (7), which may be written in either of the forms

$$i=i_0e^{-\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2}x^2} \quad \text{or} \quad i=i_0\times 10^{-\frac{\mathrm{V}ne}{9{\cdot}2\mathrm{R}\theta z^2}x^2} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

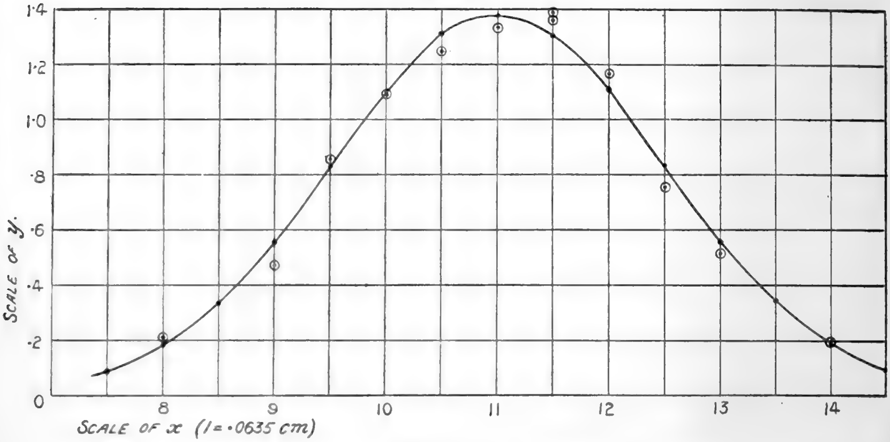
It consists in finding by trial a curve of the form $i=\mathrm{A}e^{-bx^2}$ which will fit the experimental numbers. The constant A is readily determined, being obviously the value i_0 of i when $x=0$; it is the height of the maximum ordinate of the ix curve (see fig. 1). A general method of determining b will be given below. The following table gives a series of values of i, expressed as a ratio of electrometer deflexions in the manner already described, for different values of x. The first row gives the value of x, the second the value of i for points to the right of $x=0$, and the third the value of i for points to the left of $x=0$. This is necessary as the values are not quite symmetrical as they would be under perfect conditions. The fourth row gives the mean of the two experimental values of i, and the last contains the values of i calculated from the formula $i=1{\cdot}38\times 10^{-24x^2}$.

$\pm x$ (1=·0318 cm.) ……	0.	1.	2.	3.	4.	5.	6.	7.
$+i$ (arbitrary units) …	1·35	1·38	1·17	·75	·51	·34	·19	·09
$-i$ (,, ,,) …	1·35	1·25	1·09	·85	·47	·30	·21	·13
mean i (,, ,,) …	1·35	1·31	1·13	·80	·49	·32	·20	·11
i calculated ……………	1·38	1·31	1·10	·83	·56	·34	·18	·09

The agreement between the theoretical and experimental numbers is very satisfactory. This is also shown graphically by fig. 3, in which the smooth curve is the graph of

$i=1{\cdot}38\times10^{-24x^2}$, whilst the experimental points are shown thus : ⊙.

Fig. 3.



Comparing $i=1{\cdot}38\times10^{-24x^2}$ with equation (9) we see that

$$\frac{V\,.\,ne}{9{\cdot}2R\theta z^2}=24,$$

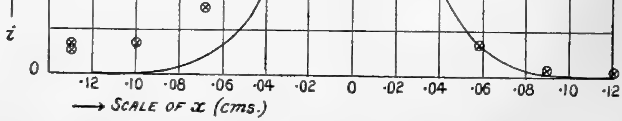
and on substituting the proper values $V=10{\cdot}6\times10^8$ E.M. units, $ne={\cdot}407$ E.M. units, $\theta=1500^\circ$ abs. and $z={\cdot}534$ cm., we obtain

$$R=4{\cdot}6\times10^3 \text{ ergs/cm.}$$

The standard value is $3{\cdot}7\times10^3$, and this is a very satisfactory agreement when all the various sources of error are taken into account.

(*b*) *Positive Ions.*—In the experiments on the positive ions a potential-difference of 78·3 volts was used. A number of series of observations were taken, of which that represented in fig. 4 is typical. The experimental points are denoted

Fig. 4.



thus : ⊕. The smooth curve drawn is the graph of $i = 3e^{-632x^2}$. It will be observed that with the exception of the last four points on the left all the rest fall on the curve within the limits of experimental error. It is probable that the high value of i for these points was due to some part of the strip having a slight twist in it, causing the electric field near that portion of the strip to throw the ions emitted from it over to the left. It is obvious that lack of symmetry of this kind is due to instrumental defects. Making allowance for these points the agreement with the theoretical type of curve is quite satisfactory.

Comparing with equation (9), we see that $\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2} = 632$. Putting $\mathrm{V} = 78 \cdot 3 \times 10^3$, $ne = \cdot 407$, $\theta = 1100°$ abs. and $z = \cdot 534$, we find $\mathrm{R} = 4 \cdot 04 \times 10^3$. The value of R is thus even nearer the standard value $(3 \cdot 7 \times 10^3)$ than that obtained with the negative ions.

A number of series of observations were taken with the positive ionization and all but two would have been approximately fitted by the curve shown in fig. 4. They would therefore have led to the same value of R, roughly, of course. But it was noticed that, with two curves taken after long continued heating of the strip, the two halves were much closer together. This indicates either a smaller amount of sideways energy or a greater charge on the ions. These curves were fairly well represented by $i = 5 \cdot 35e^{-1264x^2}$. Assuming that the value of $\mathrm{R}\theta$ had not changed this would lead to $ne = \cdot 814$ and the ions divalent. On the other hand, if we still suppose $ne = \cdot 407$ we should get about half the normal value of R. There is nothing in the present experiments which enables us to decide definitely between these hypotheses. *A priori*, the balance of probability would seem to be in favour of the kinetic energy being constant and the charge doubled ; but simultaneous measurements of e/m for the ions indicated that this also had changed, and was reduced to nearly one half its previous value. So that if the charge had doubled the mass must have increased to almost four times its earlier value. This would make it very difficult to assign these ions to any definite chemical substance. The matter evidently requires further investigation. The value of e/m for this case is the last one in the table of values of e/m for the positive ions from hot platinum in the author's * paper on that subject.

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* Phil. Mag. [6] vol. xvi. p. 759 (Nov. 1908).

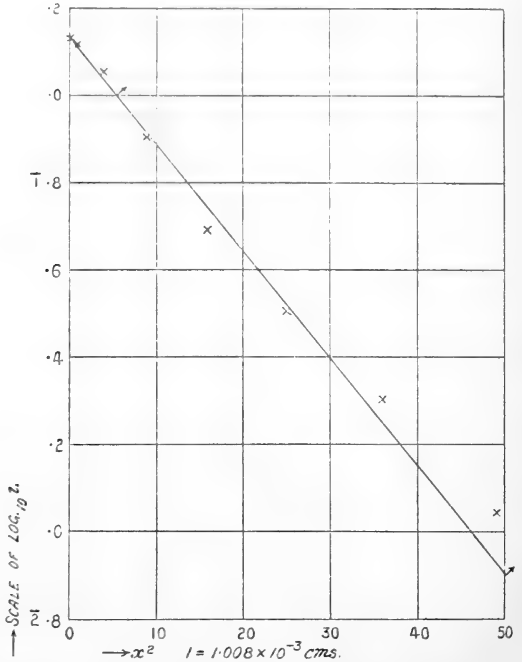
§ 5. Second Method.

(*a*) *Negative ions.*—This method is not independent of the first. It rests directly on equation (8) and is really only a more accurate method of testing the applicability of equation (7). According to equation (8) the curve obtained on plotting log i against x^2 should be a straight line. The values of $\log_{10} i$ and of x^2 have been calculated for the points shown in fig. 3 and are plotted against each other in fig. 5. It will be seen that they all lie very near to the straight line drawn on the diagram. There is a tendency for the points corresponding to large values of x^2 to lie above the line. This tendency is much more marked in the case of the positive ions, and the probable cause of it will be discussed when their behaviour is considered.

If i_1, x_1, and i_2, x_2 are any two pairs of corresponding values of i and x, it follows from equation (8) that

$$R\theta = \frac{V.ne}{9{\cdot}2z^2} \frac{x_1{}^2 - x_2{}^2}{\log i_2 - \log i_1} \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

Fig. 5.



Referring to fig. 5, we find $x_1{}^2 - x_2{}^2 = 4{\cdot}48 \times 10^{-2}$cm.^{2} and $\log_{10} i_2 - \log_{10} i_1 = 1{\cdot}1$. Substituting these and $\theta = 1500°$ abs.,

$V = 10{\cdot}6 \times 10^8$, $ne = {\cdot}407$, and $z = {\cdot}534$, we obtain

$$R = 4{\cdot}5 \times 10^3.$$

This agrees very satisfactorily both with the number obtained by the first method and with the standard value of R.

The agreement of R with the standard value shows that the mean sideways kinetic energy of the negative ions is the same as that of a molecule of gas at the temperature of the hot metal; whilst the straight line exhibited in fig. 5 shows that this energy is distributed among the different ions in accordance with Maxwell's law of distribution of energy among the molecules of a gas.

(*b*) *Positive Ions.*—The numbers used for applying this method to the positive ions were obtained by drawing as smooth a curve as possible through the experimental points shown in fig. 4. In doing this no use was made of the theoretical curve, which had not at that time been constructed. The portion of the curve to the left hand of the approximate line of symmetry was rejected as being obviously subject to a serious instrumental error. Measurements of the right-hand portion of the curve gave the values of i and x tabulated.

x (1 = ·00318 cm.).	i. (arbitrary units).	x^2 ($1 = 1{\cdot}01 \times 10^{-5}$ cm.^{2}.)	$\log_{10} i$.
0	3·02	0	·480
3	2·85	9	·455
6	2·25	36	·352
9	1·5	81	·176
14	·75	196	$\bar{1}{\cdot}875$
17	·45	288	$\bar{1}{\cdot}653$
21	·25	441	$\bar{1}{\cdot}398$
27	·12	729	$\bar{1}{\cdot}079$
38·5	·043	1480	$\bar{2}{\cdot}633$

If the numbers in the last two columns are plotted against each other the first five points will be found to lie very nearly on a straight line, from which the others show a gradually increasing divergence. This divergence is in the same direction as that observed with the negative ionization for large values of x^2, but is very much more marked. It indicates a great excess, over the requirements of the theory, of ions having very large values of the sideways energy. In other words the currents through the slit for large values of x are greatly in excess of theoretical requirements.

It seems practically certain that this arises from ions which are deviated by collisions with molecules of gas in the tube. Although the pressure of the residual gas, as registered by the McLeod gauge, was always very small (not more than 5×10^{-4} mm.), effects of this kind will be important on account of the very rapid way in which the theoretical current through the slit diminishes as we recede from the centre. The fact that this effect was much smaller in the experiments on the negative ionization is strongly in favour of this explanation. In the first place the potential-difference was only about one-eighth as great, so that the ions spread out much more by virtue of their initial energy, and scattering by collisions would be relatively less important; and in the second place the mean free path of a negative ion is some four times as great as that of a positive ion in gas at the same pressure, so that there would be less scattering of the negative than of the positive ions by collisions even under conditions which were otherwise equal.

On the above grounds it seemed reasonable to conclude that the kinetic energy effect is that which determines the slope of the graph of $\log i = f(x^2)$ in the neighbourhood of $x=0$, and that the behaviour of this graph when x^2 is large can be rejected as being due to causes which lie outside the scope of the present investigation. Substituting the values of $x_1^2 - x_2^2$ and of $\log_{10} i_2 - \log_{10} i_1$ obtained from the line passing through the points lying between $x^2 = 0$ and $x^2 = 2 \times 10^{-3}$ cm.^{2} in equation (10), together with the values of θ, ne, V, and z already given (p. 901), we find for the value of R, $R = 3{\cdot}3 \times 10^3$.

This agrees with the value previously found and with the standard value within the limits of experimental error, and the results which have just been discussed show that the sideways kinetic energy of the positive ions obeys the same laws as that of the negative.

We have seen already that a series of observations taken after the strip had been heated for a long time, when analysed by the first method gave a value of R almost one-half of the above, for the same assumed value of *ne*. This curve was also examined by the present method and, although it was somewhat unsymmetrical, both sides of the curve were made use of as there was no evidence tending to favour the rejection of one side rather than the other. With this exception it was treated in the same way as the curve in fig. 4, and led to the numbers in the next table.

	Arbitrary units.				
$\pm x$ (cms.).	$i+$.	$i-$.	$\bar{i}$ (mean).	log $\bar{i}$.	x^2 (cm.^{2}).
·00	5	5	5	·699	0
·01	4·47	4·17	4·32	·635	1×10^{-4}
·02	1·8	2·95	2·38	·376	4×10^{-4}
·03	·7	1·8	1·25	·097	9×10^{-4}
·04	·35	·70	·525	$\bar{1}$·720	16×10^{-4}
·05	·15	·30	·225	$\bar{1}$·353	25×10^{-4}
·06	·05	·13	·09	$\bar{2}$·954	36×10^{-4}

On plotting these values of log $\bar{i}$ against x^2 they behave exactly like those in the preceding table. The first four values lie on a straight line from which the others show a gradually increasing divergence. On substituting the values of $x_1{}^2 - x_2{}^2$ and of $\log_{10} i_2 - \log_{10} i_1$ obtained from this line and the values $V = 78{\cdot}3 \times 10^8$, $\theta = 1{\cdot}15 \times 10^3$, and $z = {\cdot}534$ proper to the experiment, together with $ne = {\cdot}814$, we obtain $R = 2{\cdot}8 \times 10^3$. If we had taken $ne = {\cdot}407$ we should have found $R = 1{\cdot}4 \times 10^3$. The results given by this method are therefore in general agreement with those obtained by the first method for this experiment.

§ 6. THIRD METHOD.

(*a*) *Negative Ions.*—The third method, which is independent of the first two, is based upon equation (6) and depends on the measurement of i_0, the fraction of the total number of ions which pass through the slit when in the symmetrical position, and ξ, the width of the slit. Unfortunately the present apparatus was not constructed so that this method could be applied in an accurate way. In deducing equation (6) we assumed that the slit extended the whole way across the plates and that the electrode behind covered the whole of the slit and received all of the ions which passed through it. In the experiments this was far from being the case ; the length of the electrode behind the slit was 3·7 mms., whilst the breadth of the plates was 7·7 mms. If the hot strip were indefinitely long this would easily be corrected by simply multiplying the observed values of i_0 by $7{\cdot}7/3{\cdot}7 = 2{\cdot}08$. The matter is not so simple as this, however, for the length of the hot strip was only

5·5 mms. The density of the ions received by different portions of the plates would therefore not be the same everywhere along a line parallel to the slit, as the above correction assumes, but would fall off towards the edges. Neglecting the spreading of the ions parallel to the length of the strip and assuming the temperature of the strip to be uniform throughout we should thus obtain a new correction factor, viz., 5·5/3·7 = 1·49. Since the strip is much hotter in the centre than towards the ends, this will tend to equalise the effect of the ions spreading along the length of the strip, although this will probably be accentuated by the electric field not being uniform. We shall therefore take 1·49 as being the best guess we can make as to the value of this correction factor.

In applying this method it is necessary to have absolute values of i_0, the fraction of the total number of ions which pass through the slit. The ratios of the electrometer deflexions which are given in the various curves have therefore to be divided by the ratio of the two capacities, as explained on p. 897. This ratio was not accurately determined but was known to be about 12. The uncertainty in this factor is, however, a small matter compared with the uncertainty arising out of the correction discussed in the previous paragraph.

In all the experiments described in this paper the width of the slit was ·0302 cm. and that of the strip ·026 cm.

Equation (6) may be written in the form

$$\mathrm{R}\theta = \frac{\mathrm{V}ne}{4\pi z^2} \frac{\xi^2}{\iota_0{}^2}. \qquad \qquad (11)$$

With the negative ions, in the neighbourhood of V = 10 volts, the relation $\mathrm{V}/i_0{}^2$ = constant when the other variables are kept constant, was approximately fulfilled; though this was not the case at high voltages, as we have already explained. For the data given in fig. 3 the corrected value of i_0 was found to be ·171. Substituting the values of the other quantities which have already been given we find $\mathrm{R} = 2{\cdot}52 \times 10^3$.

This value shows that the third method gives results which are consistent with the first two. It is probable that the correction is somewhat overdone in the case of the negative ions.

(*b*) *Positive Ions.*—In the case of the positive ions we have seen that the relation $i_0{}^2/\mathrm{V}$ = constant was fulfilled throughout the whole range of potential-differences employed. The method was therefore consistent over a greater range of experimental conditions although the absolute values are subject to the same kind of uncertainty as that which occurred in the case of the negative ions. The data given by fig. 4 led to the value $i_0 = \cdot 372$ and on substituting this, and the values already given, in equation (11) we find $R = 5 \cdot 4 \times 10^3$. This is also as good an agreement as could be expected. It may be that the correction is somewhat underdone in the case of the positive ions ; but we should, in any case, expect this method to give a high value for R, as the central ordinate is obviously too low, owing to some of the ions having been shot over to the left by the electric field in the manner already explained.

A large number of curves were obtained with the positive ionization which gave values comparable with the above. The curves obtained after the strip had been heated for a long time, which led to exceptional results when treated by the first two methods, were also examined by this method. The value of i_0 was found to be ·695 and on substituting this and the other numbers already given, equation (11) led to either

$$ne = \cdot 814 \quad \text{and} \quad R = 3 \cdot 16 \times 10^3,$$

or

$$ne = \cdot 407 \quad \text{and} \quad R = 1 \cdot 58 \times 10^3.$$

These results are again consistent with those given by the previous methods when applied to this experiment.

The results obtained by the third method, with an apparatus not really fitted for applying it, have been described in detail for two reasons. In the first place, it seems likely that, with slight changes in the apparatus used, this method will prove the easiest, simplest, and most reliable of the three. In the second place it seemed of great importance to show that, after making due allowance for the limitations imposed by the construction of the apparatus, this method led to the same conclusions as the others.

§ 7. All the results which have been obtained so far are consistent with the view that the distribution of the component of velocity parallel to the metal surface, among both the positive and the negative ions, is substantially that given by Maxwell's law ; and that the mean translational kinetic energy, in both cases, is the same as that of a molecule of gas at the temperature of the hot metal.

The strip used in the experiments on the negative ions had previously been exposed to high positive potentials. Dr. Brown finds that the part of the kinetic energy of the negative ions, which depends on their velocity component perpendicular to the surface, is greatly increased by previous exposure of the hot metal to high positive potentials. So far as they go, these experiments seem to show that the sideways kinetic energy of the ions is not affected by similar treatment, but this question has not yet been examined at all thoroughly.

The magnitude of the potential-difference V' through which the ions would have had to fall in order to gain the mean sideways kinetic energy assigned to them by the preceding measurements is given by $V'ne=\frac{1}{2}R\theta$. Leaving the results obtained by the third method out of account, the values are :—

For the negative ions: $\theta=1500°$ abs., mean $R=4{\cdot}55\times 10^3$, $V'={\cdot}083$ volt.

For the positive ions: $\theta=1100°$ abs., mean $R=3{\cdot}67\times 10^3$, $V'={\cdot}050$ volt.

So far we have only considered the case in which $\frac{1}{2}mw_0{}^2$ is small compared with Ve. There is one other case in which the formulæ assume a very simple form, and that is when $V=0$. If $V=0$, $x_0=0$, and ξ and ξ' are infinitesimal, the integral (4) reduces to

$$I=2n_1\frac{(km)^{3/2}}{\pi^{1/2}}\frac{\xi}{z}\int_0^\infty dw_0w_0{}^2e^{-km\left(1+\frac{x^2}{z^2}\right)w_0{}^2}$$

$$=\frac{n_1\xi}{2}\frac{z^2}{(z^2+x^2)^{3/2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If I_0 is the value of I when $x=0$,

$$I_0=\frac{n_1\xi}{2z}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

So that

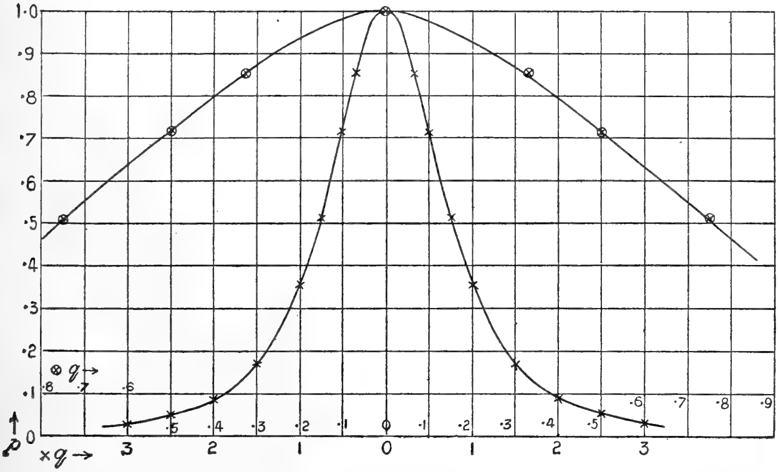
$$I/I_0=\left(\frac{z^2}{z^2+x^2}\right)^{3/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Calling I/I_0, p and x/z, q we have

$$p=1/(1+q^2)^{3/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This curve is shown with q drawn to two different scales in fig. 6. The general appearance of the curve is similar to that which obtains with high voltages except that it is spread out much more along the axis of q or x. When $V=0$ the value of I/I_0 is determined solely by the ratio x/z and is independent of the temperature of the strip and the charge on the ions. The same is true of I and I_0 separately except that these involve ξ the width of the slit and n_1 the total number of ions emitted by the strip. The latter of course is a function of the temperature.

Fig. 6.



If the distribution of the velocity components among the ions is determined by exponential functions of the type required by Maxwell's law, the formulæ (11) to (14) will hold whatever value the constant k, which determines the mean energy, may have. If this constant has different values, say k for the normal and αk for the sideways component, the distribution formulæ being otherwise as before, formula (13) becomes

$$I/I_0 = \frac{1}{\left(1+\alpha\frac{x^2}{z^2}\right)^{3/2}}.$$

The curve will thus be spread out along the x axis by an amount which would enable α to be determined.

The experimental investigation of the case when $V=0$ has had to be postponed as the apparatus employed in the rest of this investigation was unsuited to the purpose.

§ 9. All the preceding methods of analysing the experimental curves involve the principle of making a certain hypothesis as to the mode of distribution of the energy among the emitted ions and then examining the curves in such a way as to show whether they are consistent with the consequences of that hypothesis. It is important to have a more general method of attacking the problem, especially in view of the fact, demonstrated by the author and Dr. Brown (*loc. cit.*), that the distribution of the component of velocity normal to the emitting surface only follows Maxwell's law under somewhat restricted conditions. The following graphical method does not depend on any assumption as to the mode of distribution of any part of the kinetic energy.

If Ve is large compared with $\frac{1}{2}mw_0^2$ the ions which reach the plate at a distance x from the line of symmetry are emitted by the strip (of infinitesimal width) with the sideways velocity $u_0 = \frac{x}{2}\left(\frac{2Ve}{mz^2}\right)^{1/2}$. The part of their kinetic energy which depends on this velocity component is therefore

$$\tfrac{1}{2}mu_0^2 = \frac{x^2}{4}\frac{Ve}{z^2}.$$

If y is the vertical ordinate in the i, x diagram and ν is the number of ions corresponding to unit area of the figure, then the number which correspond to a strip of height y and breadth dx is $\nu y dx$. Each of these ions has the sideways energy $\frac{x^2}{4}\frac{Ve}{z^2}$, so that the total sideways kinetic energy is

$$\frac{Ve}{4z^2}\int_{-\infty}^{\infty} yx^2 dx.$$

The total number of ions is $\nu\int_{-\infty}^{\infty} ydx$, so that the average sideways kinetic energy is

$$\frac{Ve}{4z^2}\int_{-\infty}^{\infty} yx^2dx \Big/ \int_{-\infty}^{\infty} ydx. \quad . \quad . \quad . \quad (16)$$

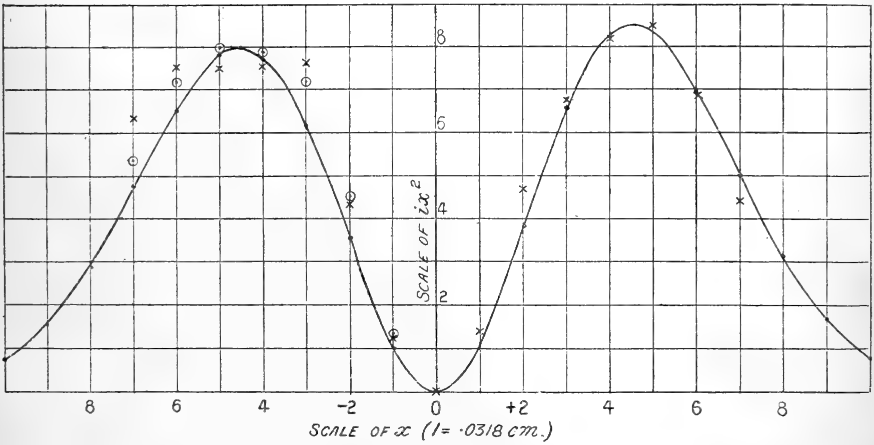
The integral in the denominator is the area included in the i, x diagram. The other can easily be obtained by plotting ix^2 against x and measuring the area enclosed by the resulting curve. The last curve, it will be observed, is a complete graphical expression of the law of distribution of u_0^2 among the ions. In a precisely similar way the distribution of u_0 could be expressed graphically.

We shall now consider the application of this method to the results already obtained, commencing with the negative ions.

§ 10. FOURTH METHOD.

(*a*) *Negative Ions.*—The values of ix^2 for the observations recorded in fig. 3 are plotted against x in fig. 7. The points marked thus, ×, were obtained by first drawing a smooth curve so as to pass actually through all the observational points in fig. 3. This was done before the theoretical curve shown in that diagram had been constructed. Corresponding values of i and x were read off this curve and the products ix^2 were calculated. The values of i are in arbitrary units but are the same for both the i, x curve and the ix^2, x curve. The points thus obtained are not quite symmetrical about the line $x=0$, so the mean values have also been plotted. These are shown thus, ⊙, on the left in fig. 7.

Fig. 7.



If $\overline{u_0}^2$ denotes the mean value of u_0^2 and if n is the number of molecules in a cubic centimetre of gas under standard conditions it is evident from equation (16) that

$$\tfrac{1}{2}nm\overline{u_0}^2 = \frac{\mathrm{V}\,.\,ne}{4z^2}\int_{-\infty}^{\infty} ix^2dx \Big/ \int_{-\infty}^{\infty} idx. \quad . \quad . \quad (17)$$

A smooth curve drawn as near as possible to the points shown in fig. 7, and completed outside the range of the points more or less in the manner of the curve shown there, gave the values $\int_{-\infty}^{\infty} ix^2dx = 8{\cdot}9 \times 10^{-2}$ and $\int_{-\infty}^{\infty} idx = 10{\cdot}4$. Substituting the values of the other quantities which have previously been given, we find

$$\tfrac{1}{2}nm\overline{u_0}^2 = 3{\cdot}2 \times 10^6.$$

On the assumption that the mean sideways energy of the ions is the same as that of a molecule of gas at the temperature θ of the metal, the value of $\frac{1}{2}nm\overline{u_0}^2$ may be calculated by the kinetic theory of gases. It is in fact equal to $\frac{1}{2}p\,\frac{\theta}{273}$, where p is the value of the standard atmosphere in dynes per cm.^{2} Putting $p=1{\cdot}01\times10^6$ and $\theta=1500°$ abs., we find

$$\tfrac{1}{2}nm\overline{u_0}^2=2{\cdot}8\times10^6.$$

This agrees very well with the experimental value.

The smooth curves drawn in fig. 7 are of the form

$$y=\mathrm{A}x^2e^{-bx^2},$$

required if Maxwell's law of distribution holds. The one on the right is

$$y=1{\cdot}141x^2e^{-{\cdot}0495\,x^2},$$

and that on the left is

$$y=1{\cdot}075x^2e^{-{\cdot}0495\,x^2}$$

(where $1x={\cdot}0318$ cm.). It is easy to deduce the proper values of the constants for these curves, since they are both determined by the coordinates of the maximum point, and this can usually be judged fairly accurately from the look of the observations. For the maximum point we have

$$\frac{dy}{dx}=\mathrm{A}(2xe^{-bx^2}-2bx^3e^{-bx^2})=0\,;$$

so that

$$b=1/x_m^2. \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Also

$$y_m=\mathrm{A}x_m^2e^{-1}\,;$$

so that

$$\mathrm{A}=\frac{ey_m}{x_m^2}=eby_m, \qquad . \quad . \quad . \quad . \quad . \quad (19)$$

where x_my_m are the coordinates of the maximum point.

By applying equation (7) we see that

$$y=ix^2=\mathrm{A}x^2e^{-\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2}x^2}\,;$$

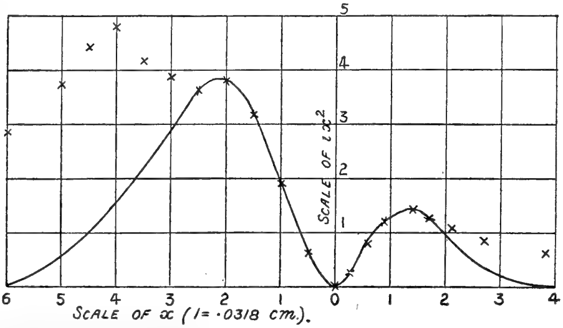
so that

$$b=\frac{\mathrm{V}ne}{4\mathrm{R}\theta z^2}.$$

Changing the units to centimetres we find from the above numbers $\frac{\mathrm{V}\,.\,ne}{4\mathrm{R}\theta z^2}=49$, which gives $\mathrm{R}\theta=7{\cdot}7\times10^6$ and $\mathrm{R}=5{\cdot}2\times10^3$. This value is somewhat higher than those obtained previously.

(*b*) *Positive Ions.*—In applying this method to the positive ions, the experimental points in fig. 4 and some additional ones from the same set of observations which fell outside the limits of that diagram were treated exactly like those in fig. 3 were treated in the case of the negative ions. The resulting values of ix^2 have been plotted against x in fig. 8.

Fig. 8.



It will be observed that this treatment greatly emphasises the lack of symmetry of the original figure. The area embraced by the left-hand portion of the curve is now very much greater than the right. It is also fairly clear that the points at a distance from the central axis do not fall on the same analytical curve as the rest. Since these correspond to very small currents they are affected by a very large experimental error in any event; but we have seen that it is quite probable that the greater part of the current through the slit at these large distances arises from ions scattered by collisions with molecules of gas in the tube and not from ions having originally the very large amounts of sideways energy indicated. Any errors of this kind are greatly emphasised by the present method of treatment. For these reasons, in calculating the mean value of the energy, the points away from the centre have not been taken into consideration, and the curves have been completed, as shown, with some regard to reasonable probability.

The value of $\frac{1}{2}nm\overline{u_0}^2$ has been determined from fig. 8 in the manner already described. Separate values have been deduced from (1) the part to the right of $x=0$, (2) the part to the left of $x=0$, and (3) the whole curve. In each case the corresponding regions of the ix diagram were used. The values obtained were :—

(1) Right-hand half... .. $\frac{1}{2}nm\overline{u_0}^2=2{\cdot}35\times10^6$ ergs.
(2) Left-hand half ..... $\frac{1}{2}nm\overline{u_0}^2=5{\cdot}9\times10^6$,,
(3) Whole curve .... $\frac{1}{2}nm\overline{u_0}^2=4{\cdot}45\times10^6$,,

The theoretical value of $\frac{1}{2}nm\overline{u}_0^2$ for this temperature (1100° abs.) was $2{\cdot}03 \times 10^6$. As with the other methods of analysing this set of experimental numbers, the right-hand half of fig. 4 gives a very close agreement with the theoretical number. The other part gives a considerably higher value, but one which is still of the same order of magnitude.

§ 11. The values of R and of $\frac{1}{2}nm\overline{u}_0^2$ which have been deduced from the foregoing experiments are collected in the following table for comparison :—

Method.	ne.	R value found.	R value calculated.	$\frac{1}{2}nm\overline{u}_0^2$ value found.	$\frac{1}{2}nm\overline{u}_0^2$ value calculated.
Negative Ions.					
I. ...	·407	$4{\cdot}6 \times 10^3$	$3{\cdot}7 \times 10^3$		
II. ...	·407	$4{\cdot}5 \times 10^3$	$3{\cdot}7 \times 10^3$		
III. ...	·407	$2{\cdot}5 \times 10^3$	$3{\cdot}7 \times 10^3$		
IV. ...	·407	$5{\cdot}2 \times 10^3$	$3{\cdot}7 \times 10^3$	$3{\cdot}2 \times 10^6$	$2{\cdot}8 \times 10^6$
Positive Ions.					
I. ...	·407	$4{\cdot}04 \times 10^3$	$3{\cdot}7 \times 10^3$		
II. ...	·407	$3{\cdot}3 \times 10^3$	$3{\cdot}7 \times 10^3$		
III. ...	·407	$5{\cdot}4 \times 10^3$	$3{\cdot}7 \times 10^3$		
IV. ...	·407	......	......	$2{\cdot}35 \times 10^6$ $5{\cdot}9 \times 10^6$ $4{\cdot}45 \times 10^6$	$2{\cdot}03 \times 10^6$
Positive Ions from old strip.					
I. ...	·407	$1{\cdot}6 \times 10^3$			
I. ...	·814	$3{\cdot}2 \times 10^3$	$3{\cdot}7 \times 10^3$		
II. ...	·407	$1{\cdot}4 \times 10^3$			
II. ...	·814	$2{\cdot}8 \times 10^3$	$3{\cdot}7 \times 10^3$		
III. ...	·407	$2{\cdot}0 \times 10^3$			
III. ...	·814	$4{\cdot}0 \times 10^3$	$3{\cdot}7 \times 10^3$		

Considered as a whole this table affords very strong support to the view that the mean sideways kinetic energy of the ions, both positive and negative, emitted by hot metals is the same as that of a molecule of a gas at the temperature of the metal.

The previous work of Richardson and Brown (*loc. cit.*) has shown that, within the limits of experimental error and under normal conditions, the part of the kinetic energy of the negative ions emitted by hot platinum which depends on the component of velocity normal to the metal surface has the same mean value as the corresponding quantity for a molecule leaving any surface drawn in a gas at the temperature of the metal; and moreover that the normal velocity component is distributed among the different ions according to Maxwell's law of distribution of the same quantity among the molecules of a gas of equal molecular weight under the same conditions. An investigation by Dr. Brown, not yet published, shows that the positive ions from hot platinum obey the same laws in this respect as the negative ions.

The present investigation, taken in conjunction with the foregoing results, shows that the ions emitted by hot platinum, whether positive or negative, are kinetically identical with the molecules of a gas, of equal molecular weight, at the temperature of the metal. This identity is true not only of the average velocity but of its mode of distribution among the different ions or molecules as well. The present investigation may be regarded as completing the evidence on which the conclusion has been based *, that the free electrons *inside* the metal have the same amount and mode of distribution of kinetic energy and velocity as the molecules of a gas of equal molecular weight at the temperature of the metal. The significance of this conclusion in other branches of physical theory has already been pointed out by Richardson and Brown (*loc. cit.*).

The argument developed by those authors, from the smallness of the currents dealt with, which compels the rejection of the continuous medium method of looking at the phenomena in favour of the atomic view, applies with equal force to the present enquiry.

In the experiments carried out in this investigation, and the others to which allusion has been made, the ions are prevented from, or helped in, returning to the metal by an external electric field. The conditions are therefore not the same as would hold in the steady state which must ultimately ensue if the metal is surrounded by a vacuous space bounded by a closed insulating surface. We are therefore not justified

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* Phil. Mag. [6] vol. xvi. pp. 374–6.

in assuming that the distribution of velocity determined by the experiments is the same as that which would hold in the steady state. Strictly speaking, this conclusion is true; but when the matter is looked at quantitively it will be seen that for all practical purposes it is false. The number of electrons which strike the bounding surface from the inside is enormous compared with the number which escape, and the number which escape must be approximately the same, whether the state is steady or otherwise, since the electric fields are too small to be appreciable within the surface layer. It follows that, even in the steady state, but an insignificant proportion of the electrons which escape from the metal will be made up of those returned to it and which do not undergo a considerable number of encounters within the metal. The number, and distribution of velocity, of the electrons emitted by the metal must therefore be the same, for all practical purposes, under the conditions of these experiments as in the steady state. We may therefore claim to have proved by direct experiment the truth of Maxwell's classical theorems relating to the distribution of velocity among a collection of material particles in statistical equilibrium.

Several of the preceding statements are true only within the limitation imposed by a considerable experimental error. There appears to be no obvious reason why the limit of error should not be materially reduced. Experiments with this object and in other directions suggested by the results of these researches are being instituted.

Princeton, N. J.,
July 6, 1908.

LXXVII. *Rotating Earth-inductor without Sliding Contacts.* *By* J. J. TAUDIN CHABOT*.

[Plate XXVII.]

As shown in a former article† it is possible—in spite of all constructions which previously apparently demonstrated the contrary—to connect together the stationary part of a circuit and the rotating coil (the rotation being continuously in one direction) by means of an unbroken conducting connexion—*i. e.* without any sliding contacts.

I have recently had an earth-inductor made according to the principle then explained, but which as constructed has

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* Communicated by the Author.

† Phil. Mag. October 1902.

FIG. 1.

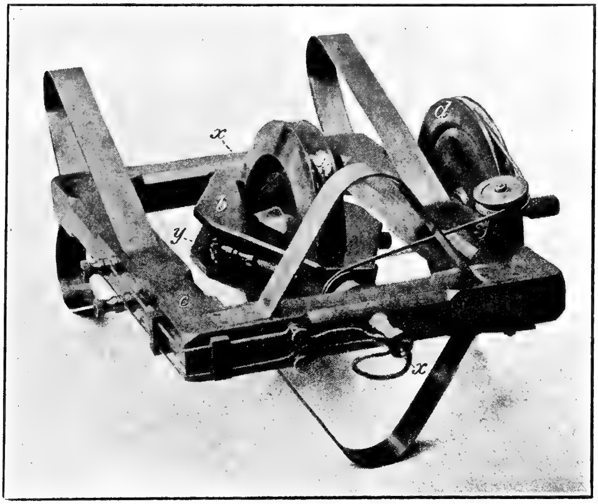


FIG. 2.

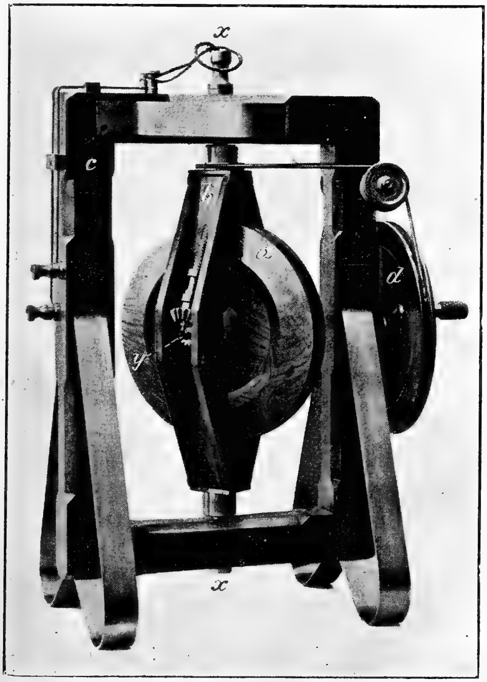
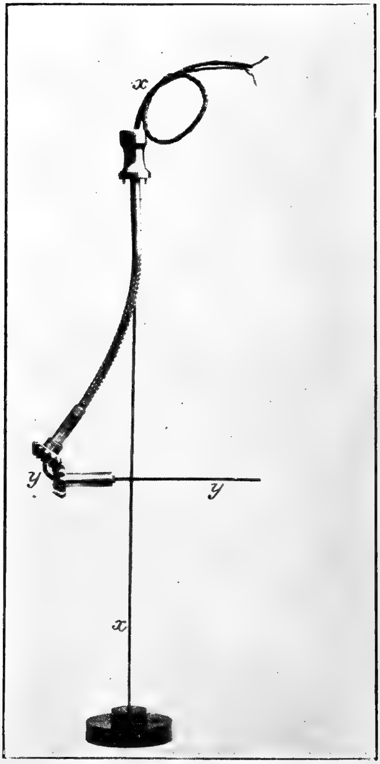


FIG. 3.



certain differences from the model previously described, which I consider to be advantageous. Hence I shall now describe the instrument in its present form with the help of figs. 1, 2, and 3 (Pl. XXVII.).

The conducting coil *a* is placed so as to turn around an axis *y* in a wooden arched-frame *b*, which is rotatable round an axis *x* normal to *y* in a fixed wooden frame *c*, which carries the driving mechanism *d*; for these axes bronze ball-bearings are employed throughout. Fig. 1 shows the instrument with a horizontal axis *x*, adapted for induction by the total magnetic field of the earth, or by the vertical component alone, according as the *x*-component runs along it transversely or longitudinally; fig. 2 shows the same with vertical axis *x* arranged for induction by the earth's horizontal component; fig. 3 shows the arrangement of the unbroken conducting path between the fixed and rotating parts of the circuit.

The brass shaft to the conducting coil *a* is hollow and terminates at the one end with a bevel-wheel gearing in the particular model, with the nearest end of another hollow shaft (which, however, is of plaited bronze wire and is therefore flexible) whose other end is fixed rigidly in the framework *c*. At each rotation of the frame *b* round the axis of *x* there occurs therefore an equal rotation of the coil *a* round the ~~axis~~ of *y* in such a manner that the conducting windings of the coil can now without further ado be connected with the stationary current circuit by a flexible cable led through the two hollow shafts. This is a concentric double cable of very fine twisted copper wire of ·0123 cm.^{2} conducting cross section for each of the two current paths. The coil is wound in a square groove of 2·1 cms. side, and has 290 turns (N) with a mean diameter of 25 cms. (D). It is made of insulated round copper wire of ·0113 cm.^{2} conducting section and 3·2 ohms total resistance (W). Accordingly there results a mean electromotive force $e=\pi 10^{-8}\mathrm{ND}^2 n\mathrm{F}$ $=5698 \,.\, 10^{-6} n\mathrm{F}$ volts, where n denotes the number of rotations per second and F the strength of the magnetic field—which must be taken as the total, vertical, or horizontal, component according to the experimental arrangement.

The constructed model allows, when worked by hand, the value $n=5$ to be attained with which a throttling by the self-inductance of the moderately wide wound induction-coil attains no appreciable value. The distance of the windings being ·15 cm. (d), the self-inductance,

$$\mathrm{L}_s = 2\pi \mathrm{DN}^2 \,(\log \text{nat}\, 4d^{-1} \,.\, \mathrm{D} - 2),$$

is about 858 kilom. (or $350^{-1}v$), so that the impedance

$W_1 = [W^2 + (2\pi n L_s)^2]^{\frac{1}{2}}$, surpasses by about 25 per cent. at the most the simple resistance, W.

Combination of several of these inductors with variously directed axes is evidently possible in the simplest manner; thence also the determination of the ratio of the magnetic components to the total field, the inclination, &c.

A special case arises, if the middle plane of the windings of the inductor-coil is placed parallel to the axis of y instead of normal to it.

In all measurements with the earth inductor by a null method (adjusting for the vanishing of the induced current) it is most effective to employ as indicator a resonance-instrument (string galvanometer or the like), whose own frequency lies within the range of the frequency of the inductor (after paying due regard to the electromagnetic constants of the entire circuit) because it means such a very great increase in the sharpness of the observations. A resonance galvanometer, *f. i.*, indicating currents of 10^{-12} ampere (I) in a circuit of 10^4 ohm total resistance (W) shows at 105 rotations per minute ($60n$) the presence of a magnetic field $F = 5698^{-1} . 10^6 I n^{-1} W = 10^{-6}$ gauss rising already at such a small variation of the earth-inductor's axis x from the axis of the geomagnetic field, that the angle will never be larger than that caused by a very small play of the rotating axis in its bearings.

Degerloch, Wuerttemberg, May 28, 1908.

LXXVIII. *An Experimental Investigation of the Nature of γ Rays.—No. 2. By* W. H. Bragg, *M.A., F.R.S., Elder Professor of Mathematics and Physics in the University of Adelaide; and* J. P. V. Madsen, *D.Sc., Lecturer on Electrical Engineering*[*].

In a previous paper (Trans. Roy. Soc. of S.A. 1908, p. 1) we have given a preliminary account of an investigation of the properties of the secondary radiation due to γ rays, and discussed the evidence thus afforded as to the nature of the rays. The first section of the present paper contains an account of further experiments, and the second a list of the properties of the secondary radiation, derived in part from the work of other observers, and in part from our own. In the third we have tried to show that the properties are

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[*] Communicated by the Authors. From 'Transactions of the Royal Society of South Australia,' vol. xxxii. (1908).

readily explained if the γ rays are supposed to be material, but are not easily to be reconciled with the æther-pulse hypothesis.

§ I.

In the former paper we showed that on the neutral-pair hypothesis the connexion between the amount of secondary β radiation emitted from the front side of a plate struck by γ rays and the atomic weight of the material of the plate should be approximately the same as for the β rays. It is, of course, known that this is actually the case. Also, we showed that the β radiation emitted from the other side of the plate, the side from which the γ rays emerge, should be the same for all substances, provided three things were true, viz.:—

(1) The γ rays were homogeneous ;
(2) The γ rays were absorbed according to a simple density law ;
(3) The β rays were also absorbed according to such a law.

If these laws did not hold, and to the extent to which they did not hold, the "emergence" radiation would not be the same for all substances.

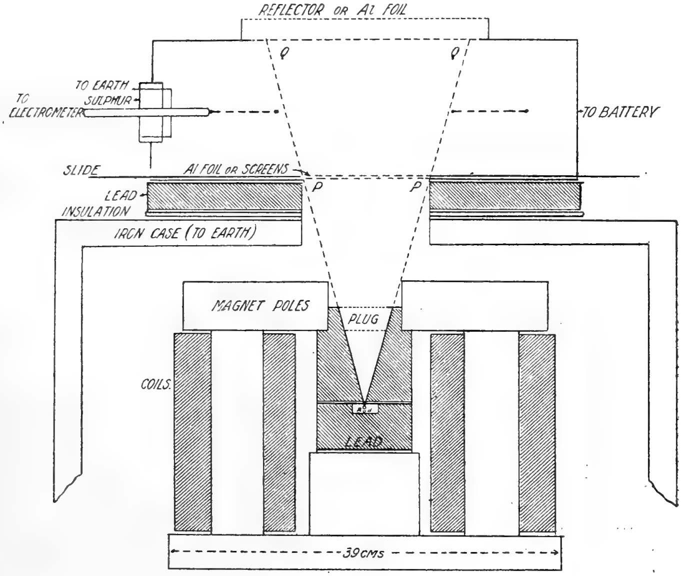
The experimental evidence which we submitted showed that the emergence radiation was not connected with the atomic weight of the material by the same law as that which held for the incidence radiation and for β rays; that it was much more nearly the same for all substances, and that such differences as existed (*e. g.*, carbon generally gave more than lead) appeared to be proper, in view of the conditions stated above. As the results we had obtained seemed to be sufficient to give a criterion between the material and the æther-pulse theories, we thought it right to publish the details of the work as far as we had carried it.

We have now made a more thorough investigation of the nature and amount of emergence radiation. We believe that we are in a position to connect together all the effects attendant on the absorption of the γ rays, and the consequent production of β rays, to a first approximation at least. Included in these effects are some which have come to light during this work, the neutral-pair theory having led us to their discovery.

It is not a very easy thing to obtain an exact measure of the emergence radiation. When a stream of γ rays is shot into an ionization-chamber through a plate forming one of the chamber-walls, a very large proportion of the ionization produced is actually due to the emergence rays of the plate. But if the plate is taken away, the place of these rays is supplied, to a varying extent, by secondary rays, made in the air or emergent from the last substance traversed by the rays. A normal stream of γ rays always contains β rays; if these are stopped by a screen, fresh β rays emerge from the other side of the screen. It is impossible, therefore, to measure the emergence rays by subtracting the value of the current when the above-mentioned plate is not in position from the value when it forms part of the chamber-wall. Such an operation might conceivably show a negative emergence radiation.

It is, in fact, necessary to remove the β rays from the stream of γ rays by some means which is more effective than a screen. A powerful magnetic field can considerably purify the γ-ray stream for a short distance along the path. Owing to the action of the air, β rays will reappear again in measurable amount after the rays have traversed a few centimetres; nevertheless, we have found the method to be fairly satisfactory so far, and will doubtless be able to improve it when better information is available for the calculation of the remaining errors. The method has already been employed by G. Kucera (*Bulletin International de l'Académie des Sciences de Bohême*, 1905), but it was finally abandoned, because the magnetic lines of induction penetrated the ionization-chamber, and affected the paths of the secondary β rays, and therefore the magnitude of the current. We therefore placed a thick iron screen (2·5 cm.) between the magnet and the chamber; the γ rays passed through a hole in the iron. This quite satisfied the purpose for which it was intended, and we were therefore provided with the means of testing the effects of a γ stream fairly free from β rays. We used a magnetic field of about 2500 units. The details and dimensions of the apparatus are shown in fig. 1. The radium was placed at the bottom of a conical hole made in a massive lead block. Plugs of various materials and different thicknesses were turned to fit exactly in the hole. The screens were brought to the position *pp* by means of a sliding frame, which passed through an opening in the side wall of the ionization-chamber. This was done to avoid the necessity of opening up the chamber, an operation which often makes readings unsteady for a short time. The electrode consisted of two concentric circles of thick copper wire, connected by short crosspieces, as shown. The chamber itself was kept at 400 volts. The radium was a fine specimen, which Dr. Herman Lawrence, of Melbourne, was so very kind as to lend us. It was contained, when we received it, in a small brass vessel covered with mica, over which a little wax had been run. Being very anxious to avoid any trace of emanation escaping into our apparatus, and at the same time to run no risk of injuring the specimen, we covered it still further with asbestos, placed the whole in a thin brass vessel, just big enough to hold it, and soldered down the lid. Thus the radium was at all times sufficiently screened to cut out most of the normal β rays, and, indeed, some of the soft γ rays as well. The Dolezalek electrometer was fitted with a fine quartz fibre : one volt moved the scale-image through four metres. The zero was fairly steady, and consecutive readings generally agreed to three per cent. ; the differences were by no means wholly due to the electrometer. As appears to be usual in the measurement of such small currents, we were somewhat troubled by unaccountable disturbances, but on most days these were not enough to interfere with the general results.

Fig. 1.



Having set up the apparatus in this way, we proceeded first to compare the incidence and emergence radiation of various substances. This was done by the measurement of the current under three different arrangements :—

(*a*) When those parts of the top and bottom walls of the chamber through which the γ rays passed were made of the thinnest Al foil (*pp*, *qq*, in the figure).

(*b*) When a plate of the substance, of proper thickness, was so placed at *pp* that the rays passed through it into the chamber.

(*c*) When a plate of the same substance was made to form part of the top wall, at *qq*, so that the γ rays struck it after crossing the chamber.

We took $b-a$ as a measurement of the emergence radiation, $c-a$ as a measurement of the incident. Some results which we obtained in this way are contained in the following table, in which the numbers refer to the movement of the scale in 30 seconds, 10=1 mm. :—

Comparison of Emergence and Incidence Radiations.

	Soft γ rays.		Hard γ rays.	
	Incidence.	Emergence.	Incidence.	Emergence.
C	170	2280	58	1150
Al	280	1810	120	795
S	340	1575	154	685
Fe	487	1350	163	560
Cu	558	...	202	523
Zn	618	1160	224	485
Sn	1051	1170	333	303
Pb	1723	2001	497	470

The figures here given show the very large want of symmetry between the radiations on the two sides of a plate. Our previous experiments proved the existence of this want of symmetry ; but it is now shown more clearly and satisfactorily.

The results still require correction before they can be considered accurate. It will be clear that $b-a$, the emergence radiation, is too small in all cases, because the screen, when placed on the bottom of the chamber, stops a certain amount of β radiation, which is made in the air just underneath the plate, and is out of reach of the magnet, as well as some fast β radiation which comes from lower down, and is strong enough to escape from the magnetic field. This is reckoned in *a*, but not in *b* ; so that on this account all the emergence radiations are too small by a certain constant amount. We have not yet succeeded in determining this constant with any accuracy. We believe it to be mainly due to the fast β rays, which emerge with hard γ rays from the upper surfaces of the magnet poles, of the lead block, and of the plug. It cannot be much less when the plug is removed, and must therefore be of more relative importance to the results for hard rays than for soft, since the total observed effects are smaller in the former case. Its magnitude is, perhaps, indicated with some accuracy by the fact that when a lead plug of 3 cm. thickness was used the emergence radiation of tellurium seemed to be nearly zero: the substance had stopped almost as much as it generated. It can easily be seen from what follows that tellurium should probably have less emergence radiation than any other substance, yet it ought to approach half the value for carbon ; and this would imply that the value of the constant was about 300 for the hard rays, and perhaps rather more for the soft. On the other hand, $c-a$, the incidence radiation, is too large, because the plate that is placed on the top of the chamber at qq not only gives rise to the incidence radiation to be measured, but also turns back to a greater or less extent the β rays striking it from below. This effect increases with the atomic weight, and must be of some importance in the case of Sn and Pb. As it is clear that these corrections will increase the want of symmetry, already obvious enough, and as we are hardly in a position as yet to make the corrections with accuracy, and as we hope to diminish our experimental errors in the future, we have for the present left these figures uncorrected.

In the first of these papers we showed that the incidence radiation should be somewhat less than p times the emergence radiation, where p is the reflexion constant of the substance in question for β rays. The above table does indeed show that the ratio of the two radiations increases with the atomic weight, and therefore with p; but the quantitative comparison appears poor. But it is to be remembered that (1) corrections yet to be made will alter the figures somewhat, making, for example, the emergence radiation of Pb greater, and the incidence radiation smaller ; (2) the quantity p is somewhat indefinite. It is true that McClelland has made careful measurements of p for various substances ; so also has H. W. Schmidt ; and the two sets of results do not agree very well. This is not to be wondered at, for the quality of the secondary radiation due to β rays is different to that of the incident, and depends on the nature of the reflector. For instance, there is some very soft radiation, of which half is absorbed in 25 cm. of air. The experimental value of p will therefore depend on how close the ionization-chamber which receives the secondary radiation is placed to the reflecting-surface. It will be largest if the surface is actually within the chamber ; and this is effectively the case in these present experiments.

Again, the incidence radiation should be *somewhat less than p* times the emergence radiation ; and the words italicized should apply specially to the case of the lighter atoms. Referring back to the argument of our previous paper, it was there pointed out that the cathode radiation, which originated in any layer of the plate and was turned back, was scattered and softened in the process. In determinations of p this effect causes the result to be too high, because slow β rays produce more ions per cm. than fast ones. At the same time, such rays contribute less to the incidence radiation than they would have done if they had possessed the same penetrative powers as the β rays which go on and emerge from the plate. This applies particularly to the lighter atoms, for it is in their case that this scattering and softening effect is so pronounced. ("Quality of Secondary Radiation due to β Rays," Trans. Roy. Soc. of S.A., Oct. 1907, p. 300.) This seems a reasonable explanation of the very large differences between the emergence and incidence radiations of the lighter atoms.

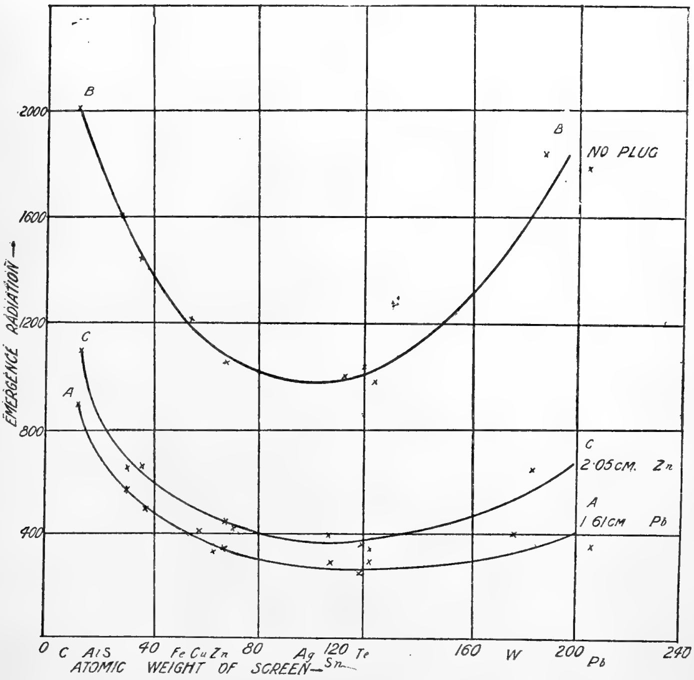
It is interesting to observe that the figures for the incidence radiations were obtained by the use of a stream of γ rays fairly free from β rays. So far as we can discover, this condition has not been realized previously. When we have successfully applied the corrections described above, the results should be of considerable interest.

Having carried these experiments sufficiently far to show clearly the want of symmetry between the secondary radiations on the two sides of the plate, we put them aside for the time, in order to compare the emergence radiations of plates of different substances. At the beginning of this paper it was stated that emergence radiations would be the same for all substances, if we could arrange to have (1) homogeneity of the γ rays ; (2) a density law of absorption for the γ rays ; (3) a density law of absorption for the β rays. All these conditions cannot be realized : but we can go a long way towards satisfying the first two. Wigger has shown that rays which have passed through 2·8 cm. of lead are then absorbed by different substances according to a density law simply: they do not recognize atomic groupings. We may safely assume that the first condition is then effectively realized also. We therefore placed a lead plug (1·61 cm. in thickness) in the conical opening (see fig. 1), and hoped to find that the emergence radiation, which we then proceeded to measure, would depend only on the absorption of the β

rays. For according to our theory equal quantities of γ rays would be converted into β rays in equal weights of different substances; and the subsequent emergence of these β rays into the ionization-chamber would be governed only by their ability to penetrate the layers intervening between their place of origin and the chamber. It is, perhaps, important to observe that we are implicitly making another assumption, viz., that the β rays originating in different substances have the same speed. On the material theory of the γ rays the assumption is natural; it is justified by the general nature of our results, and by special experiments to be described later.

Since the absorption of β rays by substances of small atomic weight is much less than in the case of the large atomic weight, weight for weight of screen; or, in the usual phraseology, since λ/ρ is smaller for light atoms than for heavy atoms, we expected the emergence radiations of C and Al to be much greater than those of, say, W and Pb. Fig. 2 shows that this expectation was realized; the results are shown graphically along the curve AA.

Fig. 2.



The representative points do not lie closely on a smooth curve. To some extent, no doubt, this is due to experimental error, for the measured quantities are very small. But we are inclined to think that the departures from regularity are to some extent real. We hope to settle this point partly by improving our apparatus, and so attaining greater accuracy of measurement, and partly by obtaining better knowledge of the corrections to be applied to the observations. For our present purpose, it is enough to draw a smooth curve such as AA, and to ignore the variations from it.

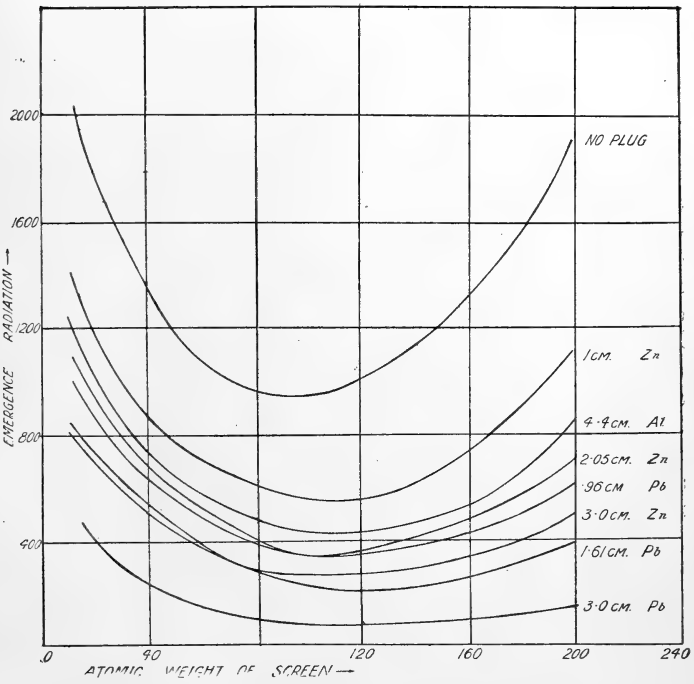
The figure shows a rapid decrease in the emergence radiations as we proceed from C to Te. There is then a small rise to W and Pb. This is easily explained, and exemplifies a very important feature of the problem. We must remember, not only that λ/ρ is fairly constant for the heavy atoms, but also that the lead screen did not completely remove the soft rays; in other words, that the pencil of γ rays was not quite homogeneous.

This will be clearly understood by comparing the curve AA with the curve BB, which represents the results we obtained when the lead plug was removed and the γ rays had passed through only the wall of the vessel containing the radium before entering the chamber. There was therefore a quantity of soft radiation in the stream of γ rays; the effect was to increase considerably the emergence radiation of Pb and W relatively to that of the other substances. This was as it should have been. We know that hard γ rays pay no attention to atomic structure, but that soft rays distinguish between atoms of different weight. In the table given by Wigger (*Jahrbuch der Radioaktivität*, 1905, p. 432) the values of λ/ρ for thin sheets of Pb and Zn are ·068 and ·039 respectively; but when the rays have been hardened by passing through 2·8 cm. of lead, each coefficient has become nearly ·02. Thus, the hard rays treat lead and zinc alike, but softer rays are more absorbed by the former than the latter, weight for weight. When a stream of γ rays is passed through a lead plate, the soft rays are rapidly converted into β rays. Consequently, a thin lead plate produces a large quantity of emergence radiation, due principally to the slow β rays produced by the soft γ rays. The effect is further discussed later on in the paper. But this is rapidly used up; consequently, the radiation measured on the far side of a lead plate is relatively large when the plate is thin, and falls off more quickly at first than it does subsequently, the plate being gradually thickened. The logarithmic curve of Pb has a rapid initial fall, as several observers have shown.

But there is a difference in the case of Al or any substance of small atomic weight. The soft γ rays give rise to much less secondary radiation, and, moreover, they are not used up so fast. Both these causes operate to make the logarithmic absorption curve of Al more nearly a straight line, as is actually the case.

It appears that a screen of any material absorbs the soft rays faster than the hard. Consequently, for example, a zinc screen or a lead screen may be used indifferently in order to reduce the ratio of the emergence radiation of lead to that of zinc. But a screen of large atomic weight acts more rapidly. If the screens of lead and zinc are chosen of such thicknesses that they absorb hard rays to an equal extent, then the former absorbs more of the soft rays than the latter. The curve CC (fig. 2) shows the results which were obtained when a zinc plug of 2·05 cm. thickness was placed in the conical opening. In both CC and AA the value for Sn is a little too small; we were not aware at the time that our Sn plate was rather too thin. In fig. 3 are drawn several curves, each showing the result of using some particular plug. In order to avoid

Fig. 3.



confusion the representative points are not marked. The effect under discussion is clearly seen on comparing, for example, the curve for 1·61 cm. of Pb with that for 3 cm. of Zn. Kleeman was the first to show that the distinction made by the γ rays between different atoms in regard to the amount of secondary radiation produced by them could be modified by screening (Phil. Mag. Nov. 1907). Our results agree with his to this extent, but they do not show any true selective absorption, such as he supposes.

We may add that when using a different specimen of radium, with which we were able to allow the γ rays to act with a minimum of previous screening, the emergence radiation of Pb was greater than that of C. It would appear probable that with very soft rays other atoms lighter than Pb would surpass C in the same way, and that it is quite conceivable that the emergence radiations should increase with the atomic weight throughout the whole range. In a letter to Nature (April 2, 1908, p. 509) Cooksey shows that in the case of X-rays the emergence radiations are greater than the incident, thus proving the parallel to our own results in the case of γ rays. He also finds that the emergence radiation increases with the atomic weight. This is the opposite to what we have found true of the γ rays in most cases ; but it is clear that it can be quite in accord with our theory.

When the screen through which the γ rays pass on their way into the chamber is gradually increased in thickness, the emergence radiation rises rapidly to a maximum, and then slowly decreases. The rise is due to increasing β radiation from the thickening screen ; the decrease to the absorption of the γ rays by the screen. There is a maximum when the two effects balance. This was clearly shown by Wigger (*loc. cit.* p. 429). If we determine the thickness which gives half the maximum value, we obtain an easy and fairly accurate measure of the penetration of the secondary β rays. It is easily shown that this particular thickness is also that which would absorb half the equally penetrating radiation from a radioactive layer, assuming an exponential law, which it is permissible to do with sufficient accuracy.

The results are shown graphically in figs. 4 to 8. In each case the curve A represents the result of an experiment in which the lead plug, 1·61 cm. in thickness, was used to screen the γ rays. The curve B shows the result with the plug removed. From each curve can be determined the thickness of screen, which gives half the full value of the emergence radiation ; the points are marked on the diagrams.

Fig. 4.

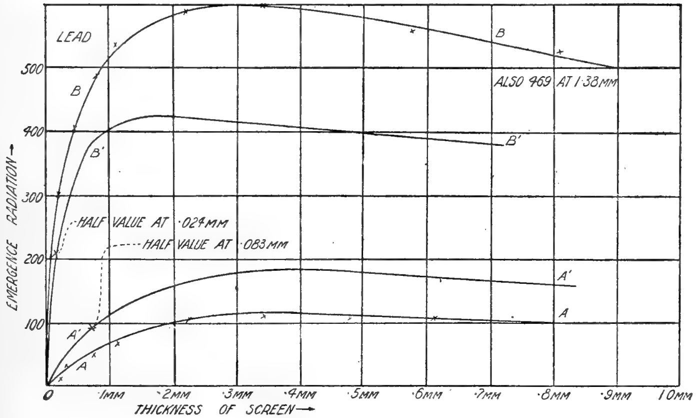


Fig. 5.

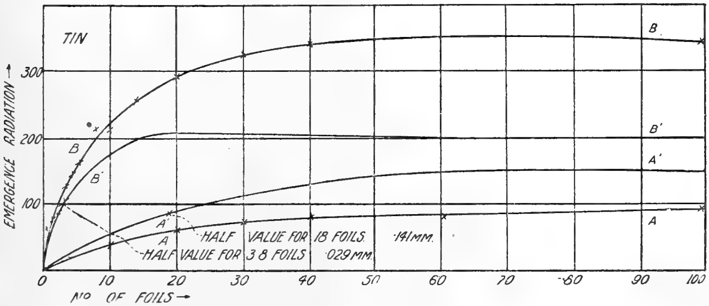


Fig. 6.

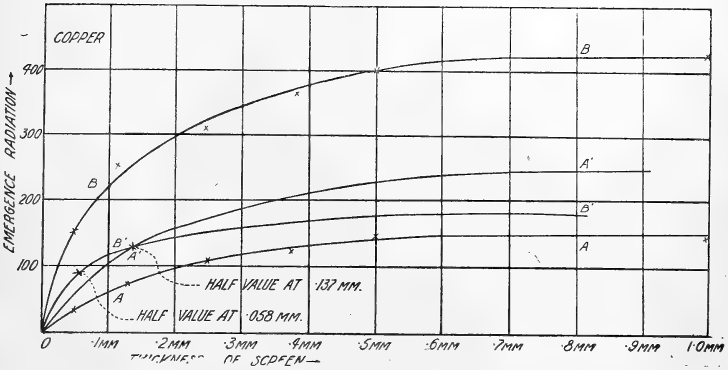


Fig. 7.

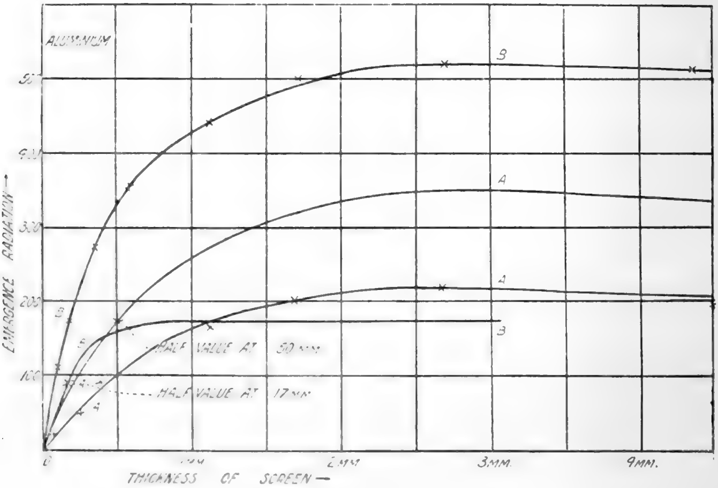
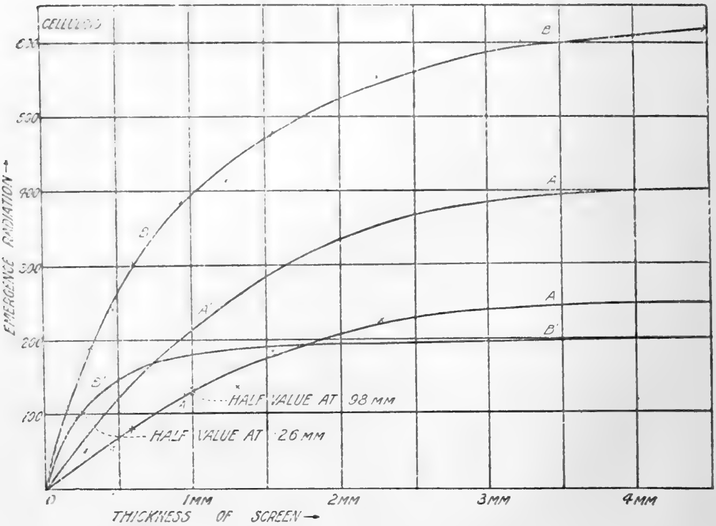


Fig. 8.



The results for the hard rays are collected and shown in the second column of the following table :—

I. Substance.	II. Thickness of screen to give half-value in mm.	III. λ calculated from II., in cm.$^{-1}$.	IV. λ for β rays. (McClelland and Hackett.)
Lead	·083	84	93
Tin	·141	50	52
Copper . . .	·137	51	55
Aluminium . .	·50	14	14
Celluloid . .	·98	—	—

The third column shows the values of λ calculated from the results in the second column. The fourth column shows the values of λ for the primary β rays of radium, as given by McClelland and Hackett (Trans. Roy. Soc. Dublin, March 22, 1907, p. 49). A comparison of the last two columns shows clearly that the secondary β rays excited by the γ rays possess nearly the same velocity, no matter in what substance they are excited, and that this velocity is the same as that of the primary β rays. Only hard γ rays have been used to excite the β rays in these experiments, while the values of McClelland and Hackett refer to β rays of ordinary heterogeneity. It is scarcely possible in the present state of knowledge to estimate what allowance should be made for this difference, but it is clear that the main conclusion cannot be affected by it. The value of λ varies rapidly with the speed of the β particle, and there is room for considerable alteration of the values in the table without any important alteration in the associated speed. Nor does much error arise from neglect of the correction discussed above, which makes the emergence radiations too small. The various curves of figs. 4 to 8 should really run a little way past the point taken as origin of co-ordinates.

If we consider the corresponding values for the soft rays, or, rather, soft together with hard rays, we find, as expected, that the β rays which they produce are of a much less penetrating character. Also, the difference between the curves A and B is most marked in the case of lead and tin, a result which is in agreement with what has gone before. For these metals the thicknesses of screen required to give half the full emergence radiation are ·030 mm. and ·048 mm. respectively, which may be compared with the values ·083 and ·141 obtained when hard rays were used. The amount of soft radiation is so large that we may consider the effect of the hard radiation mixed with it as a correction to be allowed for. The effect of the hard radiation which has been passed through the plug, 1·61 cm. of lead, is, of course, shown by the curve A. It is a little difficult to say precisely what it would have been if the rays had not gone through the plug, since the absorption coefficient for γ rays varies so much with the hardness. From ·8 cm. Pb to 1·25 cm. Pb, the value of λ is given by McClelland as ·44 cm.$^{-1}$; from 2·8 cm. Pb onwards Wigger gives ·241 cm.$^{-1}$. We have taken a value between these, towards the harder side, and drawn the curve A′ for each metal, derived from A by increasing the ordinates of A by two-thirds, a factor calculated from the absorption coefficient chosen. Subtracting A′ from B, we obtain B′, a curve which may be taken as representing approximately the behaviour of soft γ rays alone. The form of the curve for both Pb and Sn seems to suggest that the operation has been a success. The half-values are now ·024 and ·029 respectively. Thus the β rays due to these soft γ rays have only one-quarter the penetration of those derived from the harder γ rays. Possibly we have here an association with the facts stated by H. W. Schmidt (*Ann. der Phys.* Bd. xxi. p. 654), viz., that the β rays emitted by RaC consist of two groups, of which one has four times the penetration of the other. The thickness of Al screen necessary to reduce the harder set to half-value was ·53, which agrees with the ·50 given in the table above ; for the softer rays the value was ·131, nearly a quarter of the other. If there are two main groups of β rays we should certainly expect to find two corresponding groups of γ rays. Kleeman has also argued in the same direction, though for different reasons.

As will be seen from figs. 6 to 8 we have made the same attempt to sort the soft from the hard rays in respect to Cu, Al, and celluloid as in the case of Pb and Sn. The proportion of soft γ rays converted into β rays is now much less relatively. The results for soft rays are therefore of less accuracy, and depend appreciably on the allowance made for the hard rays. Nevertheless, they are of considerable interest. They show clearly the difference between the effects of hard and soft rays, and the varying proportion of soft to hard from substance to substance.

It may be gathered from consideration of all these curves that secondary γ rays play a very small part in ionizing the air within the chamber. If there were any appreciable amount of it, we should expect a gradual rise long after the effect of the secondary β rays had reached its maximum value.

§ II.

We may now give a short summary of the results of this and our previous paper :—

(1) When γ radiation is diminished in quantity in consequence of its passage through matter, β radiation appears in its place, moving at the outset in the original direction of the γ radiation, and subsequently undergoing scattering in the ordinary manner of β rays.

(2) The speed and penetration of the β radiation thus produced increase with the penetration of the γ radiation to which it is due.

(3) The speed of the β radiation does not depend on the nature or condition of the atom in which it arises.

(4) In the case of radium the speed of the β radiation produced is nearly equal to the speed of the β rays emitted by radium itself. In the case of uranium, thorium, and actinium there are indications that the law holds good also, but no exact measurements have yet been made.

(5) When very hard γ rays traverse matter the absorption and the consequent production of β rays are almost independent of the atomic structure of the matter, and a density law follows. Softer rays are affected by atomic structure, in that the heavier atoms are more absorbent than the lighter, weight for weight ; and the softer the rays are the more prominent this effect becomes.

(6) If there are secondary γ rays, the ionization which they produce is negligible compared with that produced by the secondary β radiation, at least within a moderate distance (say 100 cm. of air) of the radiator.

§ III.

Various hypotheses have been suggested as to the mode in which the secondary β radiation is produced by the interaction of the γ (or X-) ray and the atom. It is convenient to divide them into three classes, and to consider to what extent each class is able to furnish an explanation of the properties set out in the summary just given.

To the first class belong those hypotheses which suppose both the energy and the material of the β radiation to be furnished by the atom alone : the γ ray is a pulse which merely pulls the trigger. In its most recent form this idea is put forward by W. Wien (*Göttingen Nachrichten*, 1907, p. 598).

Secondly, it may be supposed that the energy of the β radiation comes from the γ ray, but the material from the atom. The γ ray is a bundle of electric energy, possessing mass, which impinges on the atom and drives out the electron before it. This is the view now held by J. J. Thomson (Camb. Phil. Soc. Proc. vol. xiv. pt. iv. p. 417).

Thirdly, both the energy and the material of the β ray may be supposed to be derived from the γ ray. The latter is not a pulse but a neutral pair, positive and negative ; in passing through some atom the bonds are dissolved, and the negative flies on (Trans. Roy. Soc. of S.A., May 1907 ; Phil. Mag. Oct. 1907).

Consider first the theory which considers that the whole of the energy of the expelled electron comes from the internal energy of the atom. It is to be supposed that the pulse as it widens finds an atom here and there which is in an explosive condition, and that in some unknown way it precipitates a catastrophe. There is, of course, one point which is immediately cleared up by such an hypothesis, viz., that the speed of the expelled electron is independent of the intensity or quantity of the primary radiation. But here we stop short, for we have also to explain why the speed of the electron is *not* independent of the quality of the primary radiation. Why should the speed be great when the primary γ rays are hard, and small when they are soft ? Why should the velocity of the shot depend on the way in which the trigger is pulled ? We might get out of the difficulty by supposing an atom to be like a battery which contained a number of different kinds of guns, and that the pulses were selective, each pulling the trigger of its own particular gun. But even if we have presumed some highly artificial arrangement of this kind, we have greater difficulties still to face. How is it that the pulses always find the guns pointing in the direction in which they are travelling themselves, so that the motion of the shot is a continuation of their own line of flight ? For if the speed of the electron is independent of the strength of the pulse, then, so to speak, the touch on the trigger must be very light indeed, and can have nothing to do with the laying of the gun. We might perhaps suppose that there were guns in the battery pointing in all directions, and that the pulse only fired the one which pointed in that direction in which it was travelling itself ; but this would require a special atomic structure to meet the case, and it would be out of all proportion to frame such an hypothesis to explain the observed effect. Nor do our difficulties end here. For if the expulsion of the electron is the result of an atomic disintegration, should we not expect the velocity of the electron to vary from atom to atom, as it does in the case of the radioactive substances? It is inconceivable that the explosion of a light atom should result in the expulsion of an electron with exactly the same speed as in the case of the heavy atom. And, further, assuming the same hypothesis, how can the production of β rays, in the case of the hard γ rays, be absolutely independent of atomic structure in all respects whatever?

Thus, after its first small success, the theory breaks down at every point. It is true that Wien makes a tentative application of a theory of Planck, viz., that energy emitted from atoms is divided into definite units, the size of which is inversely proportional to the associate wave-length. He thence deduces the law $v^2\lambda=$constant, where v is the velocity of the ejected electron, and λ the thickness of the X-ray pulse which he is considering. He thus passes by the need of explaining certain of the difficulties just discussed, and arrives at a formula from which the second and third properties in the above summary may be derived. Even then his theory fails to explain the first and fourth properties. It seems to us to be clear that the application of Planck's theory is not justified. And, generally, we conclude that the energy of the secondary β ray does not come from the atom.

We now come to the second case. In this there is no suggestion of trigger action; the energy of the β radiation is supposed to be entirely derived from that of the æther pulses. As already mentioned, this theory has lately been maintained by J. J. Thomson (Proc. Camb. Phil. Soc. vol. xiv. pt. iv. p. 417). It is also discussed by N. R. Campbell ('Modern Electrical Theory'). Since an æther pulse of the orthodox form spreads its energy over wider and wider surfaces as it radiates from its origin, and since the energy of the ejected secondary particle is immensely greater than can be imparted to it during the passage of the weak, and always weakening, pulse, it becomes a necessity on this hypothesis to concentrate the energy of the pulse along radial lines, having their centre at the place where the primary cathode particle is suddenly stopped or accelerated. Thomson speaks of "bundles of energy" occupying only a very small portion of the wave-front, the rest of the front being blank. Of course this at once suggests explanations of some of the difficulties of the γ and X-rays, such as the ionization of only a few of the atoms swept over by the wave, and the absence of relation between the velocity of the secondary electron, on the one hand, and, on the other, the intensity of the radiation and the nature of the atom. Also, it makes provision for a concentration of momentum. This theory, however, postulates a very special and complicated structure of the æther. And, in the second place, it does not even then offer an explanation of all the phenomena.

If a "bundle of energy" provides the energy with which the secondary cathode particle leaves the atom, then the energy-content of the bundle must be greater than the energy of the particle. If, on the other hand, as in the case of the X-rays, the energy of the bundle is derived from that of the arrested cathode particle, the former must be less than the latter. Now, it seems quite clear that the energy of the secondary electron is at least nearly as great as that of the primary cathode particle. For in the case of the X-rays the velocity of the secondary electron is nearly 10^{10}, and is therefore much the same as that of the cathode rays in the bulb. And we have shown above, in the analogous case of γ rays, that the velocity of the secondary β ray, produced by the γ ray, is practically the same as that of the primary β ray, which issues with the γ ray. We must, therefore, conclude on this hypothesis that the energies of the primary electron, the bundle, and the secondary electron are all equal. The whole of the energy of the cathode particle in the X-ray tube is converted into one energy bundle. This darts away from the anticathode, and sooner or later causes the ejection of an electron from some atom which it traverses, handing over to the electron the whole of its own store of energy. Replace the bundle of energy by a neutral pair, and the whole affair seems simple enough. But surely the complications of the æther structure increase the more closely we examine the process under which rapidly moving electrons in the X-ray tube disappear, and similar electrons, moving at the same rate, appear elsewhere, if we are to consider that the only links between them are little bundles of energy moving with the speed of light.

It might be said, perhaps, that one bundle contains the energy of several arrested electrons; but in that case we should have bundles of all sizes and secondary electrons of all speeds; or that several bundles might pile up their energies in one atom until there was enough for the ejection of one secondary electron; but then we should return to the difficulty of explaining why the speed is independent of the nature of the atom.

A cathode particle cannot give all its energy to a pulse unless its arrest is brought about in a very sudden and special way. The thickness of the pulse must not be greater than the diameter of the electron or corpuscle ('Cond. of Elect.,' p. 660). If the pulse is thicker than this, only a proportional fraction of the energy of the cathode particle can be converted into the energy of the pulse. Now it is generally believed that the phenomena of the X-rays require a pulse many thousands of times as thick as the diameter of an electron. It does not seem possible to reconcile these opposite requirements.

The bundle must be excessively small. If it is larger than an atom, or even than an electron, the whole of its energy cannot be given up to one electron on which it impinges. There would not be time for the energy to move in from the outskirts of the bundle to the place where it is being transformed into the motion of the electron. It must not expand or contract its borders as it moves, or else its effect will vary as it travels.

The difficulties of this theory are exactly those which would naturally arise in the attempt to transfer the properties of a material particle to an immaterial disturbance.

Let us now consider the third form of hypothesis, according to which both the energy and the material of the secondary electron are derived from the primary ray. In our previous paper on this subject, and in papers on "The Properties and Natures of Various Electric Radiations" (Trans. Roy. Soc. of S.A., May and June, 1907 ; Phil. Mag. Oct. 1907), it was shown that the hypothesis offered a reasonable explanation of all the phenomena known to date. It is only necessary now to show to what extent it fits with the properties of the γ rays enumerated in § II. of this paper. We will take the properties in turn.

As regards (1) we have simply to suppose that the negative and positive, passing united into an atom, are separated if they happen to traverse a very strong field anywhere therein ; the negative flies on and the positive becomes ineffective.

The second property is also an obvious consequence of the hypothesis. The faster the γ particle is moving the greater the initial speed of the negative.

The third is readily explainable: the electric field of the atom merely dissolves the bonds that connect the pair. It is not able to affect the speed of the negative set free.

The fourth may be taken to imply that the radioactive atom (say RaC) ejects electrons at certain speeds, some of which start off in company with a positive counterpart, some without. The former constitute the γ rays, the latter the

β rays. When the γ rays break up, the negatives so produced have the same speed as the primary β rays.

The fifth would show that there are stronger fields inside heavy atoms than light ones, and that the chance of separation of a pair increases with (a) the strength of the field, (b) the time taken to cross it.

This is all the explanation that is necessary. We can at least claim that it is much simpler and more complete than any explanation which the æther-pulse theory seems likely to afford, even in its latest form.

It is true that the neutral-pair hypothesis requires the existence of a positive counterpart to the negative electron. In a previous paper it was suggested that this might be an α particle; the results of this paper seem rather to suggest that its mass is only small, and that it may really be a positive electron. Now the positive electron has hitherto been received with little favour; but the argument has been not so much against its existence as against its presence in metals in a free state. The latter is not at all necessary to our hypothesis. We require only that the positive shall exist, that it can be torn from its attachment and carried away by a passing negative electron, and, again, that it can be left behind in some atom which the pair subsequently traverses.

The recent determination by Cooksey of the want of symmetry between the emergence and incidence radiations due to X-rays is the last experiment required to show that all the properties in the summary of § II. are true for X-rays as well as for γ rays, *mutatis mutandis.* All the properties except the first have been already shown to be true (see our first paper on this subject). The complete parallelism between X- and γ rays stands out more strongly than ever.

In conclusion, there is one aspect of the problem which seems to invite a little further consideration. The characteristics of the secondary β ray are independent, as we have seen, of the nature of the atom in which it arises, and depend only on the nature of the γ ray to which it is due. This is all the more remarkable when we consider that the characteristics of primary β rays are peculiarly dependent on the nature of the atoms whence they emerge, and are absolutely independent of physical agencies acting from without. In the one case, that of secondary β radiation, we can determine that a given material shall emit β rays of definite speed and direction, and can carry out our determination by the use of suitable agencies and dispositions. In the other case, that of primary β radiation, the whole process is completely beyond our control. It is one example of this contrast that the radioactive substances do not emit secondary radiations to an abnormal extent. It is clear that there is a sharp line of distinction between the emission of an electron from an atom as a primary β ray, and the emergence of an electron from an atom as a secondary β ray. On our hypothesis the origin of the distinction is simply that in the former case the electron was part of the atom which ejected it ; in the latter case, it was no part of the atom : it came in with the exciting ray. All the experimental evidence accords with this view. We come very close to the complete realization of an anticipation made twelve months ago (Trans. Roy. Soc. of S.A., May 7, 1907, pp. 84, 85): "All secondary radiation, other than the δ rays, seems to be in general a rough reflexion or scattering of the primary. . . . The only cases in which a secondary radiation appears, that is neither δ radiation nor reflected primary rays, are those in which β rays are produced at the impact of X- or γ rays, and in which X-rays are produced by cathode rays. . . . It may well be that further research will bring these cases into better agreement with the rest." On the neutral-pair hypothesis the exceptions mentioned here practically disappear. There remains a broad generalization, which, with all the faults natural to its kind, seems to us to be applicable to every case of which we have knowledge, and to be an important principle of the theory of secondary radiation.

LXXIX. *On the Principle of Relativity.*

A Reply to Mr. E. Cunningham. *By* A. H. BUCHERER [*].

NOTWITHSTANDING my objections Mr. Cunningham, in the September number of this Magazine, still asserts that my principle of relativity leads to the same forces as the Lorentz-Einstein principle. *Mr. Cunningham seems not to have noticed that the forces on moving electrons are quite different.* Take the concrete case realized in experiments, and let Becquerel rays traverse a uniform magnetic field. The force on the electron, according to my principle, is

$$\frac{\epsilon \mathrm{H} u \sin \alpha}{1-\frac{u^2}{v^2}\cos^2 \alpha},$$

whereas according to Lorentz the force is

$$\epsilon \mathrm{H} u \sin \alpha.$$

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[*] Communicated by the Author.

Referring to my first paper on the subject in this Magazine, I had from the first recognized that the question, which of the various theories represented the law of nature, was one for experiment to decide. I have completed the experiments foreshadowed[*], and in contradiction to Kaufmann have verified the substantial accuracy of the Lorentz formula for the electromagnetic mass, and therefore also of the Lorentz-Einstein principle of relativity, since the only serious objection to its complete acceptance has been removed.

Bonn University, Oct. 5, 1908.

LXXX. *On a Method of Showing Fluorescent Absorption directly if it exists.* *By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University*[†].

THE question as to whether the fluorescence of an absorbing medium modifies in any way its absorption appears to be still unsettled. Burke's experiments with uranium glass[‡] appeared to show that a block of the glass, when excited to fluorescence by a transverse beam of light, absorbed the fluorescent light of a second block of the same glass more strongly than when unilluminated. More recent work by Nichols and Merritt[§] showed the same effect in the case of solutions of fluorescein, and apparently confirmed the discovery of Burke. They made use of the spectrophotometer, measuring the intensity of the light of the fluorescing solution alone (F), the intensity of a source of light seen through this solution when not stimulated to fluorescence (T), and the intensity of the fluorescence plus that of the source when seen through the fluorescing solution (C). It is obvious that if the absorption is not modified by the fluorescence, we shall have F + T = C. They found, however, that in practically every case C was less than F + T. Similar results were obtained by Miss Wick[‖], with resorufin, working in the same laboratory. Camichel[¶] has, however, been unable to find any trace whatever of the effect, using similar methods.

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[*] Phil. Mag. ser. 6, vol. xiii. p. 419 (April 1907).
[†] Communicated by the Author.
[‡] Phil. Trans. cxci. p. 87 (1898).
[§] Phys. Rev. xviii. p. 447 (1904).
[‖] Phys. Rev. xxiv. p. 407 (1907).
[¶] *Compt. Rend.* cxl. p. 139 (1904).

The importance of the phenomenon, if it exists, makes a method of showing it directly much to be desired. The strangeness of the apparent laws of this new type of absorption makes one suspicious that some unforeseen error has crept in, which may account for the whole thing. The intensities are measured by varying the width of the slit of the spectrophotometer which delivers light to the comparison field, and no mention is made whether the slit was calibrated or not. It is possible that a wide slit was used in all cases, and that calibration was unnecessary. I have recently devised two methods, one for showing the phenomenon directly if it exists, and the other for detecting the error in the spectrophotometric method, should it be present.

The latter is very simple, and though I have not tried it, I recommend it in any subsequent work which may be done with the spectrophotometer upon the subject.

Substitute for the fluorescent tank a piece of thin plate glass at an angle of 45° to the axis of the collimator, which reflects light from an illuminated screen into the instrument. Measure the intensities as in the case of the fluorescent solution, first the light from the transparent reflector, then the light from the source behind the reflector, the latter unilluminated, and then both together; first adjusting the relative intensities so that they are about the same as in the actual experiment. If the method is at fault the sum of the intensities will differ from the total. It is possible that some physiological effect comes in, and I have not had enough experience with photometric work to know whether, in all cases, the sum of the intensities of two sources of light, measured separately, is numerically equal to the total intensity of the two measured simultaneously. The method which I have outlined above should answer the question however.

The method for showing the phenomenon directly, independent of any measurements, I have given a thorough trial, and can see no objections to it. In brief, I make the illuminations rapidly intermittent with a rotating perforated disk, and bring them into step and out of step in alternation. When they are in step the tank is fluorescing while it transmits the light from the source behind it. When out of step the tank is in darkness while passing the light from behind. If fluorescent absorption is present the total illumination should be greater when the flashes come out of step, for in this case there is no fluorescence during transmission.

I have tried the method under various conditions, and in no case have I found any evidence of the effect. It is possible that the experimenters who have observed it by other methods may be able to pick it up by this method, as I may have worked with too strong or too feeble illuminations, though I have varied them over wide limits. If it can be obtained by this method, all doubt as to its existence must cease, for observation errors are eliminated, and we can actually see the increase in the absorbing power.

Obviously uranium glass is not well suited, for the fluorescence, or rather phosphorescence, of this substance persists for an appreciable time after the stimulating radiations are cut off. This is not true, however, for solutions, which show no trace of continued emission, even at the highest speeds of the phosphoroscope disks.

Inasmuch as variations in the intensity of the source, provided they are not too rapid, give no trouble in the case of this method, the arc has been used in all of the work. It was found that a 220 volt arc, with a heavy ballast resistance in circuit, gave excellent results, the hissing and sputtering so common with the 110 volt current being absent.

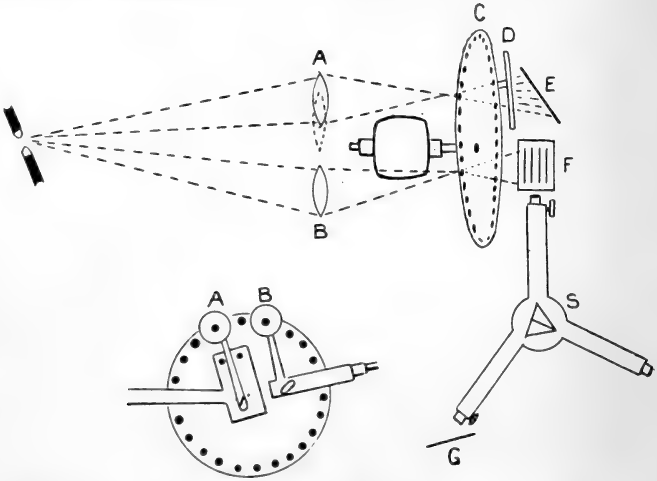
The light from the arc was focussed upon the perforated disk by means of two short-focus lenses, one fixed in position, the other arranged so that it could be rotated through a small arc about an axis coincident with the axis of the revolving disk, the length of the supporting arm being equal to the radius of the disk. The distance through which the lens could be moved was regulated by two stops, so adjusted that in one position the two images of the arc fell upon the openings of the disk simultaneously, while in the other position the image formed by one lens fell midway between two of the openings when the other was illuminated. The disk was mounted on the shaft of a small electric motor operated at very slow speed. Glass tanks filled with a very dilute solution of fluorescein were mounted behind the openings in such a position that they received the flashes of light transmitted by the disk. By this arrangement we can study the fluorescent absorption for the light emitted by the fluorescent substance, the case being analogous to that studied by Burke. The movable lens could be moved rapidly back and forth, but no flicker in the intensity of light was observed. Diaphragms were introduced to restrict the field, and the relative intensities were varied, but the effect could not be found. To render the change still more marked, if it existed, a nicol prism was placed between the two tanks, and a second nicol, with its polarizing plane parallel to that of the first, placed in front of the eye. By this arrangement we can reduce the intensity of the light coming from the fluorescing absorbing tank by one-half, without altering the intensity of the source behind it, the source of course being considered as the light after transmission through the first nicol.

The weakening by the first nicol is an advantage, for the percentage absorption is greater when the intensity of the source is small, according to Nichols and Merritt, who found that the fluorescent solution apparently absorbed a certain definite quantity of light regardless of the amount of light sent through it, a circumstance at variance with all the known laws of absorption. By the addition of the nicols the percentage change should be doubled, yet even in this case no effect could be seen, though calculation showed that with the intensities used a change of at least 20 per cent. was to be expected.

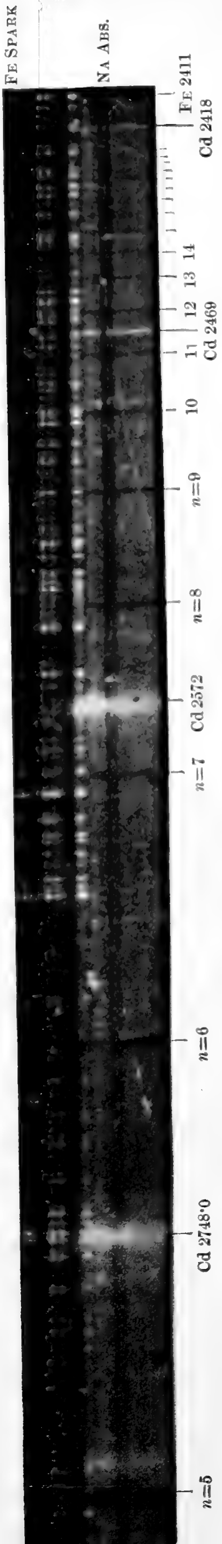
It was next determined to use a monochromatic illuminator as the source of light, and work with the wave-length most favourable for the exhibition of the phenomenon, as determined by Nichols and Merritt. The light from the slit of the instrument after passing through the rotating disk was focussed on the eye by means of a small lens, which thus appeared filled with a uniform illumination. Between the lens and the eye was placed the fluorescent tank, illuminated with a beam from the arc, coming through an adjacent aperture in the disk. The monochromatic illuminator was illuminated with a Nernst lamp, and the arc was focussed on the disk by means of the movable lens. No effect was observed in this case.

It is necessary of course in using this method to make sure that the motion of the lens and the accompanying shift in the direction of the transmitted beam causes no change in the intensity of the fluorescent solution. It is not difficult to fulfil this condition if the width of the transmitted beam and the distance of the tank are properly attended to.

As a last resort, the method was still further improved by weakening the intensity of the fluorescent tank by prismatic dispersion, and the spectrophotometer was added to the apparatus. By this means the transmitted light which we observe can be made practically monochromatic, and we see superposed on it only that portion of the fluorescent light in the same part of the spectrum. This method is therefore superior to the use of the polarizing prisms, and we have in addition a comparison field of exactly the same colour, with a vanishing line between the two fields. This latter modification is by far the best of all, for if the fields are matched when the flashes are in step, the line of demarcation should appear when the flashes are thrown out of step. The arrangement of the apparatus is shown in the figure, which is a view from above.



Light from the arc passes through the two lenses A and B, the former of which moves on a hinged arm, as shown in the lower figure, and is brought to a focus on the perforated disk. The pencil diverging from the focus formed by A falls upon a diffusing screen of thin porcelain D, and illuminates the white screen E. Light from the other lens illuminates the fluorescent tank F. One collimator of the spectrophotometer receives the light from E and F either simultaneously or in succession, according to the position of the lens A, illuminating the silver strip which crosses the centre of the field of the instrument in a horizontal direction. The other collimator receives light from the white screen G, and illuminates the remainder of the field. The telescope is set so that the field is illuminated with monochromatic light of wave-length 5180, for which Nichols and Merritt found the largest value of the fluorescent absorption, and the two halves of the field adjusted to equality, the line of demarcation disappearing. The lens A is then shifted, throwing the flashes out of step. If fluorescent absorption was present before, it should be absent now, since F is dark when the light from E passes through it, and the silver strip should consequently brighten and become visible. Absolutely no change could be seen, however, which makes it seem certain that the absorption is the same in the two cases.



EXTENSION OF THE SODIUM SPECTRUM.

LXXXI. *An Extension of the principal Series of the Sodium Spectrum.* *By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University* [*].

[Plate XXVIII.]

THE largest number of lines in a Balmer series which has ever been observed in the laboratory is thirteen, which were found in the hydrogen spectrum by Cornu and by Ames. In the spectrum of the Chromosphere twenty-nine hydrogen lines of the series have been recorded, the last line ($n=31$ in the formula) being within only fifteen Ångström units of the theoretical end of the series. In the case of sodium vapour seven lines of the principal series have been discovered up to the present time. In studying the ultra-violet absorption spectrum of the vapour I have already raised the number to thirty, though the last six lines are so close together, with the dispersion at my command, that it is impossible to determine their wave-lengths. This makes by far the most complete Balmer series ever observed in the laboratory, and places the sodium spectrum on an equal footing with the hydrogen spectrum of the chromosphere. In my opinion a further extension of the series is merely a question of vapour-density and dispersive power. No lines other than those of the principal series appear in the absorption spectrum (disregarding channelled spectra), consequently we are not obliged to hunt about in a confusion of lines for the ones which belong to the series, as is the case with the spectrum of hydrogen obtained with vacuum-tubes.

The vapour is obtained by heating the metal in a steel tube about a metre long to a dull red heat. It is almost opaque to all visible radiations, only the extreme violet being transmitted. It is best to work with a pressure of about 15 cms. of nitrogen in the tube, as in a highly exhausted tube it is difficult to get the requisite density. It is unnecessary to fill the tube with nitrogen, for the sodium vapour soon removes the oxygen, the smoke settling in a few minutes.

The source of light was the cadmium spark furnished by a large induction-coil with condenser. This gives a fairly bright continuous background, and has no bright lines which coincide with any of the sodium lines.

The spectrum was photographed with a small quartz spectrograph made by Fuess, which, though having a focal length of but 12 cms., gives in the region under investigation a dispersion about equal to that of a concave grating of

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[*] Communicated by the Author.

a metre-radius ruled with 15,000 lines to the inch. By employing an exceedingly fine slit and taking especial pains about the focus, the wave-lengths can be determined to within about 0·2 of an Ångström unit. The number of lines which appear in the absorption-spectrum increases with the vapour-density, and I feel sure that by employing a longer tube, and giving a longer exposure, many more lines would come into view. One of the photographs is reproduced on Pl. XXVIII., greatly enlarged of course, with the spark-spectrum of iron as a comparison spectrum. On the original negative the absorption-lines can be seen as far down as the cadmium line 2418, while the theoretical end of the series is at the iron line 2411. Both of these points I have indicated on the print.

The wave-lengths are as follows :—

$n = 3$	5893 (mean)
$n = 4$	3303
$n = 5$	2852·9
$n = 6$	2680·5
$n = 7$	2593·8
$n = 8$	2544·3
$n = 9$	2512·2
$n = 10$	2491·5
$n = 11$	2476·4
$n = 12$	2464·9
$n = 13$	2456·3
$n = 14$	2450·0
$n = 15$	2444·7
$n = 16$	2440·4
$n = 17$	2436·9
$n = 18$	2434·2
$n = 19$	2432·0
$n = 20$	2430·0
$n = 21$	2428·2
$n = 22$	2426·7
$n = 23$	2425·8
$n = 24$	2425·0
$n = 30$	2418·1 cal.
$n = \infty$	2409·8

Under the microscope of the dividing-machine, on which the plates were measured, five or six more lines could be seen crowded together between the last line measured and the cadmium line 2418, which is in agreement with the calculated position for the line for which $n=30$.

I hope to have an opportunity in the near future of photographing the spectrum with a large quartz spectrograph, which will make a more accurate determination of the wave-lengths possible. I feel sure that those in the table are correct to within 0·2 Å.E. I have calculated the wave-lengths from the formula given in Kayser's 'Spectroscopy,' vol. ii. page 521, for several of the lines, and found very good agreement with the observed values. As soon as more accurate values have been found with a large quartz spectrograph, a more careful comparison will be made. These results I hope to be able to publish in the forthcoming number of the 'Astrophysical Journal.' The line for which $n=4$ is not shown in the photograph. At the density employed in making this exposure it was found to be bordered on each side with what appeared to be a channelled spectrum, precisely as are the D lines, for which $n=3$. A faint indication of a channelled spectrum also appeared about the line for which $n=5$, in some of the negatives made with still greater vapour-density. I have already shown that the channelled spectrum in the green and blue region is connected in some way with the D lines, for the D lines appear in the fluorescence spectrum when the vapour is stimulated by blue-green light which is absorbed by the channelled spectrum. The fact that the other members of the principal series are also accompanied by channelled spectra is very significant.

At the present time I am making efforts to find some way of making the higher frequency members of the principal series appear in the emission spectrum, but thus far have not found the proper conditions.

LXXXII. *On a Certain Development in Bessel's Functions.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a numerical calculation of the torsion of a circular cylinder under shearing forces distributed arbitrarily over the ends, there has come to notice an apparent oversight in the usual method of determining the coefficients in certain series of Bessel's functions. The formulas used in the computation are given by Chree (Trans. Camb. Phil. Soc. vol. xiv., 1889, p. 366), who finds that in a cylinder the displacement (v) perpendicular to the radius and axis, if it is independent of the angle, must satisfy the equation

$$\frac{\partial^2 v}{\partial r^2}+\frac{1}{r}\frac{\partial v}{\partial r}-\frac{v}{r^2}+\frac{\partial^2 v}{\partial z^2}=0.$$

The solution given is of the form

$$v=\Sigma A_\lambda J_1(\kappa_\lambda r)\sinh\kappa_\lambda z,$$

where $J_2(\kappa_\lambda a)=0$, a is the radius of the cylinder, and A_λ is so chosen that

$$\nu\Sigma\kappa_\lambda A_\lambda\cosh(\kappa_\lambda l)J_1(\kappa_\lambda r)=f(r),$$

where l is the length of the cylinder, ν a physical constant, and $f(r)$ the shearing stress perpendicular to the radius on the end $z=l$. The value given for A_λ is

$$A_\lambda=\frac{2}{a^2[J_1(\kappa_\lambda \alpha)]^2}\int_0^a rf(r)J_1(\kappa_\lambda r)dr.$$

That the formula is in error is seen immediately by putting $f(r)=r$, for all the coefficients vanish. This corresponds to the most important practical case, and gives the absurd result that a cylinder experiences no torsion under a torsional force varying as the distance from the axis. It is well known that in this case v is proportional to rz.

The general theorem involved is as follows. The development of $f(r)$ into a series $\Sigma A_\lambda J_n(\kappa_\lambda r)$ where $J_{n+1}(\kappa_\lambda)=0$ is not possible. The series must include, besides the Bessel's functions, the initial term A_0r^n, a term which satisfies the same type of equation as J_n. The correct development is as follows:—

$$f(r)=A_0r^n+\sum_1^\infty A_\lambda J_n(\kappa_\lambda r),\qquad\text{from 0 to 1,}$$

where $J_{n+1}(\kappa_\lambda)=0,$

$$A_0=(2n+2)\int_0^1 f(r)r^{n+1}dr,$$

and

$$A_\lambda=\frac{2}{[J_n(\kappa_\lambda)]^2}\int_0^1 rf(r)J_n(\kappa_\lambda r)dr.$$

The initial term A_0r^n corresponds to the zero root of J_{n+1}, but its correct value cannot be obtained by a limiting process from the general coefficient.

Dini, in his *Serie di Fourier,* gives the theorem, but it is misprinted so that the first term appears as a constant. Nielsen, *Handbuch der Cylinderfunktionen,* misquotes Dini's misprinted form, while in no other book of which the writer is aware is the existence of the extra term even mentioned.

I am, Sirs,
Yours very truly,
P. W. BRIDGMAN.

The Jefferson Physical Laboratory
Cambridge, Mass., U.S.A.
July 22, 1908.

LXXXIII. *On the Rings of Saturn.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE Philosophical Magazine for April, 1908, p. 469, publishes the following paragraph written by Mr. Percival Lowell:—

"Although seen by all the observers at Flagstaff, the black core was not caught by Barnard at Yerkes, nor has it been reported from the Lick. This, however, is in keeping with the definition at the first place disclosed already by its greater space penetration for stars."

Statements similar to that made in the last quoted sentence have in the past three years been published by Mr. Lowell in several popular, semi-popular, and technical magazines; and it seems to be my reluctant and unprofitable duty finally to take note of them.

Recent observations at the Lick Observatory (soon to be published elsewhere) show that Mr. Lowell is not justified in claiming "greater space penetration for stars" for his telescope. But his article in this Magazine, quoted from above, supplies its own refutation of his claim.

1st. The inner condensation in Saturn's rings, seen double with great ease by Aitken, using the 36-inch Lick telescope, and with some difficulty (on account of poor seeing), but certainly, by Barnard using the 40-inch Yerkes telescope, was not seen double by Lowell.

2nd. Lowell located a "gap" or a "most conspicuously vacant spot" in the ring system $5\frac{1}{2}''$ west from the ball of the planet, and another one like it $5\frac{1}{2}''$ east of the ball. Aitken, observing on the same night, noticed that the light was relatively very weak at these points; but, thanks to the greater light-collecting power of the 36-inch telescope, he was able to see with certainty a faint line of light extending right across each of Lowell's "conspicuously vacant gaps."

W. W. CAMPBELL,
Director Lick Observatory.

Mt. Hamilton, California,
September 29, 1908.

LXXXIV. *Telescopic Vision.*

By G. JOHNSTONE STONEY, *M.A., Sc.D., F.R.S.*[*]

PART III.—HOW THE IMAGE IS FORMED, AND OF WHAT PARTIALS IT CONSISTS.

[Plate XII.]

Explanation of terms :—

1. u f W, undulation of flat waves, like the light of wave-length λ received from a star.
2. u s W, undulation of spherical waves, like the light of wave-length λ received from a luminous point.
3. Stellades and Punctades—see §§ 62 and 69. Observation—A u f W is a special kind of u s W; and a stellade is a special kind of punctade.
4. Complete image and its partials—see §§ 56 and 80.
5. Spile and anti-spile—see Chapter 3, in the November Phil. Mag. p. 796.

CHAPTER 5.

Outline of the Argument.

54. WE have now to enter upon the most important part of our undertaking, in which we are to find out *why* it is that when a large and a small object exactly similar to one another are examined with the same telescope, the large one will be seen satisfactorily, while the small one, though of precisely the same shape, will if small enough appear when viewed through the telescope to be transformed into something unlike itself. In the last chapter we have met with specimens of such distorted appearances and we have now to learn the cause of these imperfections, and of other imperfections due to similar causes.

Hitherto in examining these objects (see Chap. 4) we have employed diffused light as the light to illuminate object z', in order that by doing so we may reproduce in our experimental apparatus the same optical conditions as those under which natural objects are seen through telescopes, see § 80. But this mode of illumination will no longer suffice, because so long as we allow the light incident upon z' to be diffused light the whole phenomenon of the formation of its image in the pro-telescope is too complicated for investigation. It will be shown that what then happens is due to the simultaneous operation *of a vast number of optical causes* which produce different effects, and which in producing these effects *act independently of one another.* What, accordingly, we have to do is to separate these causes, and study what each does and why it does it; and then,

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[*] Communicated by the Author.

having ascertained this, we shall inquire what the final outcome will be when these causes, or any selected group of them, are allowed to come simultaneously into operation.

55. These independent causes are in fact the several u f W's (undulations of flat waves) into which the diffused light incident upon z' is resolvable and which we may call U_1, U_2, U_3, &c. A part of each of these U's passes through the opening at z' which represents in our experimental apparatus some supposed detail upon the planet which is being examined by the astronomer. The part of this U which passes through z' becomes to the left of z' what is called a 'beam' of light. This beam is of the kind which light *from a star* produces when allowed to pass through an opening in a shutter. We shall analyse this beam and find it to be a definite and complex optical phenomenon. We learn much about the u f W's (or u s W's) into which it may be resolved and of which it therefore consists, by introducing a contrivance (lens L′) by which the light of each u f W (or u s W, as the case may be, see § 68) will be concentrated into a speck of light upon plane Y′, where the simultaneous presence of the specks from all the u f W's of which the beam consists will constitute what we call the Concentration Image produced by that beam.

56. The light of the beam after becoming this concentration image upon plane Y′, continues its progress towards the left, and if it or a part of it is admitted into the pro-telescope T′, it will produce at x' within the pro-telescope that image of object z' which the light admitted to the pro-telescope is capable of forming. This is the image which the pro-telescope can furnish, when the incident light which renders object z' visible has been the light of the particular U which we have allowed to illuminate that object. Let us suppose that it is U_1 which we have so employed, and let us call the image of z', which is then formed at x', P_1. Similarly when U_2 is the incident light, the image of z' will be P_2, and so on. These P's we may call the partials, or partial images of z', which the U's when acting separately can produce. When the light incident upon z' was diffused light, all the U's were brought into operation, and the image then formed at x', which we may call the complete image, was due to the simultaneous presence there of all the partials, and may therefore be represented by the expression $P_1+P_2+P_3+$&c. The complete image therefore results from light being superposed upon light at x'. Now when light is superposed upon light, one or other of two things happens. If the lights that are superposed can permanently

interfere with one another, it is an interference effect which will result from their being both present; but if they are lights which are incapable of permanent interference, their being made to co-operate upon disk x' only causes an illumination at each point of that disk which is the sum of the illuminations which they would have separately produced at that point. As we shall presently find, it is with this second and simpler case that we have here to deal. And accordingly what we have to do is to determine what the partial images P_1 P_2 &c. are, and then to add the illuminations which they separately produce at each point of disk x', in order to learn what is the brightness at that situation in the complete image at x', *i.e.* in the image which is identical with what the astronomer can under the most favourable conditions see in his telescope.

CHAPTER 6.

Analysis of diffused light incident upon a small object.

The task with which we have to grapple is to find out by what process these images are really formed, for it requires but little consideration to satisfy ourselves that the explanation by Geometrical Optics, and other explanations which have been offered are either illusory or insufficient.

57. Geometrical Optics is a body of deductions from the supposition that light consists of rays—a supposition which is hypothesis not theory. A theory means a supposition which we think may be *true*: a hypothesis is a supposition we expect to be *useful*. The only thing to be seen to when examining a theory, is whether it is correct or incorrect; for the merit of a theory is simply to be true, irrespectively of whether man can make much or little, or indeed any, use of it. On the other hand a hypothesis is a supposition of which the express intention is that it shall be helpful, and which is legitimate if it enables us to make any real progress in our work. No doubt a hypothesis may also be a theory—in other words, a supposition which we entertain in the expectation that it will assist us in our investigation may also be the supposition which we think correctly describes what is going on in nature, but it by no means needs to be so: and in fact the best, *i.e.* the most useful, hypotheses are often of the kind that make no pretence to being true. The correct objective theory of light appears to be that light consists objectively of waves of alternating electro-magnetic stresses advancing through the æther; whereas the whole of

Geometrical Optics, which is one of our most useful sciences, is built upon the supposition that light consists of rays—a supposition which it would be an error to mistake for a theory of light, that is for an attempt to define what light really is. That which makes the supposition deserving of our acceptance is that it is eminently useful and *therefore* legitimate as *hypothesis.* In Geometrical Optics what we investigate is the succession of events, not in nature, but in a model of nature. We substitute in this model machinery more easily handled than any which operates in nature, every step in the progress of which can be foretold by the application of singularly easy mathematical analysis, can be represented by easily understood diagrams, and can be imagined and followed without difficulty by students who possess but little skill. The justification of this hypothesis is that it is so easily handled, and that it yields results *which are true within ascertainable limits.* It can be shown that the hypothesis that light consists of rays furnishes correctly positions which are in close relation with the situations really occupied by the several parts of an optical image, although what it offers as the image differs in material respects from any real image. Thus 'the Geometrical Image,' as it is called, presents us with *an unlimited amount of detail*, most of which must be regarded as false because it is detail which does not exist in the images produced by nature. The hypothesis is very useful within definable limits, but may seriously mislead if it is misapplied. Accordingly, when we seek to ascertain what the image really is, we must abandon Geometrical Optics and have recourse to an investigation based on what we are entitled to accept as theory.

58. If we place at z' in our experimental apparatus (see Plate XII.) a small object representing some feature or features upon the planet, and if we illuminate it by diffused light, we shall see in the pro-telescope at x' an image of that object.

The diffused light which is to be incident upon z' may be light which has issued from an image of the sun as in § 39 (see p. 801 of last month's Phil. Mag.), or, when we do not need it to be of great intensity, it is often more convenient to provide it by a suitably placed piece of illuminated white paper or by light reflected from a cloud. Whatever is the source of the light it will be convenient to call it σ; and what we have now to ascertain is the succession of events by which a part of the light emitted by σ succeeds in becoming an image of z' at s' in the pro-telescope.

59. This sequence of events naturally divides itself into three stages—1°, From σ, the source of light, to the object z'; 2°, From the object to the pro-telescope; and 3°, Within the pro-telescope—in correspondence with whch our study of the events will have to consist of three inquiries: 1°, How the light emitted by σ and incident upon z' is to be analysed? 2°, What happens to the portion of this light which gets past z', upon its journey between plane Z′ and plane Y′, which latter stands in front of the pro-telescope? And 3°, By what further behaviour does this light or some part of it afterwards form the image at x'? In the present Chapter we shall deal with the first of these inquiries, reserving the second and third for consideration afterwards.

60. To fix our ideas we may suppose the source of light σ to be a bright round disk of paper two inches in diameter placed at the situation of s' in Plate XII., *i. e.* at a distance of about a metre and a half to the right of object z'; and we may conceive of this disk as though it were divided into patches $d\sigma_1$, $d\sigma_2$, &c., hexagonal like a honeycomb, and of sufficiently small size (which they will be if about $\frac{1}{3}$ mm. across). Then the light of wave-length λ emitted from these small $d\sigma$'s and reaching z' will, under the theorem proved in § 29 (see p. 335 of the Phil. Mag. for last August), be equivalent to u f W's (undulations of flat waves) travelling towards z', which will be of the same number as the patches inasmuch as one will advance from each $d\sigma$ in the direction of the line from the middle of that patch to the middle of z'—together with an exceedingly small amount of r l (residual light) due to the rulings formed on plane Z′ by the P's and —Q's described in § 29. These rulings produce scarcely any illumination at the part of plane Z′ where z' is situated. In fact, if the $d\sigma$'s are as small as we have described them and if the object z' is of sufficiently moderate size, this residual light will be so faint that in making experiments it may be quite left out of account, and the whole of the light of wave-length λ reaching z' may be regarded as exclusively consisting of the same number of u f W's as there are $d\sigma$'s in σ, one arriving at z' from each of the $d\sigma$'s.

61. Hitherto we have considered only light of one wave-length, whereas the light emitted by σ being white light contains light of all the wave-lengths included within the visible part of the spectrum. Accordingly, the light transmitted from each one of the $d\sigma$'s to z', is to be regarded as consisting of u f W's of all these wave-lengths, all travelling in the same direction, viz., in the direction of the line from the middle of the $d\sigma$ to the middle of object z'. These from

the mathematician's point of view will be infinite in number, since he requires to be able to push matters to their limit, in order to comply with the requirements of mathematical analysis; but when our object is either to interpret experiments, or to deal with nature, the whole range of wave-lengths may be divided into groups, $d\lambda_1$, $d\lambda_2$, &c., each of a sufficiently small range, and then, as explained in § 31, a single u f W may be substituted for each of these groups. When this has been done the light incident upon z' from any one of the $d\sigma$'s will consist of a large but finite number of u f W's, of different wave-lengths all travelling in one direction. Let m be the number of these 'groups,' *i.e.* of the $d\lambda$'s, within the visible part of the spectrum, and let n be the number of $d\sigma$'s in disk σ, then will the entire of the visible light incident upon z' consist of mn u f W's, of which m of the u f W's of different wave-lengths will have issued from each $d\sigma$—together with traces of r l (residual light), too faint to need to be taken into account.

62. The visible light which inhabitants upon the earth receive from a white star is of the same kind as that received by the z' of our experimental apparatus from any one of the $d\sigma$'s of the source of light. They both consist of the same u f W's, of different wave-lengths, with in addition a tiny amount of residual light, which is too faint to need to be considered. It will be convenient to have a name for this kind of light, and it will in the present paper be called a stellade; which will therefore mean light of the same kind as we receive from a star. The statement at the end of the last paragraph may now be put into the following more convenient form:—

If σ, the source of light, is divided into n sufficiently small patches, $d\sigma_1$, $d\sigma_2$, &c., and if the wave-lengths present within the visible part of the spectrum are divided into m sufficiently small groups, $d\lambda_1$, $d\lambda_2$, &c., then will the visible light which is thrown by disk σ upon object z', consist of n stellades, one from each $d\sigma$, advancing along the n directions from the centres of the $d\sigma$'s to the centre of z'; and each of these stellades will consist of m u f W's, of the wave-lengths that correspond to the middles of the small groups, $d\lambda_1$, $d\lambda_2$, &c.—together with the residual light referred to in § 29, which is so very faint that it may legitimately be disregarded.

This resolution of the light incident upon z' into n stellades, and of each stellade into m u f W's, answers the first of the three inquiries proposed in § 59, viz.: How is the light in its first stage, *i.e.* between σ and z', to be analysed?

63. It should be borne in mind that the u f W's into which

we have here resolved the incident light are of the complex type referred to in § 31 (August no. of the Phil. Mag. p. 337), that is to say, they are u f W's the waves of which need not be alike except as regards wave-length, but in which, throughout the whole extent of each wave, there will be no difference between one part of that wave and another part of the same wave. Restrictions seem to limit the differences that actually prevail between the successive waves on any one u f W, consequent upon events that go on within the superficial molecules of visible matter. This is a subject one part of which is discussed in a paper in Vol. IV. of the Scientific Transactions of the Royal Dublin Society (1891), p. 563, from which discussion it appears that the light emitted by a visible body is due to the activities of the negative electrons within its molecules, and that the motion of any one electron, however intricate its path, is resolvable into elliptic partials each of which will emit light of a definite wave-length *.

CHAPTER 7.

Analysis of a beam of light.

When we intend that the light incident upon object z' in our experimental apparatus (see Plate XII.) shall be diffused light, we employ a source of light which we have called σ. A part of this light will ultimately become the image of z' which may then be seen in the pro-telescope T′ at x'; and in order to trace how this comes to pass we have divided the advance of the light from σ to x' into three stages.

64. The first stage of this progress, which is from σ to z', we have studied in the last chapter, and have found that if σ be divided into n sufficiently small patches $d\sigma_1$, $d\sigma_2$, &c., each of these will transmit towards object z' a single stellade of light (light of the kind we receive from stars), and that each of these stellades will consist of m u f W's (undulations of flat waves), one for each of the m wave-lengths of which we have found that white light may legitimately be regarded as consisting—along with a residuum of light obeying a different law of propagation, which however at the middle of object z' and for a certain distance round that point is so

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* We have some reason to suspect that the more definite motions of negative electrons are accompanied by surgings of the associated positive electricity. It may be to these less definite displacements of positive electricity that we are to look for the explanation of subsidiary effects which have been observed, even possibly including anomalous dispersion.

faint that its presence may be disregarded unless object z' is too large. We shall be careful not to make it too large; and may therefore regard the light incident upon z' as consisting of n stellades and each stellade of m u f W's, these stellades advancing upon z' in the n directions represented by lines from the middles of the $\bar{d}\sigma$'s to the middle of z'.

65. Let us now select some one of these stellades and study what further happens to it. To do this we must be able to deal with it separately; that is we must free it from the presence of the other stellades which will accompany it so long as σ is the source of light. This is easily done by removing σ from the experimental apparatus and employing s', the pro-star, as the source of light. The pro-star will then illuminate z' with a single stellade, and this may legitimately take the place of the stellade whose future history we want to trace, if we make its light fall upon z' in the right direction. This we can do by availing ourselves of the adjustments provided at the B end of the board BE. See § 22, p. 333.

66. What we have in the present Chapter to study are the events that will then occur between object z' and the plane Y$'$ which stands in front of the pro-telescope. To do this satisfactorily, we must confine our attention to light transmitted to the astronomical telescope from some definite object upon the planet, and the object we shall select as the first to be dealt with is an object like the planet Neptune, and in some degree like the Solis Lacus upon Mars, at longitude 87° and south latitude 27° upon the maps of the so-called 'canals upon Mars.' The Solis Lacus is a small but conspicuous spot upon the image of the planet, of a shape not far from round, and of a diameter on the planet which when the planet comes nearest to us subtends at the distance of the earth an angle not far from our standard angle ϵ. We are not at present concerned with the faint traces of detail which are supposed to have been at times detected upon its image, since the question to which we are at present seeking an answer is, what appearance *the outline* of an object of some such shape and size will have in the astronomical telescope, if such an object exists upon the planet? The object we shall suppose will, for simplicity, be an object exactly round, and subtending exactly angle ϵ at the distance of the astronomical telescope from the planet. The object which we have assumed to exist upon the planet will be adequately represented in the experimental apparatus by a round hole in copper-foil at z', illuminated by light coming from beyond it. This will present in the pro-telescope the appearance of a bright object with dark surroundings, whereas the Solis

Lacus is seen as a dark object with brighter surroundings; but this difference is immaterial, since the optical conditions for seeing a bright object upon a dark background, and a dark object of the same shape and size upon a bright background, are known to be the same.

67. The object on the planet which we have chosen for our first experiment being a round object of such a size that it subtends angle ϵ ($2''\cdot 062648$) at the distance of the earth will be adequately represented in the OEA (observatory experimental apparatus) at z', by a round hole 1 mm. in diameter, in the screen of copper-foil Z′, when the carpenter's square which supports the screen has been pushed into its place near the right-hand surface of lens L′, with z' opposite to the middle of the lens. This is to be illuminated by the single stellade of light issuing from pro-star s', and the observer can bring the direction in which this stellade is incident upon object z' into any of the directions along which light from the various parts of a source of diffused light, such as σ, would reach that object. When the incident light reaches screen Z′, most of the light is stopped by that screen, the only light which is allowed to advance beyond the screen being that which passes through the round opening z'. We need not consider what happens to the rest of the light as we are concerned only with what is called the 'beam of light' which advances past the hole.

68. We have to find out what this beam of light is. It is plainly no longer the simple stellade which encountered screen Z′, and which consisted of u f W's of different wave-lengths *all travelling the same way*. But it is light of some kind, and as such may be resolved into u f w's or in any other way that is legitimate. One of these legitimate resolutions (and the one which will most assist us when experimenting with an apparatus in which lens L′ has a focal length less than the whole of the distance from that lens to plane Y′) is a resolution into u s w's (undulations of spherical wavelets) which shall radiate from the several points of a surface W (see Plate XII.), of such a form and so situated that its points are the conjugate foci with reference to lens L′ of the several points of plane Y′ which stands in front of pro-telescope T′. The positions of these conjugate foci may be determined by Geometrical Optics, since this is a case in which Geometrical Optics leads to a correct result. Furthermore, instead of employing all the points of surface W as the centres of innumerable undulations of infinitesimal intensity, we may, as in other similar cases, distribute a large but finite number of points over surface W at sufficiently short intervals and

regard these as the centres of u s W's (undulations of spherical *waves*) each of which will take the place of a sheaf of the u s w's and may be bright enough to be seen. It is accordingly into these u s W's that, when dealing with experiments, we shall resolve the light between object z' and lens L′.

69. Let p_1, p_2, &c. be the numerous but not innumerable points which we have supposed to be distributed over surface W, and which are the centres of the spherical undulations into which we have resolved the light within the limited space between screen Z′ and lens L′. As this light contains light of all the wave-lengths present in white light, there will, in general, be spherical undulations of some or all of these wave-lengths emanating from each of the p's. Any complete system of undulations of the different wave-lengths with which we are concerned, and all of them consisting of spherical waves which have one common centre we shall find it convenient to call a *punctade* of light, which will then mean light of the same kind as that which issues from a luminous punctum or optical point, whether white or coloured. Accordingly we may regard the light within the limited space between screen Z′ and lens L′ as resolved into punctades P_1 P_2, &c., which have their centres at the points p_1 p_2, &c.; and each of these punctades will consist of the u s W's of different wave-lengths into which we may resolve white or coloured light emanating from a point.

70. Having got so far, we shall facilitate the next step of our inquiry by substituting instead of the real source of light s', and the obstruction it meets with at screen Z′, the much simpler machinery which we can imagine by making the hypothesis that this source of light and that obstruction have been removed, and that at the same time the puncta p_1 p_2, &c. upon surface W have been rendered luminous and are now what emit the light which exists between plane Z′ and lens L′. This is a hypothesis of the same legitimate kind as the familiar one which we make when we find it convenient to treat light reflected from a plane mirror as having come directly from the virtual images of the objects in front of the mirror instead of indirectly from those objects themselves.

71. When we view matters in this way we see that these punctades are incident upon lens L′, and accordingly that lens L′ will concentrate the light of any one of them, suppose of P_1, into an image of the kind which that lens is capable of forming of the luminous punctum from which we have asked the reader to regard the light of this punctade as having issued. This will be into an image which we may call Q_1, formed upon a small patch of plane Y′, which we shall call

q_1, and of which the middle point will be the point upon that plane which is conjugate to point p_1 upon surface W. How small the patch is which will be occupied by this image, may be seen from the following considerations. The image of a point formed by a lens is of the same kind as the image which we have called a star-burst. This image was investigated by Airy and consists of a central boss of bright light (sometimes called the spurious disk of the star) surrounded by relatively faint coloured rings, of which, usually, only a few of the inner ones can be seen. A very large percentage of the light is concentrated into the central bright boss and nearly the whole into it and the two inner appendage rings. Now, from Airy's formulæ we find that in the author's apparatus the patch occupied by the central boss and its two inner appendages is less than a tenth of a millimetre in diameter, and that the central boss in which most of the light is concentrated is only a few hundredths of a mm. in diameter *. We are therefore justified when making experiments in regarding the light of each of the u s W's incident upon lens L′, as being concentrated into an image small enough to be regarded as a speck of light upon plane Y′. In the author's apparatus there are about 100 of these specks in every square mm. of plane Y′; and, of course, the size of these specks can be made as much smaller as the observer chooses by substituting for L′ a lens of correspondingly larger aperture.

72. Accordingly, what the observer will see on looking through his Steinheil lens at B will be the image which we have called the concentration image upon plane Y′. This he may regard as consisting of the specks of light which occupy the patches q_1, q_2, &c. into which plane Y′ has been divided. He should then reflect that each one of these specks, as we may call them, is the concentrated light of one of a definite set of punctades of light into which the beam of light which has advanced to the left of screen Z′ has been able to resolve itself; and that what he sees on plane Y′ supplies the following information about that resolution. In the first place the position of the speck upon plane Y′—let us suppose that it is q_1—can be made to indicate to him the direction in which

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* The image in the author's apparatus is in fact larger, because of the large spherical aberration of telescope objective L′ when employed to form an image of a *near* object. This might have been corrected by using as lens L′, two telescope objectives put back to back, but this more elaborate arrangement was not adopted, as the simpler arrangement was found to work well in practice.

the component travelled, which has been concentrated into that speck *.

In the next place, the intensity at the various situations of the concentration image tells the observer the relative intensities of the several components of the beam which are concentrated into the corresponding specks.

And, thirdly, the colours of the concentration image at those situations indicate in some degree the various proportions in which wave-lengths are mixed in the components, whether they be punctades or stellades. This very considerable amount of information is increased when the observer adds to it what he may infer from the circumstance that all this light has been furnished by the single stellade emitted from pro-star s', which is the light that illuminates object z'. This light reached z' in the same phase and in the same state of polarization throughout each wave-front. Accordingly, all the light which advanced beyond screen z', and with which alone we are concerned, started from z' in the same phase and in the same state of polarization, and accordingly if at any subsequent stage the different parts of this light are brought together again after having spent equal times in their several journeys from z', they will arrive at that destination (as, for instance, at x' in the pro-telescope) under such conditions that they can produce there the kind of persistent interference effects of which human eyes can take cognizance. This we shall find a very important circumstance: upon it depends the competence of this light to form at x' the image which it displays there.

73. An object upon the planet which is small enough to subtend not more than a few seconds of angle at the distance of the earth may have its *outline* correctly represented by the boundary of a mere hole of the proper shape and size at z'. And the experiments that can then be made with it will

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* The direction in which that component of the beam travelled across whatever free space was left for it to the left of screen Z′, is made known to the observer by the position upon plane Y′ of the speck of light into which the light of that component is concentrated. He has only to picture to himself the ray (of Geometrical Optics) from that speck to the optical centre of lens L′, with its continuation to the right of lens L′. The portions of this ray which are in air are parallel to one another, and their direction when reversed indicates the direction in which the component in question was travelling until it encountered lens L′; that is to say, this is the direction in which the stellade advanced, if the resolution of the beam is regarded as being into stellades, and it is the direction of the central radius of the punctade, if the resolution is into punctades. Either of these resolutions is legitimate.

show what approach the astronomical telescope can make to reproducing this outline in its image of the planet. If the astronomical telescope shows further detail upon the image of the small object, the conditions under which this further detail becomes visible must be made the subject of a separate investigation. What a simple hole at z' suffices to do is to investigate the vision which can be obtained of the outline, and this is usually what is wanted in practice. In the few cases when more is required we must substitute something other than a mere hole at z'. However, for the present we confine our attention to mere holes, and to those of elementary shapes such as round, rectangular, or triangular. For forms less simple much the best course is to inspect, and if necessary measure, the concentration image in the OE apparatus, which will then give the astronomer the information he requires.

74. A circular opening is the first with which we shall deal, inasmuch as with a small hole of this shape in screen Z′ it is specially easy to foresee what the optical effect on plane Y′ will be, when light from the pro-star s' is admitted through that opening. For, in the first place, since object z' is small the light which reaches it from the pro-star is not appreciably distinguishable from the light which would reach it from a luminous point on surface W, and accordingly we may regard the light which reaches z' as light that has emanated from that luminous point, which we may call w. Again, objective L′ and the Steinheil lens at B may be regarded as the objective and eyepiece of a telescope with which the observer is looking at luminous point w. The aperture of his telescope is limited by the size of the round hole z', which we shall suppose cuts it down to being one millimetre. It thus appears that what the observer sees through his Steinheil lens is the image of luminous point w which the telescope just described has been able to form when its aperture is only 1 mm. Now the image of a luminous point in a telescope is of the same kind as the image of a star. It is the kind of image which we have called a star-burst, all the principal details of which are known to us from Airy's investigation, and the dimensions of which can be computed by his formulæ. The image consists of a very bright central boss of nearly white light, often spoken of as the spurious disk of the star, surrounded by coloured rings which are so much fainter and so rapidly deteriorate in brightness, that Airy's formulæ only give full particulars for the central boss and the two inner rings which are nearly all that can be seen of the phenomenon in astro-

nomical telescopes. The sizes of these depends upon the wave-length of the light, and therefore differs for the different colours of the spectrum. With light of one wave-length everything would be definite. At the centre the intensity is a maximum, and at a certain distance from the centre it falls to cipher. This distance will be the radius of a circle of no intensity, which will separate the central boss from the first ring; and similar circles of no intensity separate the successive luminous rings from one another. By slightly simplifying Airy's formulæ (see Transactions, Cambridge Philosophical Society, vol. v. 1835, p. 287), the angular radii of the innermost three of these, as seen from the optical centre of lens L′, are found to be

$$\theta_1=(1{\cdot}22)\frac{\lambda}{\mathrm{A}},\ \theta_2=(2{\cdot}27)\frac{\lambda}{\mathrm{A}},\ \theta_3=(3{\cdot}24)\frac{\lambda}{\mathrm{A}}, \quad . \quad (1)$$

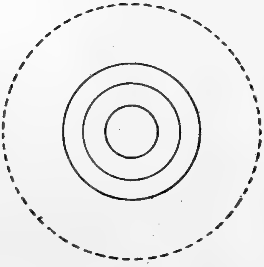
where θ_1 θ_2 and θ_3 are the angular radii as seen from the optical centre of the objective, λ is the wave-length of the light for which the computation is made, and A is the aperture of the telescope, which in the case supposed is 1 mm. Hence, on plane Y′ which is about a metre from the objective, the radii of these innermost dark circles will approximately be

$$\left.\begin{aligned}t_1&=1000(1{\cdot}22)\lambda\\ t_2&=1000(2{\cdot}27)\lambda\\ t_3&=1000(3{\cdot}24)\lambda\end{aligned}\right\}, \quad . \ . \ . \ . \ . \quad (2)$$

and if we insert 0·7 of a micron for λ, which is about the longest wave-length of the conspicuous parts of the spectrum, we find that for that wave-length the radii of the three dark circles will be

$$t_1=0{\cdot}854 \text{ mm.},\ t_2=1{\cdot}589 \text{ mm.},\ t_3=2{\cdot}268 \text{ mm.} \quad (3)$$

These the observer sees magnified seven times by his Steinheil lens. But in the annexed figure they are magnified only four times, as this magnification will make the diagrams in



Part of concentration image.

this paper of convenient size. When white light is used the central boss will occupy the space within the inner circle, and the innermost two appendage rings will occupy the spaces between the circles, since the overlapping of spectra does not become conspicuous till farther out. If the phenomenon is particularly well seen three or four more of the luminous rings will also be visible. The space within the dotted line of the figure would include five of the appendage rings, which are usually all that we need consider. If one wishes to see what the more definite effect is with monochromatic light, the absorbing contrivance known as a thallium screen may be held before the eye.

75. By these considerations we learn that when the opening at z' is round, and when the light incident upon z' has been a single stellade of light, its concentration image will be identical except in size with the image of a star as seen in a telescope. It is what we have called a star-burst, and with a round opening is the kind of star-burst which Airy investigated. If the opening at z' is of some other shape, the concentration image on plane Y′ produced when z' is illuminated by a single stellade will still be a star-burst or image of a star, for in fact it will be the kind of image which a telescope would furnish if its objective had this new shape. Several such images produced by stars were examined by Sir John Herschel, and some of them are figured in Plates IX. and X. of his article on Light in the *Encyclopædia Metropolitana*. But they are displayed in fuller detail by the OE apparatus, and with great additions to what can be made visible by examining the images of stars in telescopes. The astronomer when using the OE apparatus should bear in mind that in all cases the concentration image produced by a single stellade of incident light must be essentially a star-burst or image of a star whatever the shape of the opening at z' may be. It is the image which the telescope would furnish if its objective were of the shape of the opening or openings which he has made at z'. And he will find a study of the concentration image which will result from different forms of openings or from rows of openings most suggestive. When the form of the opening is polygonal the spectra which are associated in its concentration image with a central boss of light are no longer circular as they are when z' is a round hole. They become detached patches of coloured light, and some of the more distant ones are more conspicuous than the corresponding spectra when z' is round. This is a very instructive fact. It must be remembered that it is the same light which

produces the concentration image, or some part of this light, which afterwards develops the image of object z' which is seen at x' in the pro-telescope; and if z' is of an angular shape, the light of the more distant spectra must be admitted to the pro-telescope in order that the vertices in the angular image may be seen sharply defined. If the aperture of the pro-telescope is unable to admit the light of these distant spectra, the angles in the image of z' will appear blunt and not reaching out as far as they should. This seems to be the case with most if not all of the polygonal spiles in the image of Mars which are bounded by the dark streaks in the image which have been called canals. And this is a state of things which must apparently cause dark specks to present themselves at the angles, and may be the true account of the dark specks upon Mars which have been interpreted as representing oases upon the planet.

76. Before closing this chapter it may be well to refer to a property common to all concentration images, which the reader is requested to keep constantly in view when investigating the process by which the light emitted by objects at z' forms images at x' in the pro-telescope. This property is that objects at z' which are similar but of different sizes will give rise to concentration images on plane Y' which will also be similar, but of linear dimensions which will be inversely as the linear dimensions of the objects. See fig. 1, § 83 (p. 969).

The concentration image has a double meaning. It as it were looks backwards and analyses for us the beam of light which has passed through the opening at z'; and it looks forward and furnishes the information about the image in the telescope which will occupy our attention in the next chapter.

CHAPTER 8.

How a Telescopic Image is formed.

78. By combining what we have learned in the last two chapters, we obtain a complete reply to the second of the three questions propounded in § 59, in which we are asked how a beam of light is to be analysed. If, for example, the beam has come from the sun through a hole in a shutter, which opening may be of any form, we are first to conceive that a sheet of star-like bodies, sufficiently close together and sufficiently bright, take the place of the sun as the source of light. In Chapter 6 we found that the light reaching an opening of limited size in the shutter will be for practical

purposes the same whether it comes from the sun or from this sheet of stars. Regarding it as coming from the stars, we at once see that the sunbeam may be regarded as an aggregate of star-beams, one coming through the opening in the shutter from each of the stars in the sheet of stars. The light which reaches the shutter from each star is the kind of light we have called a stellade; and lights from any two of these stellades, having come from independent sources, are lights incapable of producing with one another visible interference effects. One consequence of this is that the intensity of the sunbeam at any situation will be the mere sum of the intensities which the starbeams would separately produce at that place.

Knowing that light of any kind and therefore that a star-beam is capable of resolving itself into components which may be either stellades or punctades, we learn in Chapter 7 much about these components. To gain this knowledge the observer inspects that concentration image which by the help of lens L′ will be produced upon plane Y′ whenever light from pro-star *s*′ passes through an opening at *z*′ and becomes a star-beam. Knowing that each luminous speck of this concentration image is the concentrated light of one of the components of the star-beam, he is told by the position of the speck upon plane Y′ in what direction that component travelled between screen Z′ and lens L′; and from the intensity and colour of the speck he learns what the intensity and colour of the component are. When to this information we add that all parts of the light of this concentration image have started from *z*′ in the same phase and in the same state of polarization at each instant of time, but that the light of any two of the concentration images may have been in various other phases and in various other states of polarization—when these particulars are added we have all the information we shall need in the inquiry upon which we are now to enter.

79. Let light from the pro-star *s*′ be allowed to fall on screen Z′. A portion of this light passes through the opening at *z*′, and becomes a starbeam between screen Z′ and lens L′, and this starbeam by the intervention of lens L′ produces the image on plane Y′ which we have called the concentration image. After forming this image the light continues its advance so that the pro-telescope can be placed in such a position that the whole or some part of the advancing light will enter the pro-telescope, and will then form at *x*′ the image of object *z*′ which the portion of the light which gains admission to the pro-telescope is able to yield.

80. The image formed from light that originally came from a star or pro-star we shall call a partial image, or partial. The partial image cannot be the same as the image of the corresponding feature on the planet which would be presented to the observer in his astronomical telescope. This is because the planet is an opaque body, the superficial molecules of which have been rendered luminous by light which has reached them from in front, and which has set up such activities in their superficial molecules as *scatter light in all forward directions.* To represent this correctly in our experimental apparatus the light reaching z' from behind must be light that advances *in all forward directions*, or in other words it must be diffused light. And the image of z' which is then formed, and which is identical with that formed by the corresponding feature on the planet, is entitled to be spoken of as the complete image of z'. To form this complete image in our apparatus it would suffice to illuminate z' from behind by light coming from a sheet of pro-stars instead of from a single one. This makes it obvious that the complete image is that image which is formed when all the partials formed by the individual pro-stars are simultaneously present on disk x'. These partials, however, we can in the experimental apparatus study one by one. As they arise from light coming from different pro-stars, viz. from $d\sigma_1$, $d\sigma_2$, &c., they come from independent sources of light, and therefore when they are all thrown down simultaneously upon disk x', the portions of light which they individually contribute and which form images at x' are unable to produce further interference effects than those which they separately produce. Hence we arrive at the important conclusion that when we have studied what the partials are when examined one by one, we can arrive at the brightness at any point of the 'complete' image, by simply adding together the illuminations which will be produced at that point by the partials when they are made to present themselves in succession.

81. In order to see the general outcome of this state of things, we shall examine how the principles that have been laid down will work out when applied to a special instance. The feature to be seen we shall suppose to be the simple boundary of the whole planet, when the planet is 1°, Neptune in opposition, and 2°, Mars when nearest to the earth in 1909. In other words the objects are nearly circular disks, and these we shall represent by circular openings of the proper sizes, at z', respecting which we are to discover of what partials their images in the pro-telescope will be built up

when the pro-telescope is successively made to correspond to astronomical telescopes with apertures of 40, 24, and 12 metric inches, *i.e.* with apertures of 100, 60, and 30 centimetres.

82. The angular diameter of Neptune in opposition is about $1\frac{1}{3}\,\epsilon$, and the maximum diameter of Mars in 1909 will be $11{\cdot}655\,\epsilon$. We shall first deal with these magnitudes in the most obvious way, which is also the way best fitted for computation; and we will afterwards indicate another way of dealing with them which is more convenient to the experimentalist. The first or more obvious course is to imagine round openings in copper foil with diameters $1\frac{1}{3}$ mm. and 11·655 mm. to be placed successively at z', and to illuminate these by a single stellade of light incident upon them from the right. They, and the round opening 1 mm. in diameter with which we have been already experimenting, would any of them produce on plane Y′ the same kind of concentration image. These, however, would be of different sizes, their linear dimensions being inversely as the linear dimensions of the openings at z' to which they are due. Hence we can deduce the sizes of the others from the dimensions given in § 74; where we found that the concentration image presented when z' is a round hole 1 mm. in diameter furnishes the values:

$$t_1 = 0{\cdot}854 \text{ mm.},\ t_2 = 1{\cdot}589 \text{ mm.},\ t_3 = 2{\cdot}268 \text{ mm.}, \quad . \quad (3)$$

where t_1, t_2, and t_3 are the radii of dark circles which separate the central boss of light and the first three of the appendage rings which with the central boss form the whole of the concentration image produced by light of wave-length $\lambda = 0{\cdot}7$ of a micron. This wave-length and wave-lengths shorter than it are all that we need take into account, as this range includes all the brighter parts of the spectrum of white light. Accordingly the central boss and its two inner appendage rings will lie within a circle of which the radius is 2·268 mm. Airy's formulæ do not enable us to calculate the radii of the limiting circles that lie farther out; but their position can be seen and measured in the experimental apparatus, and it thus appears that a circle with a radius of 4·2 mm. would nearly include all of the fifth ring. Appendage rings that lie farther out become so faint that they need not be taken into account unless we are considering the vision of a much brighter object than a planet. We may therefore safely assume that the whole of the effective part of the concentration image is bounded by a circle 4·2 mm. in radius. This radius we shall call T.

83. Accordingly, when z' is a hole 1 mm. in diameter, the radius of the whole of the efficient part of its concentration image upon plane Y′ will be

$$\left.\begin{array}{c} T = 4{\cdot}2\ \text{mm.} \\ \text{and the radius of its central boss of very} \\ \text{bright light will be} \\ t_1 = 0{\cdot}854\ \text{mm.} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From these values we can compute what they would become if the diameter of the opening at z' were made successively $1\frac{1}{3}$ mm. and 11·655 mm. so as to represent planets Neptune and Mars. We thus find that a round hole at z' which would represent Neptune in opposition, would make

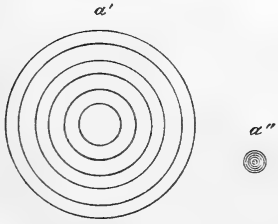
$$\left.\begin{array}{l} 4T' = 12{\cdot}6\ \text{mm.} \\ 4t_1' = \ \ 2{\cdot}562\ \text{mm.} \end{array}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and that the hole at z' which would represent Mars when nearest to us in 1909, *i.e.* on the 18th of September, would make

$$\left.\begin{array}{l} 4T'' = 1{\cdot}44\ \text{mm.} \\ 4t_1'' = 0{\cdot}293\ \text{mm.} \end{array}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In writing these we have introduced a single dash when the equations refer to Neptune, and a double dash when they refer to Mars; and the radii have been multiplied by 4 because the annexed diagrams need to be on a larger scale than the scale on which the originals present themselves on plane Y′. In these diagrams each inch upon the objective of the astronomical telescope is represented by a millimetre.

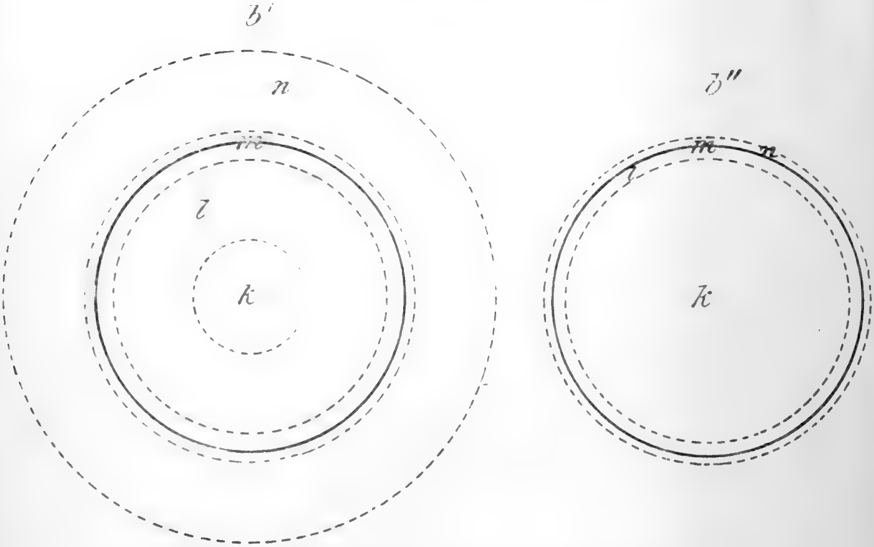
Fig. 1.



Concentration images of Neptune and Mars.

In fig. 1 a' is four times the size of the concentration image upon plane Y′ when z' represents Neptune, and a'' is four times what its size becomes when z' represents Mars. Fig. 2 will illustrate what kind of vision can be obtained *of the outline* of these planets if examined with a telescope of which the aperture is a metre (*i.e.* 40 metric inches), *and if the optical state of our atmosphere is sufficiently good*, which it of course very rarely is. In this diagram the continuous line is the circumference of the objective, and the dotted circles separate it and the neighbouring space into four regions k l m and n. The dotted lines nearest to the continuous line are at distances from it $=4t_1'$ in the left-hand figure, and $=4t_1''$ in the right-hand figure; while the outermost and the innermost circles are distant from the outline of the objective, at distances from it $=4\mathrm{T}'$ in the left-hand figure, and $=4\mathrm{T}''$ in the right-hand figure[*].

Fig. 2.



Efficiency of a 40-inch telescope upon the outline—
of Neptune. of Mars.

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[*] In the right-hand diagrams of figs. 2, 3, and 4, the distances of the four dotted circles from the continuous circle should be the lengths given for $4\mathrm{T}''$ and $4t''$ in equation (7). Of these only the more distant dotted circles, at the distance $4\mathrm{T}''$ from the edge of the objective, can be represented in the diagrams. The other two, between which lies region m, can be imagined though too close to the continuous circle to be drawn.

84. To make use of these diagrams we must remember that the 'complete image' in the pro-telescope is due to the simultaneous presence in that telescope of all the partials, and that a partial is produced whenever the whole or any part of the concentration image represented in fig. 1 is able to enter the pro-telescope. Now fig. 1, *a′* is the concentration image formed by a stellade of light incident upon the pro-Neptune at *z′*; and obviously if the direction of the incident stellade to which it is due, brings its middle point *o* anywhere within space *k*, then the whole of the efficient light of that concentration image has got into the pro-telescope, and therefore the 'partial,' the image of *z′* which it will form, will be an image so good that we may practically regard it as an optimum partial. On the other hand, if *o* the centre of fig. 1 falls anywhere within space *l*, only part, although it will be the greater part, of the concentration image gains admission to the pro-telescope. The resulting 'partial' formed at *x′* will fall short of being the optimum, the defect being slight if *o*, the centre of the concentration image, reaches a part of region *l* which is distant from the margin of the objective, while the defect goes on increasing the nearer that *o* comes to the margin of the objective. This *l* group of partials may be called fair images of *z′*, and will some of them be almost good, others only mediocre.

The next stage is when *o* the centre of the concentration image reaches space *m*. Under these circumstances part even of the light of its central boss is excluded from the pro-telescope and the resulting partial will be a decidedly bad image of *z′*, and this defect becomes still worse when the centre of the concentration image lies farther from the objective within region *n*. If the centre of the concentration image lies farther out than region *n*, none of its light gets access to the pro-telescope and we are therefore not concerned with it. Now when the light incident upon *z′* is diffused light, as it must be when we want to represent correctly what occurs in nature, this light when analysed will furnish stellades that would send the centres of their concentration images to all the points represented in fig. 3, so that *all* the partials which have been described above are present upon disk *x′* and cooperate to produce there the 'complete image' of *z′*. It is obvious that in the state of things represented in fig. 2, *b′*, this complete image cannot be a very satisfactory one. It is to be regretted that when using a telescope we are unable to exclude any of the partials. It is convenient to divide them into the four groups which we call *k l m* and *n*, depending upon the situations on plane Y′ (the plane of the figure) which the centres of their concentration images reach. The partials belonging to class k, if all the rest were excluded, would acting together form *an exceedingly good image* at x', since the partials of this group are all optimum partials. This is a state of things which the microscopist can realise by closing the iris-diaphragm under his condenser sufficiently to exclude the light which would develop any other partials than those of class k. This in using the microscope is called 'clearing the image.' We can do the same in the author's experimental apparatus, by calling into requisition an iris-diaphragm provided at F (see Plate XII.). But the astronomer has no means of accomplishing it with his telescope. He must put up with all those mischievous bad partials, being present in the image which the telescope presents to him. And under the conditions represented in fig. 2, b', they contribute so largely to the image that the resulting 'complete image' cannot yield a really good image of the outline of Neptune, which is what we want to see, although the astronomer would probably consider it quite a fair image. This is partly because of a very curious power which the experienced observer acquires of, in such cases, being able in some degree to detect the image which the better of the contributory partials would form, and being able to distinguish and exclude from his consideration some at least of the added defects.

By the movements provided at the B end of the board BE, the observer can bring the concentration image successively into all the positions described in the last paragraph, and can then see for himself the partial images in the pro-telescope, which will result; and the astronomer would do well to familiarise himself with these details.

85. We have now to contrast with the above the image which the same telescope will furnish of an object of the same shape but of larger angular size, when the feature to be seen is the outline of the disk of planet Mars. Here when we distribute the partials into the four groups k l m and n, we find this distribution represented by fig. 2, b''. This diagram shows us that the optimum partials, which are those of group k, are greatly more numerous[*] than they were when Neptune was the object, and at the same time the partials of the three other groups, l m and n, are much fewer. Hence the 'complete image' of the outline of the planet Mars which will result from their being all present,

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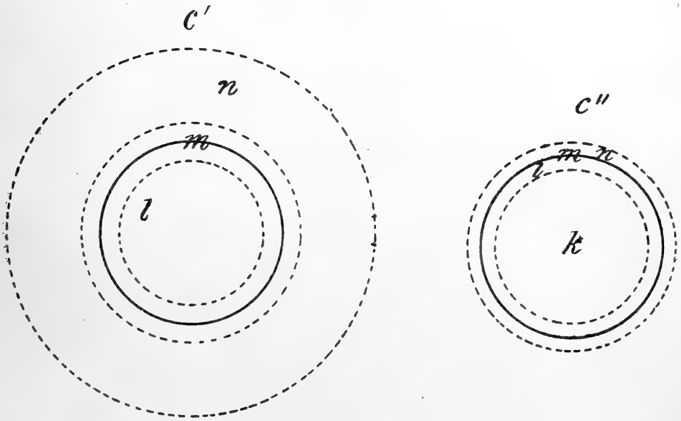
[*] The numbers of the partials of each group are proportional to the areas allotted to them in figs. 2, 3 and 4. The intensities of the partials have however to be taken into account as well as their number.

is chiefly characterized by this great preponderance of optimum partials. The state of things which now prevails will furnish an image of the edge of the planet which any astronomer would pronounce to be an exceedingly sharp * image. Of course this will only happen, if the observation is made on one of those rare occasions when 'seeing' is very good.

86. We shall next consider how these same objects would appear in telescopes of less aperture, such as those with which the most successful observations have hitherto been made upon the images of Mars in telescopes. The apertures we will consider are apertures of 24 inches and of 12 inches. Proceeding as before, we find that the following figures indicate the proportions in which the four classes of partials will be present in these images when the objects under examination are the contours of Neptune and Mars.

Fig. 3.



Efficiency of a 24-inch telescope upon the outline—
of Neptune. of Mars.

From fig. 3, *c′*, we learn that when Neptune is examined with an aperture of 24 inches, the image will contain no partials of class *k*, *i.e.* none of the best kind; but that there will be present a considerable contingent of the partials of class *l* (without however the best of that class). Those of class *l* that are present would produce a fair image, were it not for the large admixture of partials of the other two

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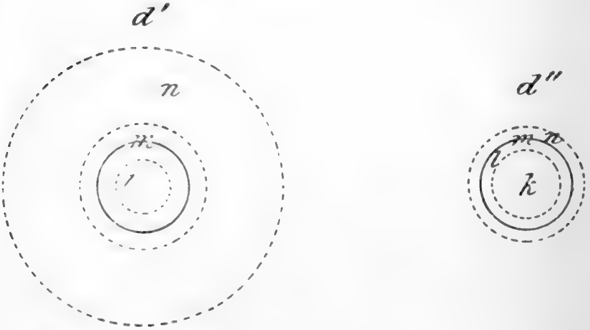
* This does not in the least imply that such vastly smaller details as the profiles of mountains upon the edge of the planet could approach to being made visible by a 40-inch telescope.

classes, m and n, which are the kinds of partials which most tend to spoil an image. Owing to their presence the image of the edge of planet Neptune as seen in a 24-inch telescope cannot be assigned a higher place than that of a barely fair image of that feature of the planet.

87. The state of things will of course, become worse, if the aperture of the telescope is cut down to 12 inches. What will then happen is depicted in fig. 4 d'. From this diagram we see that the image of Neptune's outline is made up chiefly of partials of the two bad classes m and n, superposed upon only a few of those of class l, and they only the less efficient of this class. The resulting 'complete image' will therefore poorly represent the real margin of the planet.

Fig. 4.



Efficiency of a 12-inch telescope upon the outline—
of Neptune. of Mars.

88. As before, we shall find a great contrast to the state of things described in the last few paragraphs when we turn the same telescopes upon planet Mars. The visions which they will afford of the outline of Mars are expressed diagrammatically in fig. 3 c'' and fig. 4 d''. From these we learn that even with the 12-inch telescope, the image of the contour of Mars when nearest the earth in 1909, will be decidedly well seen on a good night. The image will include a considerable number of the k partials—the partials of the best kind—with not a very large admixture of partials of the three inferior kinds l m and n. With the 24-inch telescope this satisfactory state of things will be improved on. The proportion in which the k partials will now stand to the three other classes will have become a much greater proportion, with a corresponding improvement in the resulting "complete

image' of the outline of the planet, which will be of the kind that an astronomer would pronounce to be excellent.

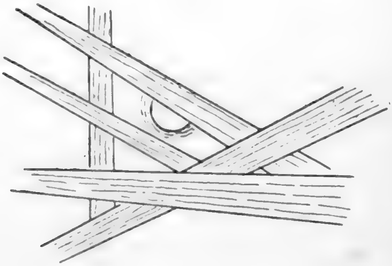
89. In order to show the efficiency of the proposed method of investigating telescopic vision, and of discovering the reason why it is encumbered with the imperfections which become troublesome when we endeavour to see minute objects, it has been thought that the best course was to describe how to apply the new method to some one class of objects; and the class chosen has been round or roundish objects such as are some of the spots on the image of Mars, including the polar caps at the times when these appear to be roundish or oval objects. The telescope is more successful in dealing with objects of this kind than with objects of angular or other irregular form. This is because in the latter case, as experiments with the OE apparatus will show, the concentration images which they develop upon plane Y′ do not, as with round objects, consist of a boss of white light surrounded by annular spectra alike in all directions round the boss and which after the first four or five become excessively faint, but consist of a central boss of some other form surrounded by spectra occupying detached patches upon plane Y′, of very unequal intensity in the various directions round the boss, and in some directions retaining sufficient brightness to need to be taken into account, when considerably farther from their central boss, than the fifth annular spectrum which is the most distant we have thought it necessary to retain when inquiring as to the vision of round objects. Long rows of exceptionally bright spectra are in such cases apt to radiate out in some directions from the central boss, and the more distant of these will be excluded if the aperture of the telescope is insufficient. This must have often happened when the 24-inch telescope and in a more intense degree when the 12-inch telescope have been employed to examine polygonal patches subtending at the telescope so small an angle, as do those brigher regions upon Mars which are enclosed by whatever on Mars correspond to the 'canals' upon the image, or by the darker 'seas.' When these outlying spectra are excluded from the telescope, one effect will be that the angles of the polygon will be rounded off, and such appearances as 'oases' and 'carets' will present themselves.

90. In all such cases the astronomer can make at z' a hole which will represent both in size and shape any supposed polygonal feature upon Mars. This is to be illuminated by the pro-star s', and he can then see through the Steinheil lens the concentration image it produces on plane Y′, and

can measure the distance from the centre of the concentration image to the most distant appendage spectrum which ought to be retained. The distance so measured he is to employ as his T in constructing diagrams like those of figs. 2, 3, and 4, which will then reveal to him the kind of vision of the supposed object upon the planet which his astronomical telescope would be competent to supply.

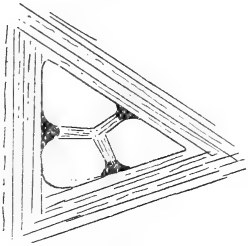
91. Many experiments with the microscope throw additional light upon this interesting subject. One of these I may mention. The object was the proboscis of the Blowfly, and the part of the specimen which was made use of was a small triangular patch of bright light which happened to be shut in between three of the hairs or bristles which grow near the base of the proboscis. These hairs had been pressed when mounting the specimen, so that they lay near to one another and nearly in a plane perpendicular to the optic axis. Another thinner hair which we may call the canal crossed the triangle and lay parallel to one side. This canal divided the triangle of light into a smaller triangle below, and a quadrilateral space above the canal. Within this quadrilateral was seen about half of the base of another small hair, presenting the semicircular appearance in fig. 5, and being somewhat darker on the right-hand part of the semicircle than on the left. The rest of this hair lay outside the triangle of light to which attention is being called.

Fig. 5.



This object was examined through one of Zeiss's 24 mm. apochromatics, over which an iris diaphragm had been fitted to enable the observer to diminish its aperture to any desired extent. The succession of appearances while the aperture was being diminished was most suggestive. The object was fairly well seen until the aperture became rather small, but then on still further contracting the aperture a succession of new phenomena sprang into existence, until at a certain stage the appearance became that represented in fig. 6*, and was then utterly unlike the real object. The semicircle has

Fig. 6.



disappeared and instead of it and the one straight canal across the triangle we have what appear to be three canals of nearly equal thickness and abutting nearly perpendicularly upon the three sides of the entire triangular space. And at the same time 'carets' have developed themselves at the outer ends of these three optically produced canals. These misleading appearances, which sometimes metamorphose an object into something utterly unlike itself, are of the same kind as those by which the Astronomer who occupies himself upon minute details, is but too liable to be misled, unless he diligently avails himself of some such aids as those which the author has ventured in this memoir to recommend.

NOTES.

NOTE 1. *On control observations upon the Moon.*—When in last month's Phil. Mag. (see p. 807), recommending the Astronomer diligently to make control observations upon the Moon when nearly full, the author omitted to point out that valuable observations of this kind can be made without having to provide the auxiliary telescope there suggested. With that telescope the *exact* optical conditions of the observations upon Mars can be reproduced, including the vision of Mars in the astronomical telescope, and of the Moon in the control apparatus, under equal magnification.

To make observations with the naked eye we have only to

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* In looking at fig. 6 the reader is requested to exercise his imagination, for none of the features as seen in the microscope had the hard outlines of our diagram of them. The three 'canals' were dusky streaks with straight but nebulous edges, and the boundary of the triangular bright space was also nebulous. The 'carets' were the darkest parts of the image.

provide round holes of the sizes given in column 4 of the table on p. 807. With a little care, these can be made with needles in softened copper foil (see § 26, p. 331). Of these holes that one is to be selected which corresponds to the angular size of Mars at the time, which is given in the Nautical Almanac (see column 2 of the table). On looking with the naked eye through this hole at the full Moon, we see the Moon under the same optical conditions as when we view Mars through the astronomical telescope armed with a magnifying power equal to the number which is found in column 3 of the table. If we wish to have at our command an opportunity of using other powers, we must provide the small auxiliary telescope suggested in § 48.

NOTE 2. *On the size of the Eidolon.*—In the text (see § 13) we have described the Eidolon, or object which appears to the observer to be what he is looking at, as of one special size. In this it was assumed that the observer had focussed his telescope so as to be able to scrutinise the eikon, the image presented to his eye, with most success. By adjusting the focus differently the eikon could be made to give the impression of a larger object at a greater distance; but it is best, as in the text, to focus in the way that enables the observer to scrutinise the image he sees to most advantage.

And, when focussing his telescope, the experienced observer will judge as to whether it is focussed correctly by the vision he obtains of whatever is *the most distinctly seen feature of the image* presented to him. This in the case of Mars will be the contour of the planet and not any of the objects upon its disk, and especially not any phenāko-spile.

NOTE 3. *On lens L′ of the OE apparatus.*—Since the focal length of lens L′ is less than a metre, we have the concentration image affected by the spherical aberration spoken of in the footnote on p. 960. However, it is found that this defect does not *sensibly* impair the image even when the focal length of L′ is as short as it is in the author's apparatus. Neither is it sensibly the worse because s' is a little farther from z' than surface W, the conjugate of plane Y′. If on the other hand the focal length were longer than a metre, the specks of the concentration image which are formed by each of the punctades (or stellades) into which the beam is analysed, would dilate and become less definite as seen upon plane Y′, and if the focal length were excessive (which would have the same effect as removing lens L′ from the apparatus) the diffuseness of its specks would impair our vision of the concentration image. This is what renders it necessary to retain lens L′ as part of the apparatus. The concentration image upon plane Y′ can be seen, but very poorly seen, without its intervention.

Of course, the experimental apparatus would most closely represent the Cosmical Apparatus described in Chapter 1, if the focal length of lens L′ were a metre, and if at the same time a collimating lens were introduced between z' and s', to parallelize the light from pro-star s'.

NOTE 4. *On the analysis of light into* u f w 's.—In all Mathematical and experimental investigations into Nature, what in each case we deal with is not the whole of the activities that are going on, but some immense simplification of them effected by ignoring the bulk of what is really taking place, and considering only the small residues which are what can be perceived by man. Thus we can perceive a wind in air, which is in fact only a residual effect, a slight preponderance in one direction of all the momentums which are consequent upon the vastly swifter motions of the molecules between their encounters ; and these motions are themselves only the residues which remain over as a preponderance in one direction of the enormously more subtile momentums that are going on within those travelling missiles.

So also, in his investigations of wave motion, the mathematician finds it necessary to substitute untextured mediums, devoid of all that majority of events which he ignores,—he has to substitute this simplification of nature for the real, immeasurably more complicated activities that are really in operation. The untextured medium is the mathematician's hypothesis ; and is legitimate because, under his handling of it, it furnishes results *which are correct under certain definable circumstances,* though incorrect under others. They are correct whenever we have not to deal with distances that approach to being molecular. The mathematician, however, in order to carry out his work, has to explore the whole field, as he has to base his reasoning upon limiting conditions which occur within the part of the field that, when he comes to interpret his results, is the very part that must be rejected. Resolutions into u f w's,—undulations of *wavelets* —are of this kind, and are of value because although the results to which they lead at close quarters are incorrect, all the results to which they lead beyond those limits are true, and may be used in the present memoir which nowhere has occasion to explore the extremely small in space, or the extremely brief in time.

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END OF THE SIXTEENTH VOLUME.

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